Supporting Information

Highly Efficient and Ultra-Narrow Bandwidth Orange Emissive Carbon Dots for Microcavity Lasers

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METHODS

Materials: 1, 4-diaminonaphthalene (AR, 97%) was purchased from Alfa Aesar, part of Thermo Fisher Scientific. Dichloromethane, acetone, dimethyl formamide and ethanol were analytical pure and bought from Sinopharm Chemical Reagent Co., Ltd. All the reagents used as received without further purification. Deionized water was used in all experimental processes.

Synthesis of CDs: 1, 4-diaminonaphthalene (0.05 g) was ultrasonic dissolved in ethanol (20 mL) to form a transparent solution. Then, the solution was sealed into autoclaves and placed in oven for heating at 200 ºC for 12 hours. After cooling to room temperature, the obtained suspensions were purified with a silica column chromatography using dichloromethane and methanol as the eluent. Finally, four CDs were obtained with violet, blue, green and orange emission named v-CDs, b-CDs, g-CDs and o-CDs after evaporation to remove the eluent.

Microcavity fabrication and lasing measurement: The microcavity was fabricated by coating the o-CDs on a glass fiber (diameter ~6 μm). The bottle-like microcavity was formed by surface tension of the o-CDs. The 532 nm pulsed laser (continuum surelite II) was focused into a stripe, which was perpendicular to the length of the glass fiber on the microcavity through a semi-cylindrical lens, and light emission was coupled into a spectrometer (Horiba iHR 320) via an optical fiber. For lasing measurement under different temperature, the measurement was performed in a temperature controllable heating and freezing stage (linkam HFS-600).

Characterizations: JEM- 2100F instrument (JEOL, Japan) and Multimode 8 instrument (Bruker, Germany) were used to investigate the morphologies of CDs including TEM and AFM images. Excalibur HE 3100 (Varian, USA) and ESCALab250i-XL electron spectrometer (Thermo Fisher Scientific, UK) were used to record the chemical constitutions, such as FT-IR and XPS of CDs. Fluorescence spectra, UV−vis absorption and transmittance spectra were measured on F-4500 instrument (Hitachi, Japan) and U-3000 instrument (Hitachi, Japan). The resolved fluorescence lifetimes measurement was recorded using LP920 instrument (Edinburgh instruments, UK). Absolute QYs were obtained using an integrating sphere connected by a FLS980 system (Edinburgh Instruments, UK).

Table S1. The dimension and optical parameters of as-prepared four CDs.

CDs	PL (nm)	FWHM (nm)	Abs. (nm)	QYs (%)	average diameter (nm)	size distribution (nm)	τ_{avg} (ns)	E_g (eV)
v-CDs	445	84	411	18	4.0	2.0-5.5	3.21	2.78
b-CDs	452	54	420	26	3.7	2.7-5.3	7.03	2.70
g-CDs	557	80	451	46	3.5	2.0-5.0	8.25	2.24
o-CDs	581	30	532, 570	82	2.7	2.0-3.2	10.13	2.03

Table S2. The illustration of reported CDs with their emission wavelengths, full width at half maximum (FWHM) and quantum yields (QYs).

λ_{em} (nm)	FWHM (nm)*	QYs (%)	Source
441	82	88	*Adv. Mater.,* 2012, 24, 1716.
450	54	94	*Scientific Reports,* 2014, 4, 5214.
519	38	63	*J. Mater. Chem. C,* 2013, 1, 4902.
443 515 572 715 745	108 97 85 71 55	54 41 51 43 13	*Small,* 2018, 14, 1800612.
430 513 535 565 604	80 95 71 85 90	75 73 58 53 12	*Adv. Mater.* 2017, 29, 1604436.
570 580 608	90 95 95	——	*Adv. Mater.,* 2015, 27, 1663.
435 535 604	65 70 75	10.4 4.8 20.6	*Angew. Chem. Int. Ed.* 2015, 54, 5360.

580 625	95 95	—— 24	*ACS Nano,* 2016, 10, 484.
580	120	46	*Adv. Mater.,* 2016, 28, 3516.
568	90	32.5	*ACS Appl. Mater. Inter.,* 2015, 7, 23231.
680	100	——	*Nat. Commun.,* 2014, 5, 596.
570 609 628 680	115 125 120 85	——	*Nanoscale,* 2015, 8, 729.
610 710	110 120	7 6	*Angew. Chem. Int. Ed.,* 2015, 54, 2970.
555 630	120 145	——	*Chem. Commun.,* 2015, 51, 2544.
683	~30	16.8	*Nanoscale,* 2016, 8, 17350.
640	80	22.9	*Chem. Mater.,* 2016, 28, 8659.
710	90	26.28	*Adv. Mater.,* 2017, 29, 1603443.
640	125	9.6	*Small,* 2017, 13, 1700075.
628	75	53	*Adv. Mater.,* 2017, 29, 1702910.
598	30	54	*Nat. Commun.* 2018, 9, 2249

* The FWHM is estimated according to photoluminence spectra.

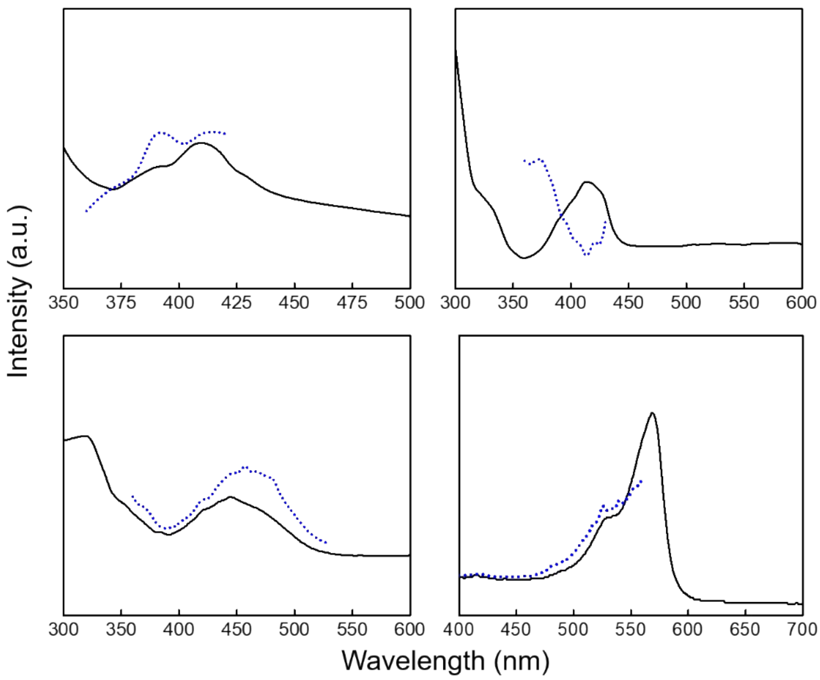


Fig. S1. UV-vis absorption (black line) and PL excitation spectrum (blue dotted line, emission wavelength are their emission peak) of v/b/g/o-CDs.

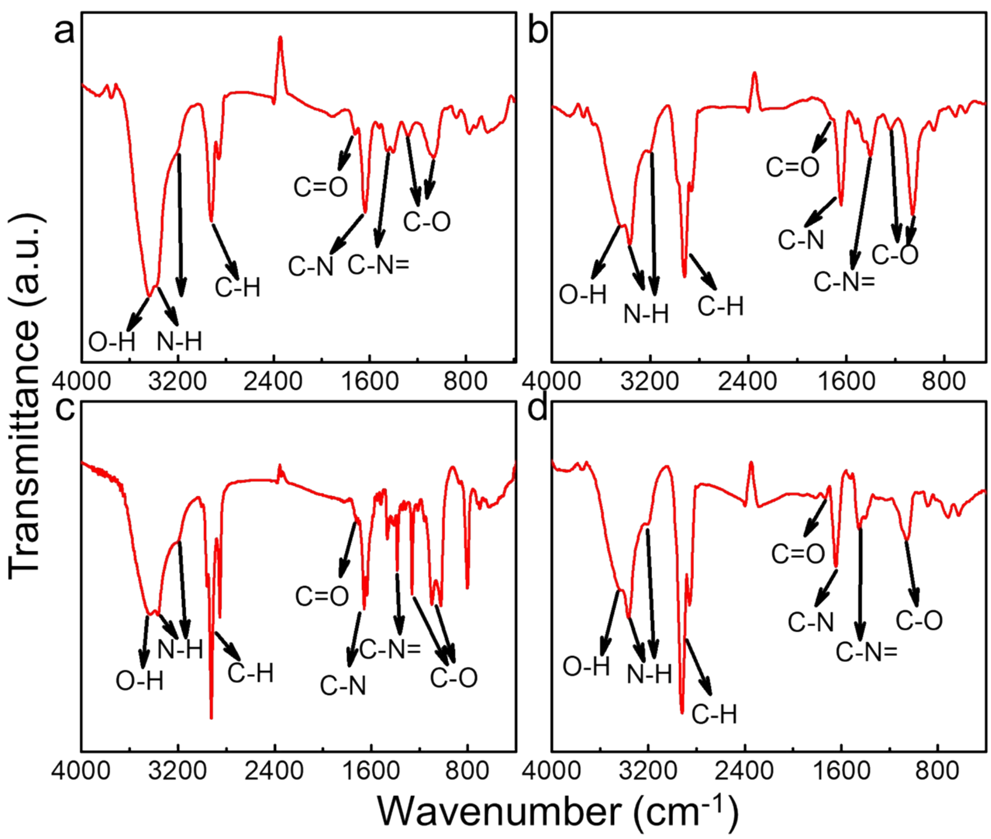


Fig. S2. FT-IR spectra of v-CDs (a), b-CDs (b), g-CDs (c) and o-CDs(d).

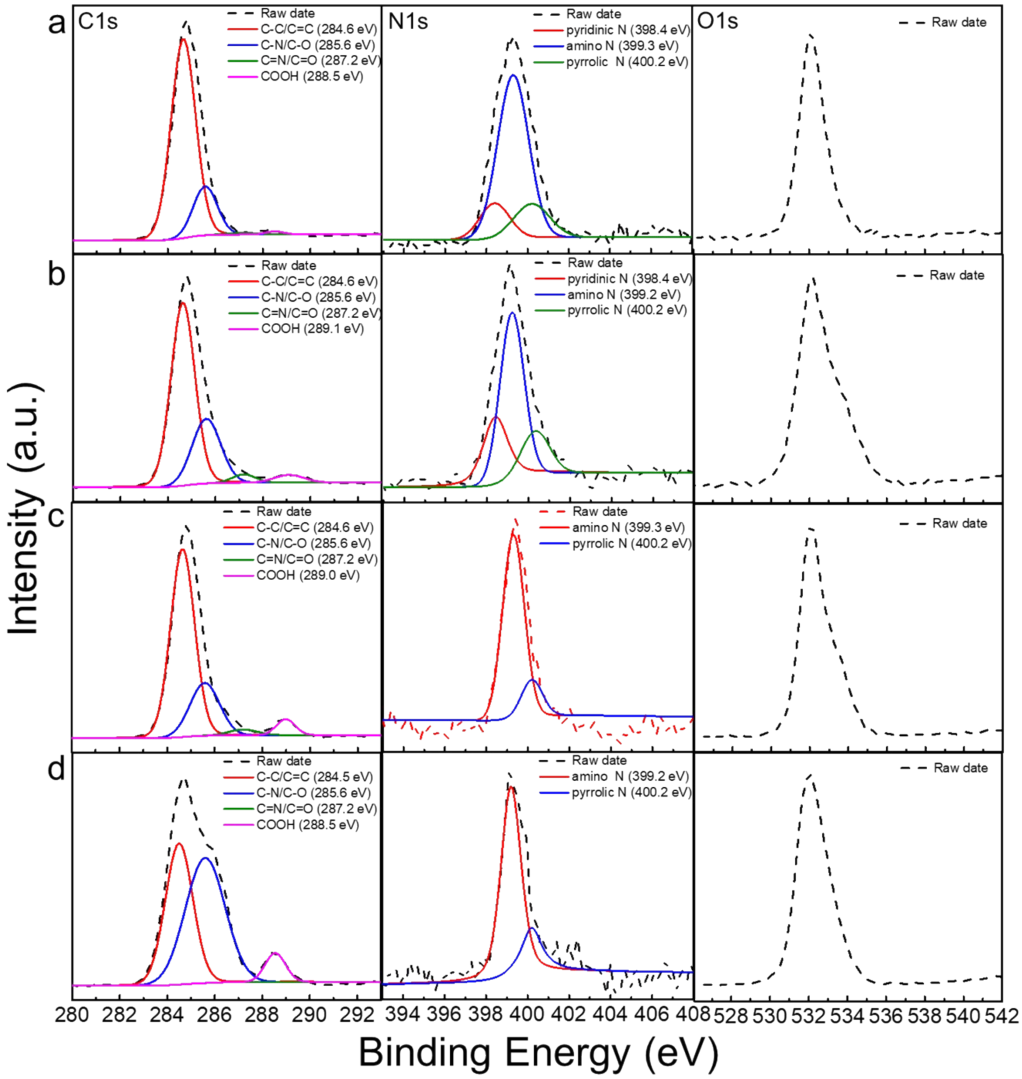


Fig. S3. High-resolution XPS C1s, N1s, and O1s spectra of v-CDs (a), b-CDs (b), g-CDs (c) and o-CDs (d).

Table S3. The relative contents of C, N and O atoms for v/b/g/o-CDs according to XPS surveys.

Samples	C (%)	O (%)	N (%)
v-CDs	80.98	14.25	4.77
b-CDs	79.77	16.44	3.79
g-CDs	72.09	24.97	2.94
o-CDs	67.89	29.78	2.33

Table S4. XPS analyses of the C1s (1), N1s (2) and O1s (3) spectra of v/b/g/o-CDs.

(1)

Samples	C=C/C-C (%)	C-N/C-O (%)	C=N/C=O (%)	COOH
v-CDs	79.59	18.66	0.82	0.93
b-CDs	70.12	24.19	2.50	3.19
g-CDs	69.62	23.37	2.47	4.54
o-CDs	41.86	51.00	1.01	6.13

(2)

Samples	Pyridinic N (%)	Amino N (%)	Pyrrolic N (%)
v-CDs	14.62	68.97	16.41
b-CDs	27.87	55.53	16.60
g-CDs	0	84.24	15.76
o-CDs	0	76.20	23.80

Table S5. PL decay lifetimes τ and the relative fluorescence intensity percentages f for CDs' ethanol solution, and χ^2 is the reduced Chi-Square value for τ_{avg}.

Sample	τ_1	f_1	τ_2	f_2	τ_{avg}	χ^2
v-CDs	2.308 ns	85.87%	8.713 ns	14.13%	3.21 ns	2.035
b-CDs	1.633 ns	0.01%	7.029 ns	99.99%	7.03 ns	1.938
g-CDs	2.005 ns	7.33%	8.741 ns	92.67%	8.25 ns	1.282
o-CDs	4.404 ns	5.05%	10.433ns	94.95%	10.13 ns	1.283

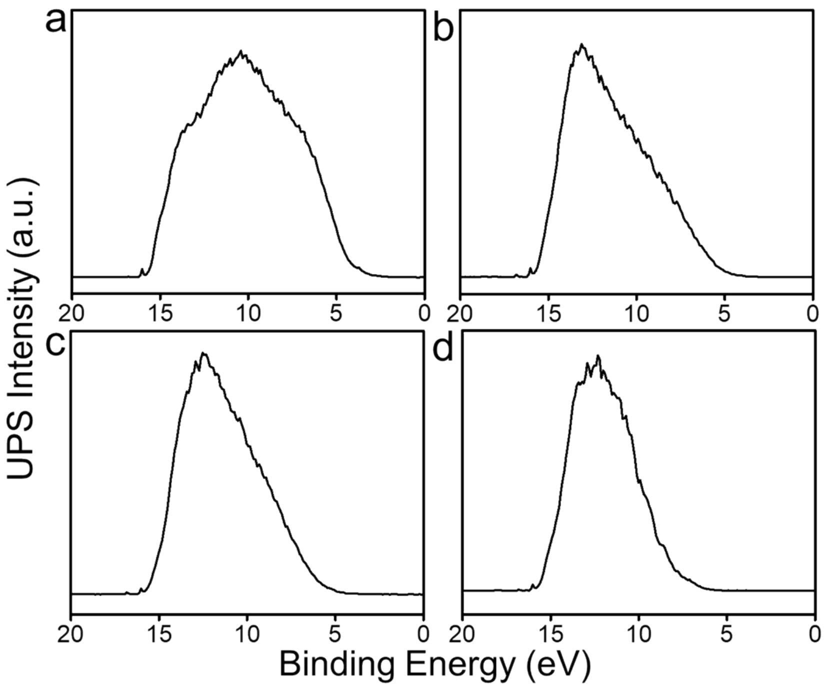


Fig. S4. UPS spectra of v/b/g/o-CDs.

Table S6. The calculation results of energy level of CDs according to UV-vis spectra and UPS spectra.

Sample	v-CDs	b-CDs	g-CDs	o-CDs
Eg (eV)	2.78	2.70	2.24	2.03
HOMO (eV)	9.55	10.75	11.36	12.22
LUMO (eV)	12.33	13.45	13.60	14.25

Energy gap is calculated by this equation:

$$E_g = \frac{hc}{\lambda_{Abs}}$$

Where h=4.13×10^{-15} eV·s and c=3×10^8 m·s^{-1}. λ_{Abs} is UV cut-off wavelength[1].

Work function is calculated by this equation:

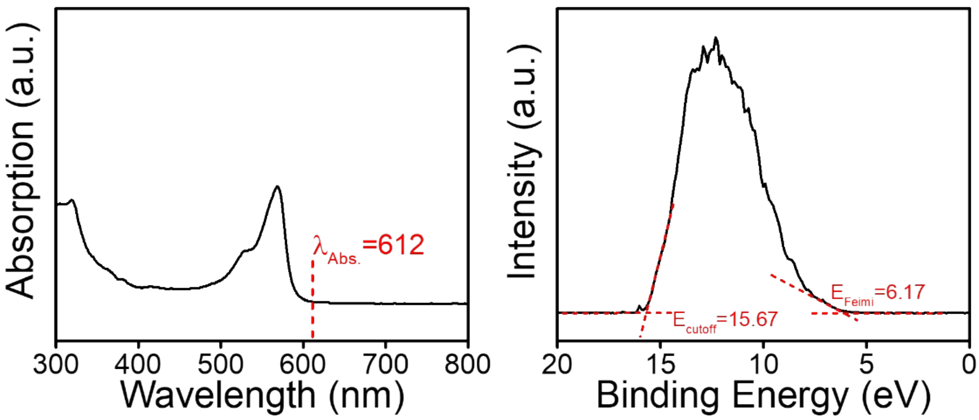
$$\Phi = h\nu - (E_{cutoff} - E_{Fermi})$$

Where hv=21.22 eV, E_{cutoff} is the cutoff of secondary electron and E_{Fermi} is the Fermi level[2].

HOMO is calculated by this equation:

$$Eg= LUMO\text{-}HOMO$$

Take o-CDs for an example:



Eg=1240/612 eV ≈2.03 eV; HOMO=21.22-(15.67-6.17) ≈12.22 eV;

LUMO=12.22+2.03 =14.25 eV

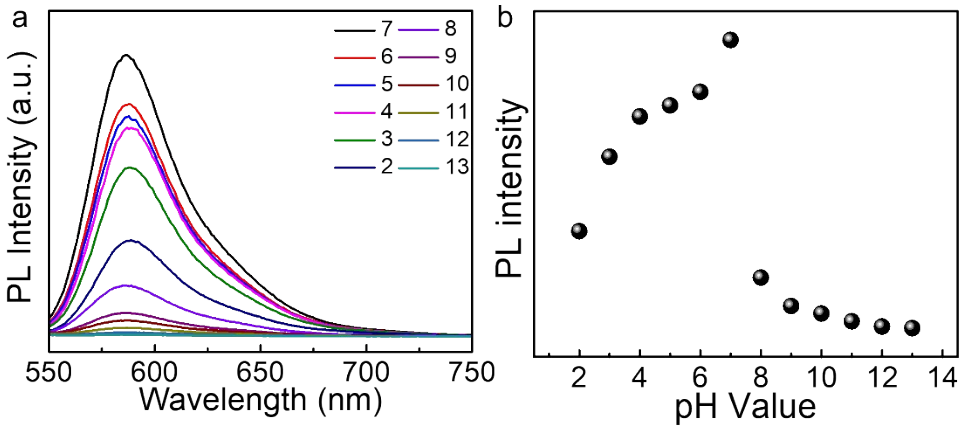


Fig. S5. (a) PL spectra (λ_{ex} = 581 nm) of o-CDs in different pH surroundings; (b) The relationship between PL intensity and pH value.

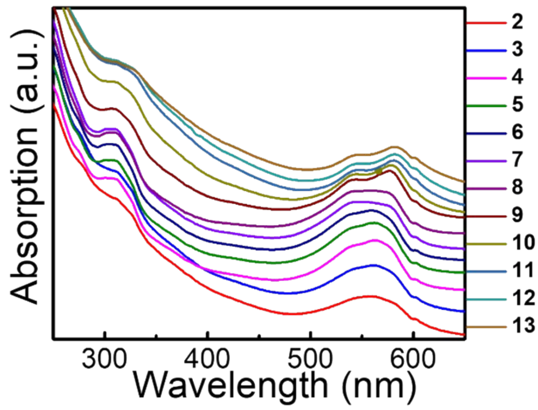


Fig. S6. UV−Vis absorption spectra of o-CDs in different pH surroundings

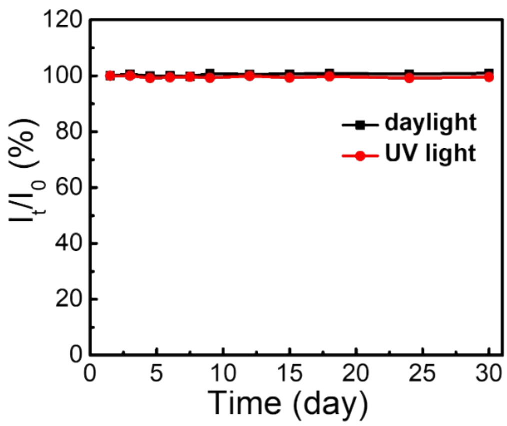


Fig. S7. The photostability of o-CDs ethanol solution under continuous radiation with daylight and 365 nm UV light for one month.

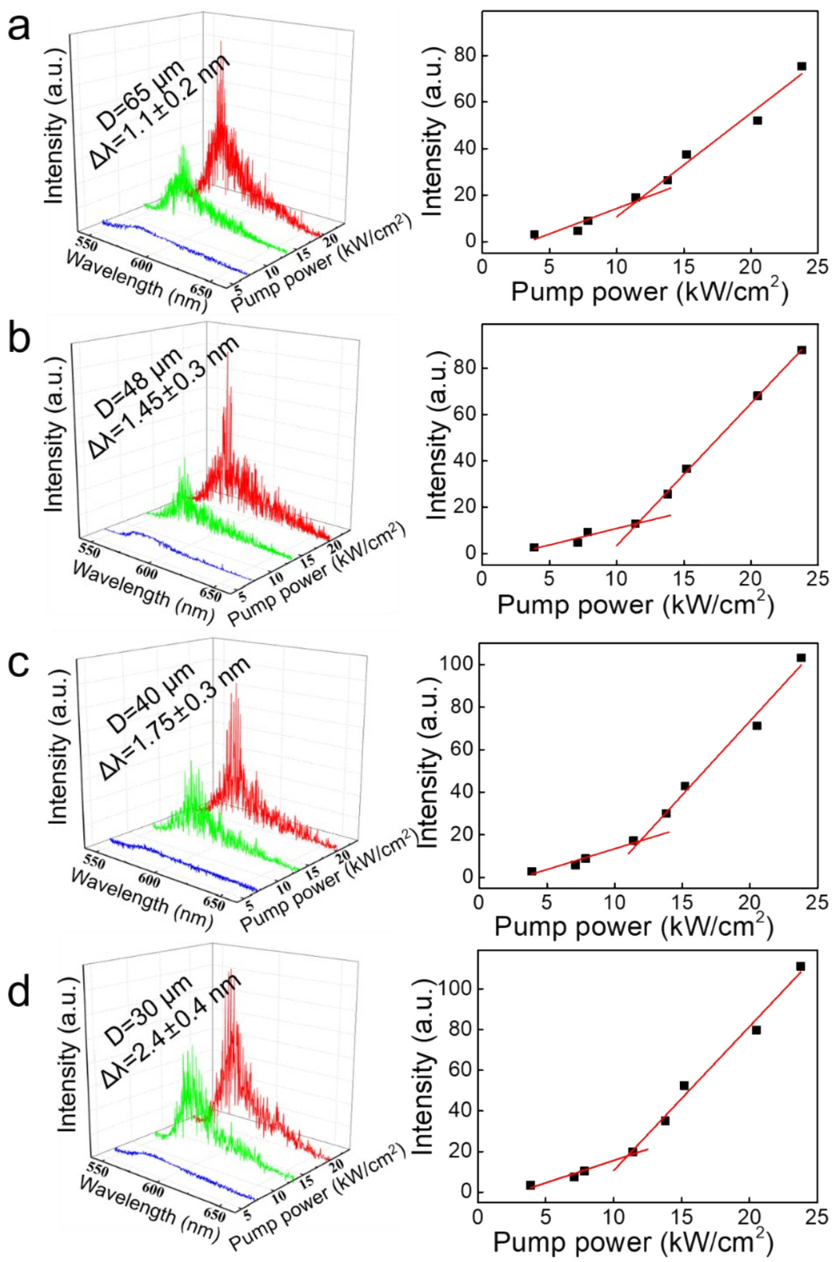


Fig. S8. Lasing spectra of the microcavity and plot of lasing intensity to different pump powers with different diameters D of 65 μm (a), 48 μm (b), 40 μm (c), 30 μm (d).

References

[1] Sista, P.; Hao, J.; Elkassih, S.; Sheina, E.; Biewer, M.; Janesko, B.; Stefan, M. Synthesis, characterization, and computational modeling of benzodithiophene donor–acceptor semiconducting polymers. *J. Polym. Sci. Polym. Chem.* **2011**, 49, 4172-4179.

[2] Zhong, J.; Qin, X.; Zhang, J.; Kera, S.; Ueno, N.; Wee, A.; Yang, J.; Chen, W. Energy level realignment in weakly interacting donor-acceptor binary molecular networks. *ACS Nano* **2014**, *8*, 1699-1707.