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Supporting Information

Room Temperature Phosphorescence from Moisture-Resistant and Oxygen-Barred Carbon Dot Aggregates

Yonghao Chen, Jiangling He, Chaofan Hu, Haoran Zhang, Bingfu Lei, and Yingliang Liu**

Experimental Section

Materials

All reagents were used as received without further purification. The EDA and ethanol are analytical pure reagents. The degree of polymerization of PVA is 1750 ± 50.

Synthesis of NCD Powder

PVA (1 g) was dissolved in deionized water (20 mL) and then EDA (0.75 mL) was dropped into this solution. The mixture was then transferred to a Teflon autoclave (volume of 30 mL) and hydrothermal treatment was carried out at 220 ^{o}C for 10 hours. After this reaction, the brown suspension was obtained and then a certain amount of acetone was added to precipitate the excess PVA. The precipitation of PVA was removed by centrifugation (12000 rpm) and then the transparent solution was further purified by dialysis (the molecular weight cutoff is 1000 Da) in deionized water. The yellow NCD powder was obtained by freeze-drying of this NCD solution.

Synthesis of PVA_{220} Powder

PVA (1 g) was dissolved in deionized water (20 mL). The mixture was heated at 220 ^{o}C for 10 hours in a Teflon autoclave (volume of 30 mL). After this reaction, the brown suspension was obtained and then a certain amount of acetone was added to precipitate the excess PVA. The precipitation was removed by centrifugation (12000 rpm) and then the transparent solution was further purified by dialysis (the molecular weight cutoff is 1000 Da) in deionized water. The grey PVA_{220} powder was obtained by freeze-drying of this PVA_{220} solution.

Synthesis of NCD/PVA film

PVA (1g) was dissolved in NCD aqueous solution (20 mL, 0.5 mg mL^{-1}) and under stirring at 80 ^{o}C for 1 hour. The mixture was then casted on a mold and placed in an oven of 60 ^{o}C to form the film.

Characterization.

Transmission electron microscopy (TEM) images were taken in a FEI Tecnai12 transmission electron microscope. Scanning electron microscopy (SEM) images were carried out using a XL-30-ESEM (FEI). The UV-Vis absorption spectra were collected in an ultraviolet-visible spectrofluorometer (UV-2550, Shimadzu). Photoluminescence spectra and phosphorescence decay curves were measured by a fluorescence spectrofluorometer (F-7000, Hitachi). The thermogravimetric-differential thermal analysis (TG-DTA) was carried in a DTG-60 (Shimadzu). The Brunauer-Emmett-Teller (BET) was carried out by an automatic volumetric sorption analyzer (ASAP 2020, Micromeritics Instrument Corp).

Table S1. Exponential fitting results of phosphorescence decay.

Sample	A_1	t_1 (ms)	A_2	t_2 (ms)	R^2	t_{ave} (ms)
NCD	0.58356 ± 0.00139	1.70290 ± 0.00824	0.37412 ± 0.00137	15.45885 ± 0.07124	0.99863	13.4
PVA_{220}	0.57882 ± 0.00098	42.90458 ± 0.21711	0.40337 ± 0.00101	2.19575 ± 0.01214	0.99834	41.5

The double exponential equation:

$$I = A_1 \times e^{-t/t_1} + A_2 \times e^{-t/t_2}$$

Where I is the intensity; t is the time; t_{ave} is the average lifetime; t_1 and t_2 are the lifetimes, and A_1 and A_2 are the amplitudes of each component.

Table S2. Fitting results of phosphorescent and fluorescent response to temperature.

Sample	I_0	A	T_0 (°C)	R^2
Phosphorescence	0.32762 ± 0.01481	3.66107 ± 0.47659	17.48198 ± 1.34392	0.99097
Fluorescence	1.29864 ± 0.01136	-0.00948 ± 0.00018	\	0.99566

The double exponential equation for phosphorescence:

$$I = I_0 + A \times e^{-T/T_0}$$

The linear equation for fluorescence:

$$I = I_0 + A \times T$$

Where I is the intensity; T is temperature; I_0, T_0 and A are constants.

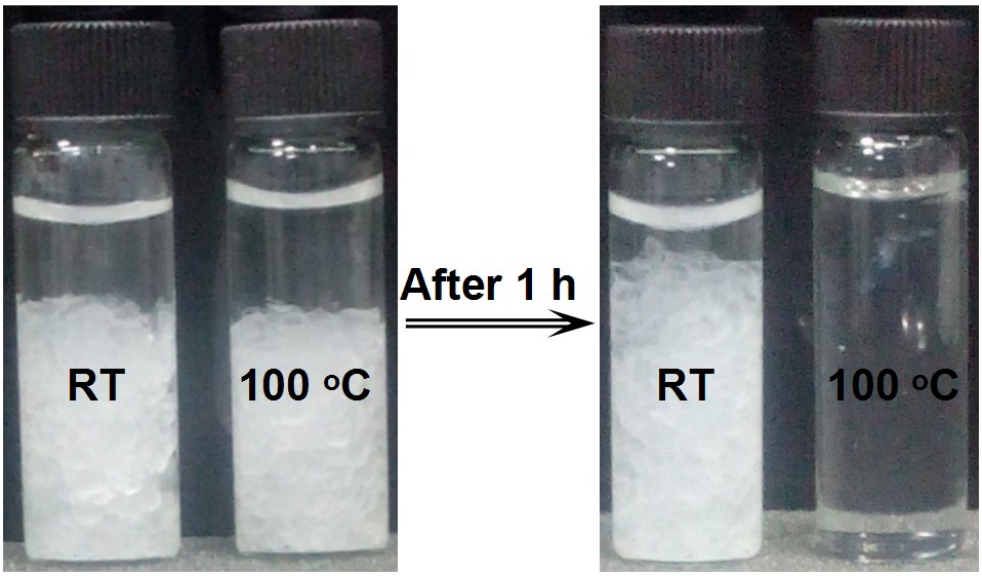

Fig. S1. Photographs of the behaviors of PVA in water at room temperature (RT) and 100 °C. The former just swelled even though it stayed in water for 1h. The latter was placed into an oven of 100 °C for 1h, it dissolved as transparent viscous solution.

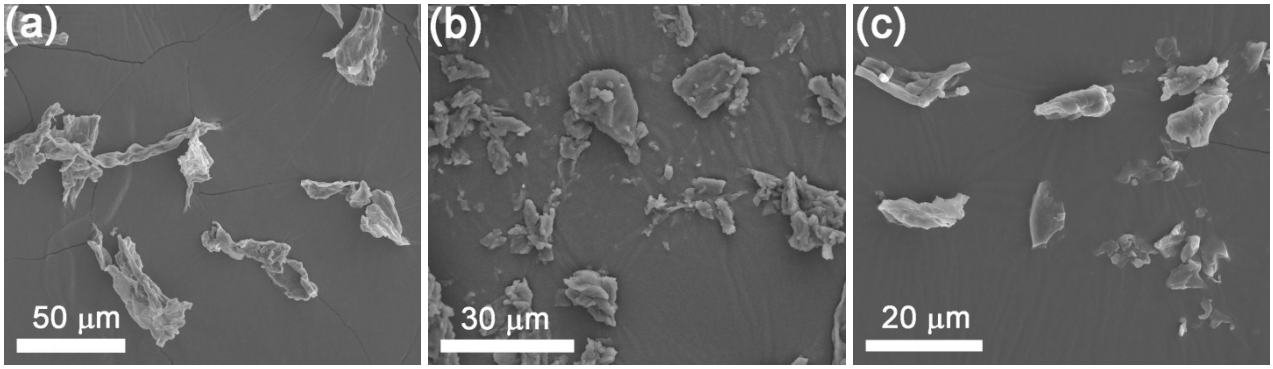

Fig. S2. SEM images of NCD powder (a) under 25 % RH, and (b) under 85% RH, and (c) after drying at 65 ^{o}C from (b).

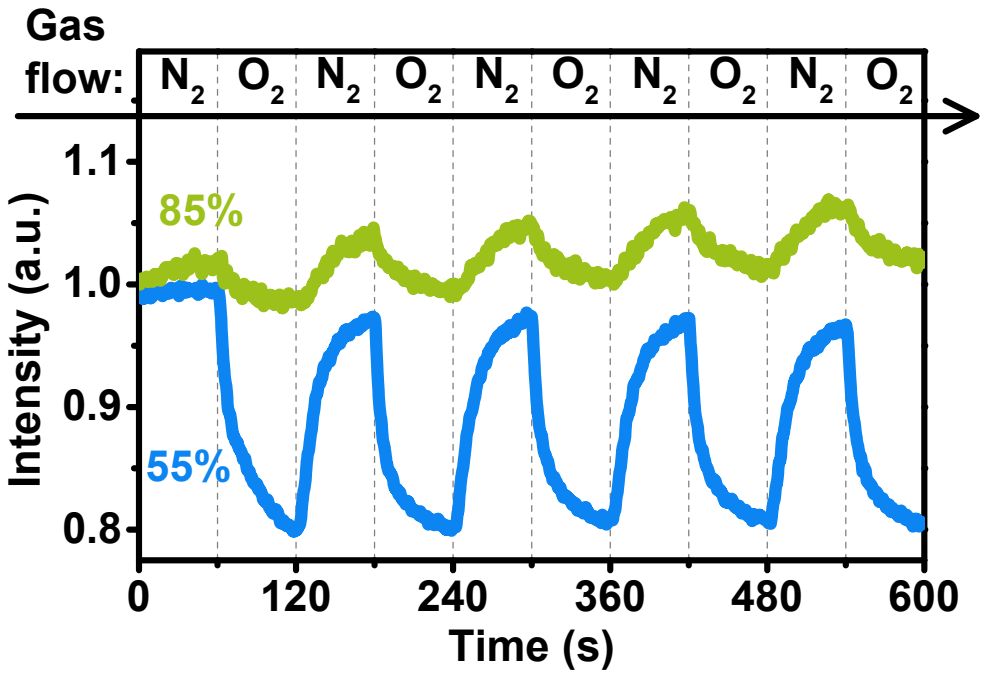

Fig. S3. Nitrogen-oxygen responsive curves of NCD Powder after being placed at 55% RH and 85% (15^{o}C) for four days.

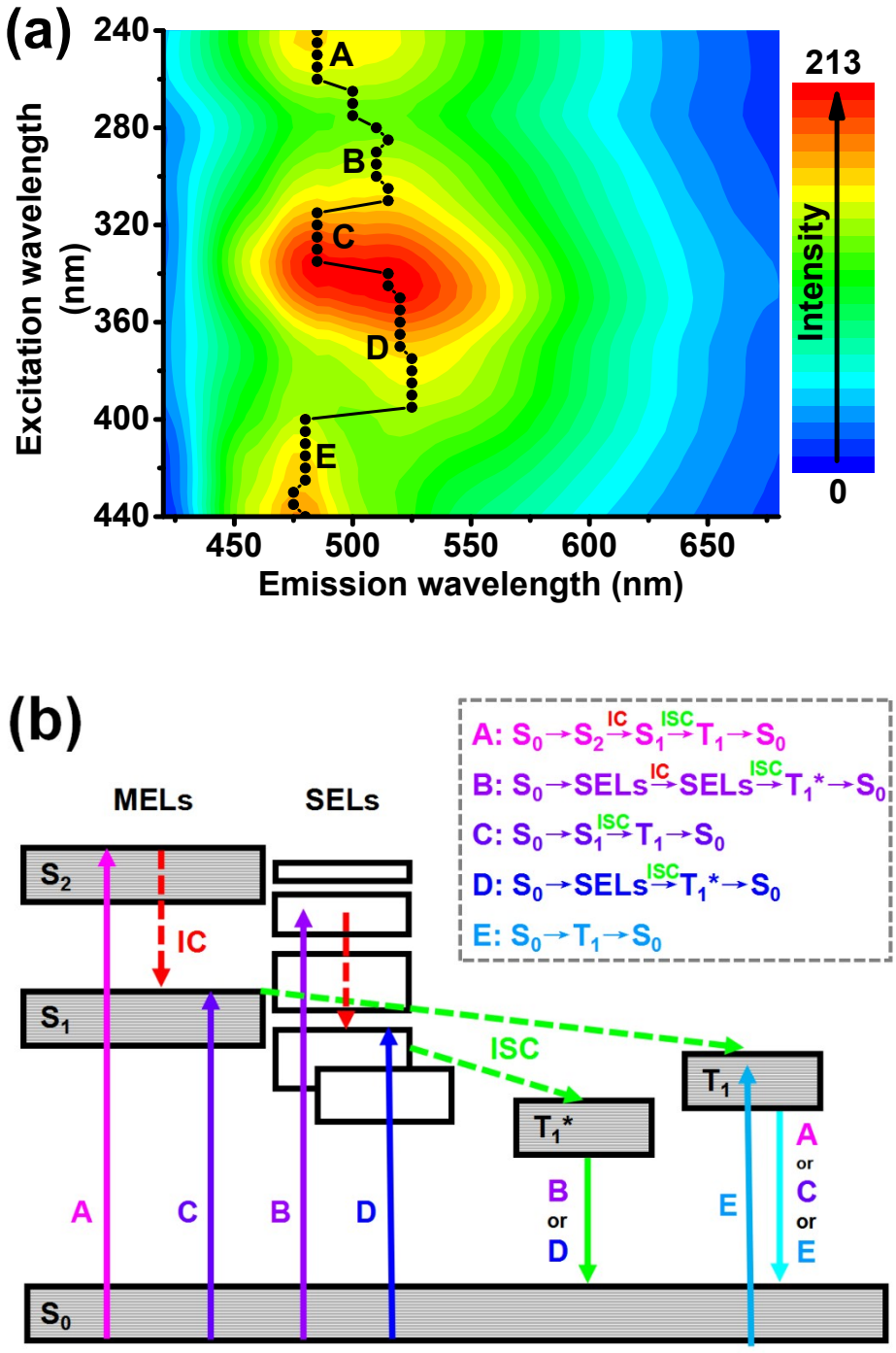

Fig. S4. (a) RTP isoline spectra of NCD/PVA composite. Dotted profile: the maximums of emission corresponding to different excitation wavelengths. (b) Jablonski Diagram: the mechanism of (a). A-E indicates the electron transition pathway related to different absorption. Red dash arrows: internal conversion (IC). Green dash arrows: intersystem crossing (ISC). Up and down arrows: absorption and fluorescence, respectively.

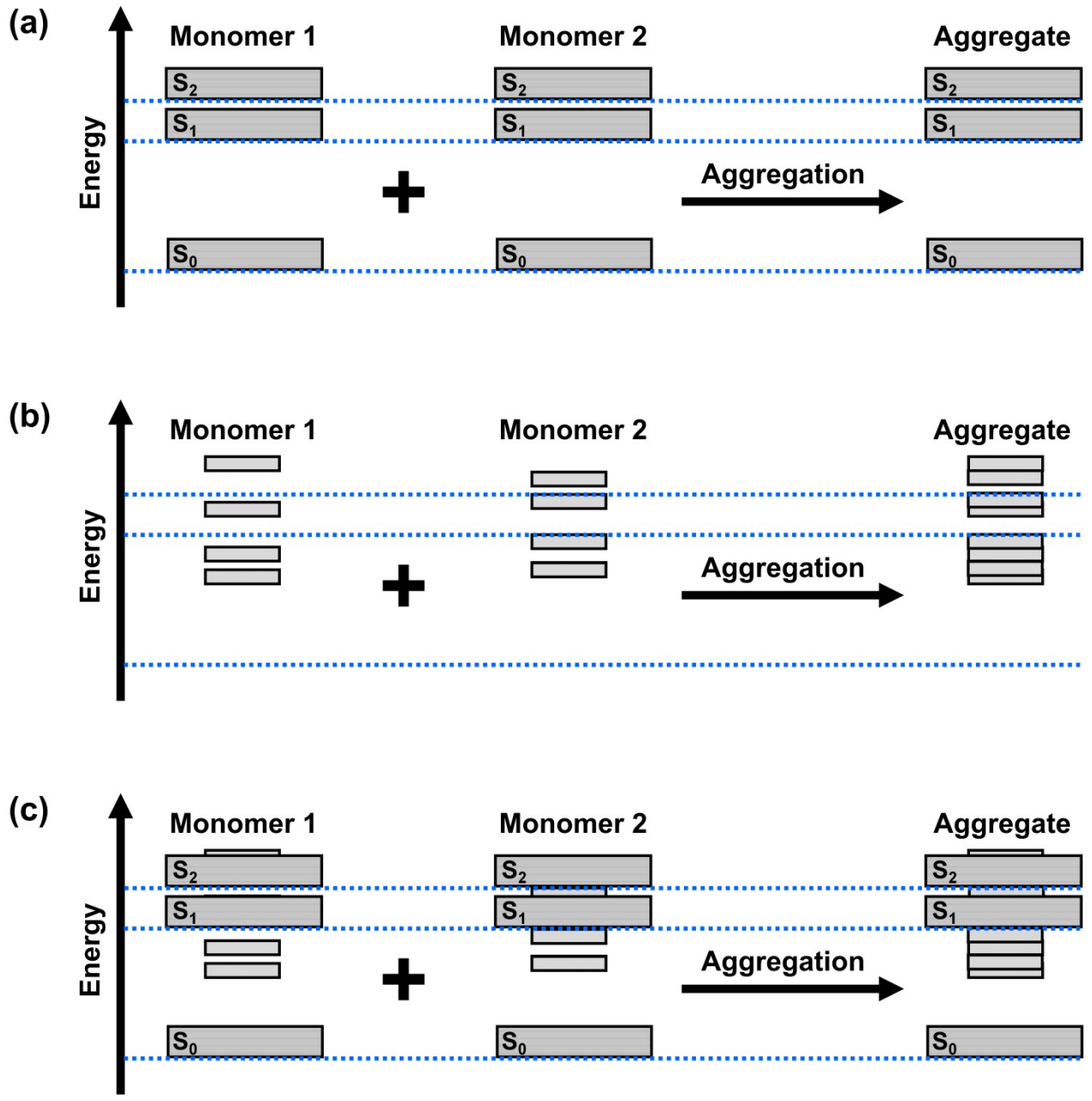

Fig. S5. Respective integration of (a) MELs and (b) SELs after NCD monomers aggregating. (c) The merged behavior of (a) and (b) which probably occurs in NCD aggregates.

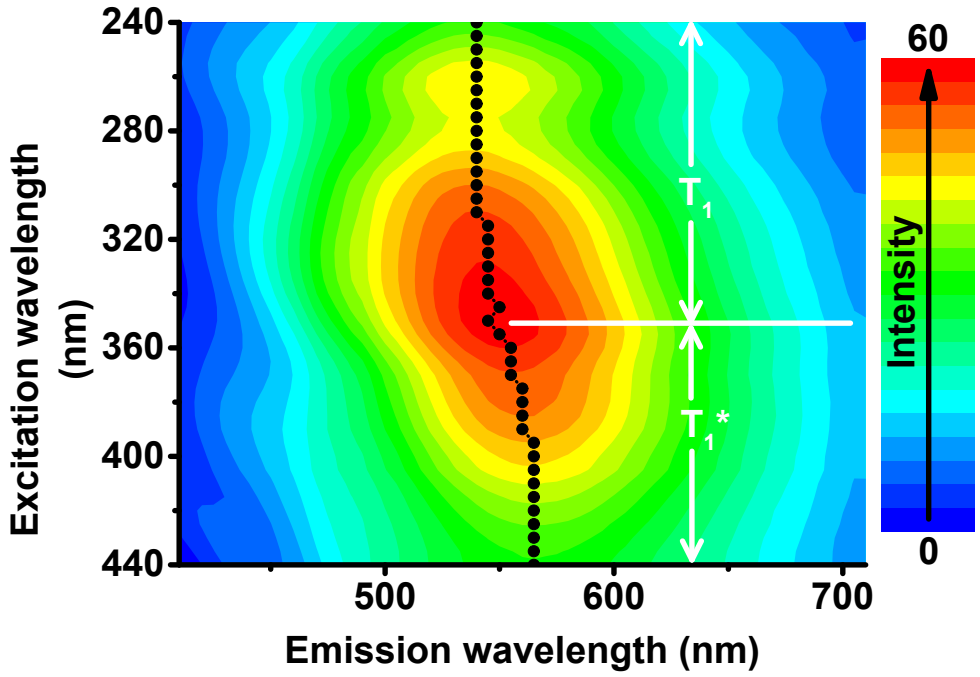

Fig. S6. RTP isoline spectra of PVA_{220} powder. Dotted profile: the maximums of emission corresponding to excitation wavelengths.