Electronic Supplementary Information

Bright, Stable, and Tunable Solid-State Luminescence of Carbon Nanodot Organogels

Zhixing Gan,^{*a,b,**} *Lizhe Liu*,^{*b,*} *Li Wang*,^{*c*} *Guangsheng Luo*,^{*c*} *Chunlan Mo*,^{*c*} *and Chenliang Chang*^{*a*}

a. Key Laboratory of Optoelectronic Technology of Jiangsu Province, School of Physics and Technology, Nanjing Normal University, Nanjing 210023, China. *E-mail: zxgan@njnu.edu.cn*

b. Collaborative Innovation Center of Advanced Microstructures, National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China.

c. School of Materials Science and Engineering, Nanchang University, Nanchang 330031, China



S1. (a) Schematic illustration of the formation of organogels embedded with CNDs. The citric acid (CA) melted to liquid firstly. As temperature increased and heating continued, a part of the CA polymerized to form carbon nanostructures, which were dispersed in the liquated CA. After cooling down, the liquated CA cured to form transparent organogel and CNDs were embedded in the organogel. (b) Contrast experiment was performed to prove the fluorescence does not come from the organogel. The CA was heated to 200 °C. After the CA was liquated, the heating was stopped immediately. In this situation, it is supposed that little CND formed in the

organogel due to the low processing temperature and short heating time. And no remarkable fluorescence can be detected in that organogel without CNDs.

	Reactants in preparation		Elemen	tal fraction	n of the	obtained
	(mg)		nanodots (at%)			
	Citric acid	L-cysteine	С	0	Ν	S
CND	2000	0	66.12	32.97	0.67	0.24
N,S-CND-1	2000	200	67.68	28.36	2.56	1.4
N,S-CND-2	2000	400	66.73	29.15	2.67	1.45
N,S-CND-3	2000	600	69.06	23.54	4.35	3.05

S2 Table. Details of sample preparation and elemental fractions based on XPS results.



S3. Locally enlarged PL (a) and PLE (b) spectra corresponding to the selected regions of Fig. 4b and ESI S4b, respectively.



S4. (a-d) PLE spectra of aqueous solutions of CNDs (a), N,S-CND-1 (b), N,S-CND-2 (c), and N,S-CND-3 (d). To display the weak peak more clearly, an enlargement of the marked area in (b) is shown in ESI S3b. (e-h) PLE spectra of solid organogels of CND (e), N,S-CND-1 (f), N,S-CND-2 (g), and N,S-CND-3 (h).



S5. PL (a,c,e,g) and PLE (b,d,f,h) spectra of CND aqueous solutions with different concentrations. The concentration is c (a,b), c/2 (c,d), c/4 (e,f) and c/16 (g,h). If the concentration further decreases to c/32 or c/64, PL and PLE spectral profiles remain unchanged except for decreased intensities.



S6. PL spectra of CND solutions with different concentrations under excitation of 380 (a) and 480 nm (b). (c) Peak intensity of emissions excited at 380 nm *versus* concentration. (d) PL decay curves of CND solutions with different concentrations, excitation wavelength: 405 nm and monitoring wavelength: 450 nm.

Concentration	CND	N,S-CND-3	N,S-CND-3	
Concentration	450 nm (ESI, S6d)	450 nm (Fig. 5d)	520 nm (Fig. 5e)	
С	7.06 ns	7.02 ns	9.18 ns	
<i>c</i> /2	7.81 ns	7.87 ns	9.18 ns	
c/4	9.64 ns	9.63 ns	9.18 ns	
c/16	10.96 ns			

S7. Table. Lifetime parameter fitted by a mono-exponential decay function.



S8. PL (a,c,e,g) and PLE (b,d,f,h) spectra of N,S-CND-3 aqueous solutions with different concentrations. The concentration is c (a,b), c/2 (c,d), c/4 (e,f) and c/16 (g,h).



S9. (a) PLQYs of CND aqueous solutions and CND solid organogels. (b) PLQY of CND aqueous solutions with different concentrations under excitation of 370 nm. When the concentration increases from c/32 to 2c, the PLQY increases first and then decreases. In the concentration range of c/16 to 2c, PLQY monotonically decreases with increasing concentration, confirming the strong concentration induced PL quenching. (c) The calculated relationship between photon escaping probability (η_{esc}) and external PLQY (η_{ext}), when assuming the internal PLQY $\eta = 0.5$.

Taking into account of photon reabsorption, the external PLQY (η_{ext}) can be estimated as follow [*Nat. Commun.* **2016**, 7, 13941]:

$$\eta_{ext} = \eta_{esc} \cdot \eta + (1 - \eta_{esc}) \cdot \eta^2 \cdot \eta_{esc} + (1 - \eta_{esc})^2 \cdot \eta^3 \cdot \eta_{esc} + \cdots$$
$$= \eta_{esc} \cdot \eta \sum_{k=0}^{\infty} (1 - \eta_{esc})^k \cdot \eta^k = \frac{\eta_{esc} \cdot \eta}{1 - \eta + \eta_{esc} \cdot \eta}$$

where η_{esc} is the probability that an emitted photon will leave the solution before reabsorption, the higher η_{esc} value means lower photon reabsorption degree. And η is the internal PLQY without photon reabsorption. For example, assuming the $\eta_{esc} = 0.2$ and $\eta =$ 0.5, the external PLQY is only 16.7%. According to this euqation, the calculated relationship shows that external PLQY decreases when photon reabsorption increases, in agreement with trend of experimental results (from c/16 to 2c). Therefore, there is a trade-off between the emission wavelength and PLQY. Strong photon reabsorption is required for long-wavelength emission, but leading to a loss of PLQY.



S10. Normalized PL spectra of the N,S-CND-3 aqueous solutions with different concentrations under excitation of 300 nm. Upon the concentration increases, the emission at 420 nm drops down while the emissions at 520 to 650 nm remarkably increase, clearly indicating the concentration induced reabsorption.



S11. Absorption spectra of CND and N,S-CND aqueous solutions. All the solutions have an identical concentration of c/4. Normally, the two main absorption bands at about 240 and 350 nm are attributed to π - π * transitions of C=C and n- π * transitions of C=O transitions, respectively. However, recent research suggested that both π - π * and n- π * transitions contribute to the main absorption band at ~350 nm, contrary to common assignment of exclusive n- π * transition [J. Phys. Chem. Lett. 2017, 8, 1044–1052]. Additionally, the generally perceived core-state transition at ~250 nm, involving sp²-networked carbogenic domains shielded from external needs to be reassessed because it fails to explain the observed fluorescence quenching and spectral shift.



S12. The size distribution and carbonization degree were controlled by changing the reaction time of pyrolysis. After CA was liquated. Heating was continued and kept for 10, 15, and 20 min, the acquired samples were designated as CND-10 min, CND-15 min, and CND-20 min, respectively. (a-c) Size distributions of CND-10 min (a), CND-15 min (b), and CND-20 min (c). (d-f) PL spectra of CND-10 min (d), CND-15 min (e), and CND-20 min (f) solutions. (g) the most probable size and maximum PL position as a function of reaction time. (h) Normalized PL spectra of CND-10 min, CND-15 min, and CND-20 min solutions excited at 400 nm.

Dynamic light scattering (DLS) measurements were performed to estimate the size distribution (Malvern Zetasizer Nano-ZS). The results show that the particle sizes monotonously increase with reaction time (a-c). It is expected that carbonization degree also increases along with the size. Thus, the strongest bands of the PL spectra redshift with the heating time (d-f). The most probable size and maximum PL position as a function of reaction time are plotted in (g). When the concentration kept constant, the maximum PL only tunable from 450 to 500 nm. Furthermore, when excited by an identical wavelength, different samples almost emitted at the same wavelength (h). It indicates that the Stokes-shift is independent on the size and carbonization degree.

Firstly, CNDs and N,S-CNDs presented in the main text were synthesized under the same conditions. Due to the aggregations, the sizes cannot be compared directly. The elemental contents based on XPS results (ESI, S2) manifests the carbon contents in different samples are very close, suggesting the divergence in carbonization degree is small. Thus, it is reasonable to speculate the difference in PL emission caused by carbonization degree and size is also tiny. Secondly, Fig 3a shows that CNDs, and N,S doped CNDs emit different colors identically excited at 400 nm. The Stokes-shift gradually increases from CND to N,S-CND-3. Therefore, the modulated fluorescence of the N,S-CNDs is caused by the higher aggregation degree, rather than the increased particle size or carbonization degree.



S13. PL intensities of CND organogel with exposure to a continuous UV lamp (365 nm, 2 W). The integrated PL intensity drops by less than 5% after 3 h irradiation. In additional, the CND organogels also exhibit good chemical stability. After storing for three months, the PL spectra of the samples are rechecked. Both PL intensities, peak positions, and spectral shapes remain unchanged.



S14. (a) Diagram illustrating the fabrication of a LED by the color converting cover and emitting diode chip. (b) photograph of the covers filled with CNDs and N,S-CND gels excited by a UV lamp (365 nm) and LED operated at a current of 350 mA. (c-e) EL spectra of three LED operating at different currents. Blank represent the cover is empty without any carbon nanodots. (f-h) Peak positions (f), illuminance (g), and conversion efficiency (h) *versus* operating current, respectively.



S15. The chromaticity coordinates of the LED in CIE (Commission Internationale de l'Éclairage) color space.

Device fabrication and test: LED were fabricated based on semi-finished commercial products. The liquated organogels containing luminescent CNDs were injected into the transparent covers directly. Then the covers were encapsulated over the diode chips. A DC source was used to drive the chips. The light output was measured by an integrating sphere (ISP 250) connected to an array spectrometer (CAS 140CT) from Instrument Systems.

As illustrated in S14a, the electroluminescent (EL) diode chip emits at 400 nm. A cover injected with organogel is encapsulated upon the diode chip. S14b shows that the covers filled with CND and N,S-CND gels exhibit fluorescence from blue to green. However, the fluorescent intensity evidently drops due to the deterioration in transmittance. Herein, three of them are fabricated to prototype LED and the photograph of the LED operated at a current of 350 mA is shown in S14b. The EL spectra of the three LED are shown in S14c-e, respectively. The peak positions and illuminance *versus* operating current are plotted in S14e and f. The emission wavelength keeps constant and the illuminance increases with operating current. The emission

wavelength can be tuned to a longer wavelength by simply increasing the doping concentration, however, with an evident decline in intensity. The chromaticity coordinates in CIE (Commission Internationale de l'Éclairage) color space is depicted in S15. The efficiency of the color converting layer is plotted in S14g. The conversion efficiency is calculated as

$$\eta = EQE_{with \ cover} / EQE_{without \ cover},\tag{1}$$

where EQE = Luminescent power/Electrical consumption power. The conversion efficiency of CNDs (LED-1,2) is about 12%, consistent with the PLQY. While the conversion efficiency of N,S-CND-3 (LED-3) is 3%, which is much lower than the PLQY measured by a backscattering geometry due to the poor transparency. More characterization on the device and improvement of the performance will be conducted in our future work.