Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supplementary Information

## Searching for the True Origin of the Red Fluorescence of Leaves-Derived Carbon Dots

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## Experimental

*Chemicals*

Camphor leaves, hellebore leaves, oleander leaves, clover leaves and bamboo leaves were picked in Southeast University (Nanjing, China). Chlorophyll ab mixture was purchased from Nanjing Dulai Biotechnology Co., Ltd (Nanjing, China). Anhydrous ethanol (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd (China). Deionized water (18.1 MΩ cm) was obtained using the Milli-Q water purification equipment.

*Characterization*

Transmission electron microscopy (TEM) images were obtained using a Talos F200X microscope operating at 200 kV. Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Tensor 27 ATR-FTIR spectrometer with KBr pellets. X-ray photoelectron spectroscopy (XPS) was carried out with Thermo ESCALAB 250XI instrument. The decomposition temperature thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209F3 thermogravimetric analyzer under a nitrogen atmosphere from room temperature to 600 ℃ with a heating rate of 10 ℃/min. UV-vis absorption spectra were performed with a Shimadzu UV-2600 spectrometer. Photoluminescence (PL) spectra were collected using a Horiba Fluoromax-4 fluorescence spectrophotometer. Raman spectra were obtained on a Horiba Scientific LabRAM HR Evolution *via* a microspectrometer with an excitation wavelength of 785 nm laser. PL lifetimes were collected on FLS 1000. Absolute QY was measured on FLS

1000 with an integrating sphere.

*Preparation of c-CD$_{180}$/c-CD$_{200}$/c-CD$_{280}$*

Fresh camphor leaves were cleaned to remove mud, dried in an oven at 100 ℃ for 1 h and ground into fragments by a micromill while still hot. Than 0.20 g smashed leaves were scattered in 30 mL anhydrous ethanol and transferred to a poly (tetrafluoroethylene) lined autoclave (50 mL). The solvothermal reaction was performed in an oven at 180 ℃ for 6 h (named *c*-CD$_{180}$, 180 represents reaction temperature). After cooling down to room temperature, the products were purified by silica column chromatography using ethanol as the eluent. The solvent removal *via* rotary evaporation and drying under vacuum. 0.20 g smashed leaves and 30 mL anhydrous ethanol were added into a 50 mL autoclave and heated to 200 ℃ for 10 h (named *c*-CD$_{200}$). 0.20 g smashed leaves and 20 mL deionized water were transferred into a flanged stainless steel reactor liner (25 mL) and heated to 280 ℃ for 10 h (named *c*-CD$_{280}$). The subsequent purification and drying steps for *c*-CD$_{180}$ were equally applicable to *c*-CD$_{200}$ and *c*-CD$_{280}$.

*Preparation of chlorophyll-CD$_{180}$/chlorophyll-CD$_{200}$/chlorophyll-CD$_{280}$*

0.10 g chlorophyll ab were scattered in 30 mL anhydrous ethanol and transferred to a poly (tetrafluoroethylene) lined autoclave (50 mL). The solvothermal reaction was performed in an oven at 180 ℃ for 6 h (named *chlorophyll*-CD$_{180}$). 0.10 g chlorophyll ab and 30 mL anhydrous ethanol were added into a 50 mL autoclave and heated to 200 ℃ for 10 h (named *chlorophyll*-CD$_{200}$). 0.10 g chlorophyll ab and 20 mL deionized

water were transferred into a flanged stainless steel reactor liner (25 mL) and heated to 280 ℃ for 10 h (named *chlorophyll*-$CD_{280}$). After the *chlorophyll*-$CD_{180}$, *chlorophyll*-$CD_{200}$ and *chlorophyll*-$CD_{280}$ solution were cooled to room temperature, the subsequent purification and drying steps were as shown above, respectively.

*Preparation of various ethanol dispersions*

Fresh and withered camphor leaves, hellebore leaves, oleander leaves, clover leaves and bamboo leaves were cleaned to remove mud, dried in an oven at 100 ℃ for 1 h and ground into powder while still hot, respectively. 0.02 g of each of the above powder was added in 6 mL of anhydrous ethanol to make different ethanol solution, respectively. And the ethanol solution of chlorophyll ab was prepared by directly dispersing 0.02 g of chlorophyll ab powder into 6 mL anhydrous ethanol.

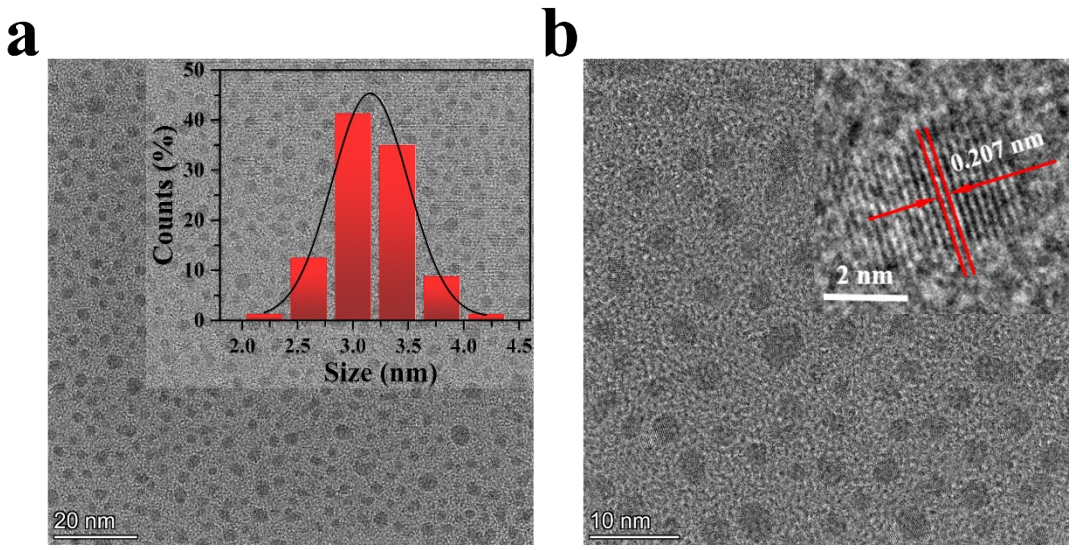


**Fig. S1** (a) TEM image and corresponding dots diameter distribution histogram of *c*-$CD_{180}$. (b) HRTEM image of *c*-$CD_{180}$.

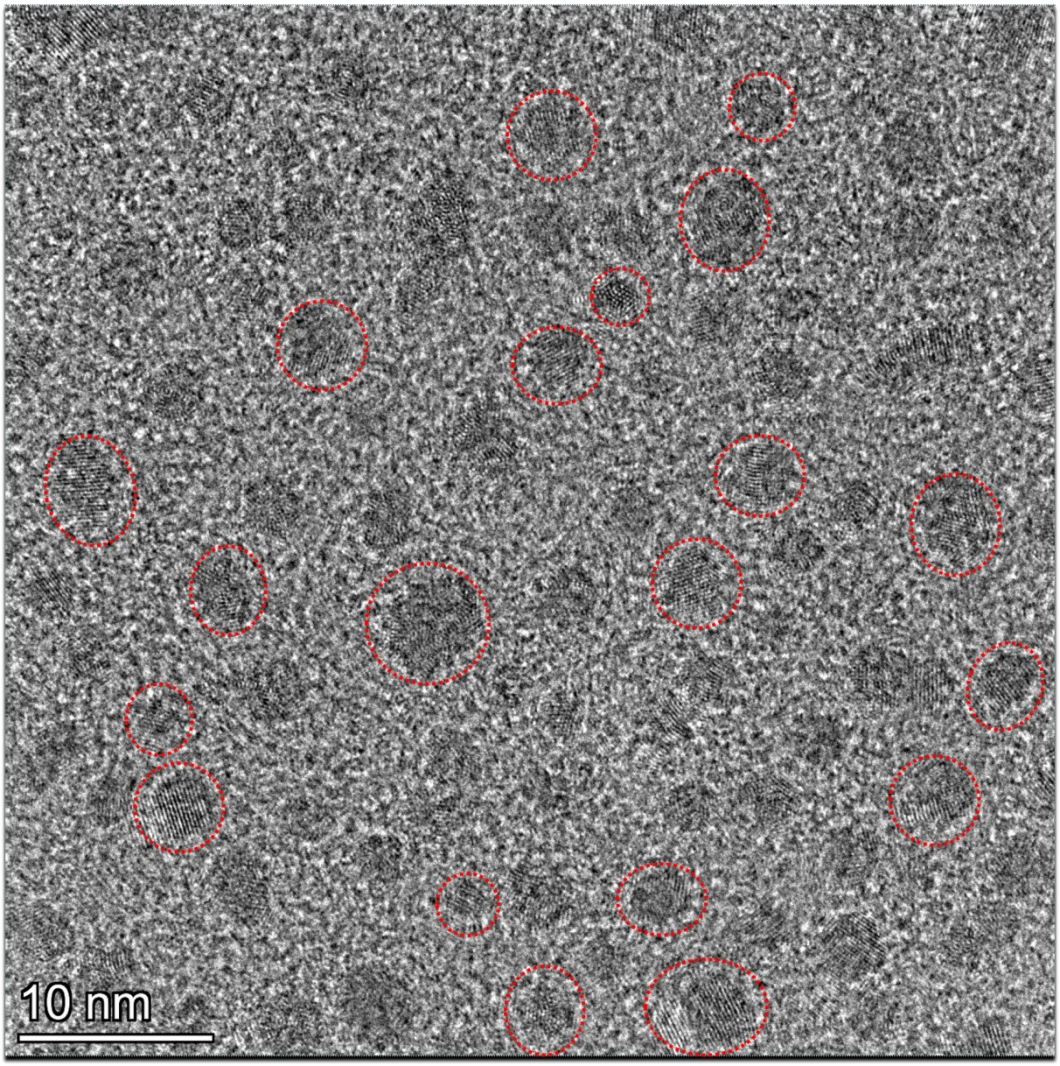


**Fig. S2** The enlarged TEM image of *c*-$CD_{180}$.

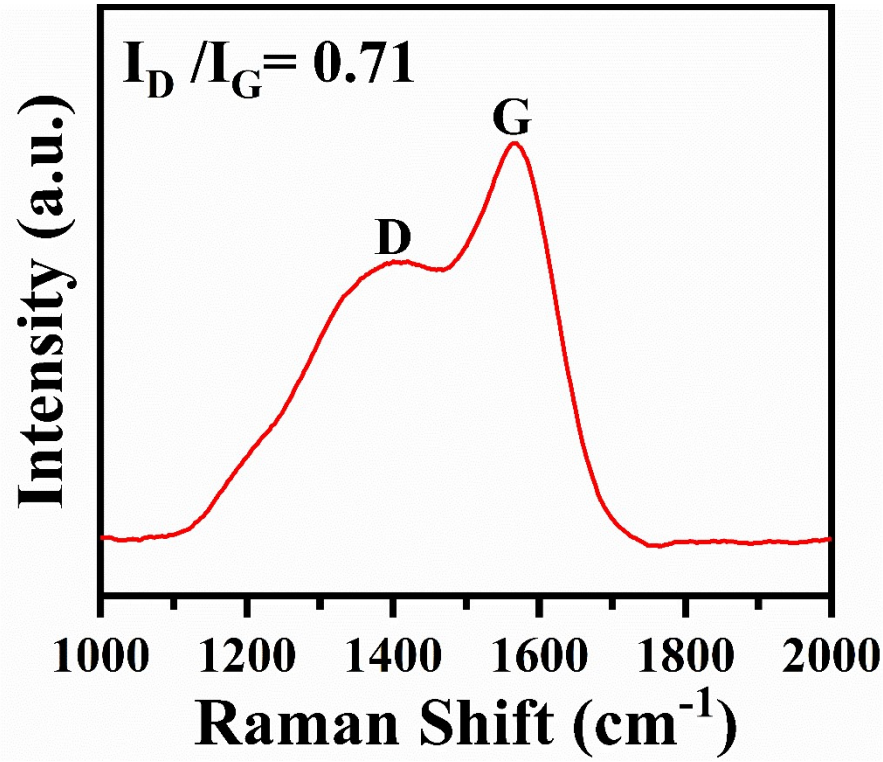


**Fig. S3** Raman spectrum of the *c*-$CD_{180}$.

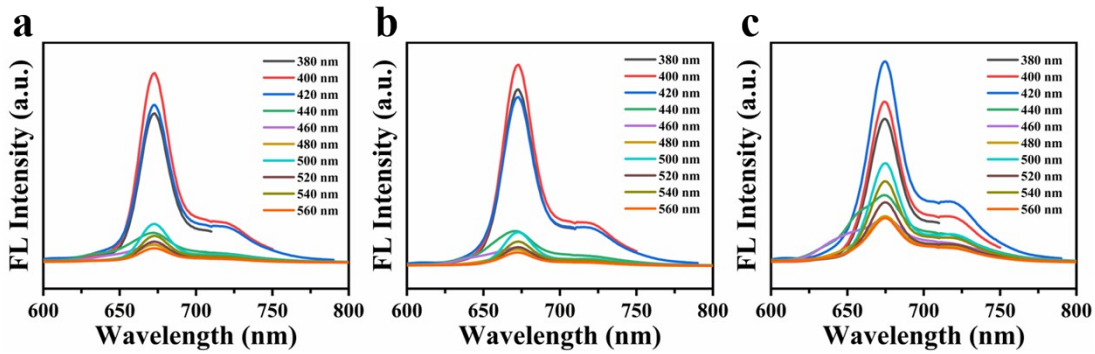


**Fig. S4** Fluorescence spectra of (a) 0.05 g camphor leaves, (b) 0.1 g camphor leaves and (c) 0.4 g camphor leaves in ethanol solution after solvothermal reaction at 180 ℃ for 6 h.

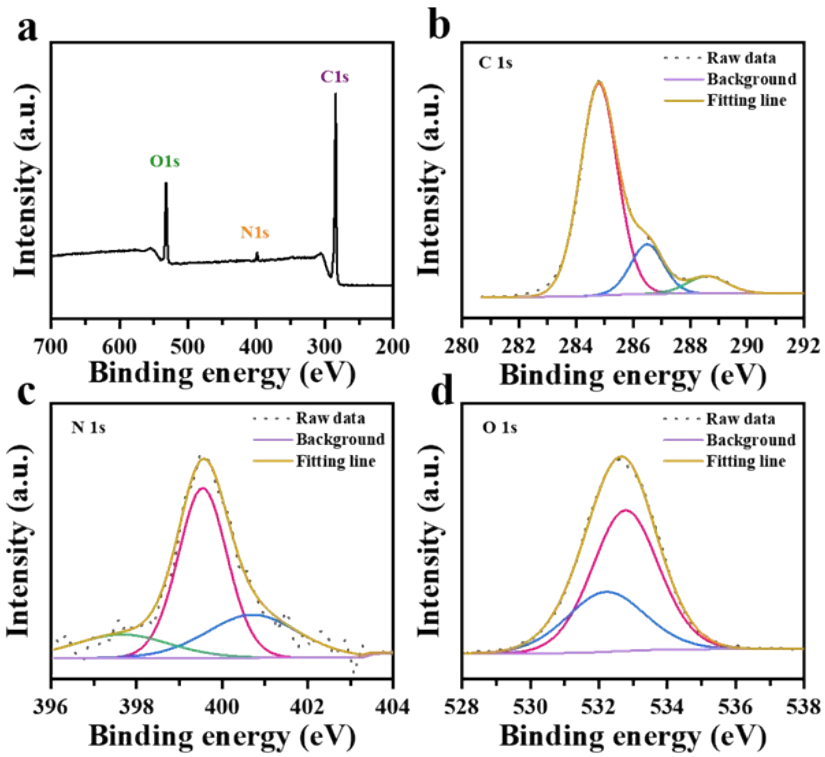


**Fig. S5** The full XPS spectrum (a), high-resolution (b) C 1s, (c) N 1s and (d) O 1s spectra of camphor leaves powder.

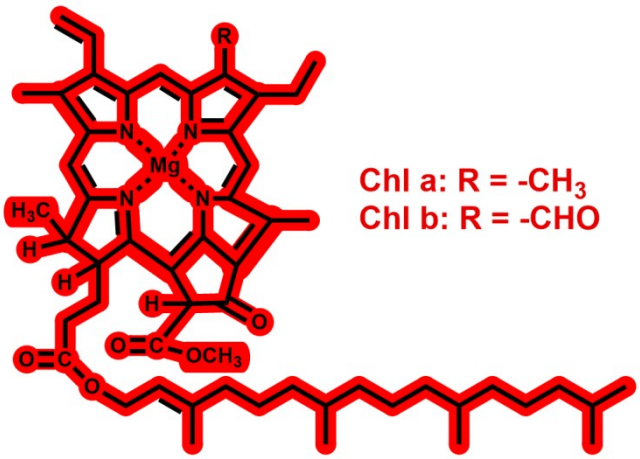


**Fig. S6** Molecular structure of chlorophyll ab.

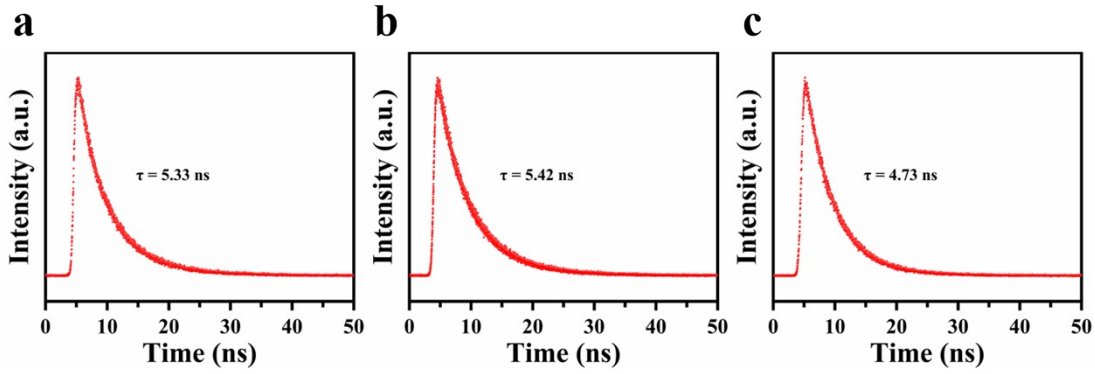


**Fig. S7** (a) Fluorescent decay curves of *c*-$CD_{180}$ in ethanol solution. (b) Fluorescent decay curves of fresh camphor leaves powder ethanol solution. (c) Fluorescent decay curves of pure chlorophyll ethanol solution.

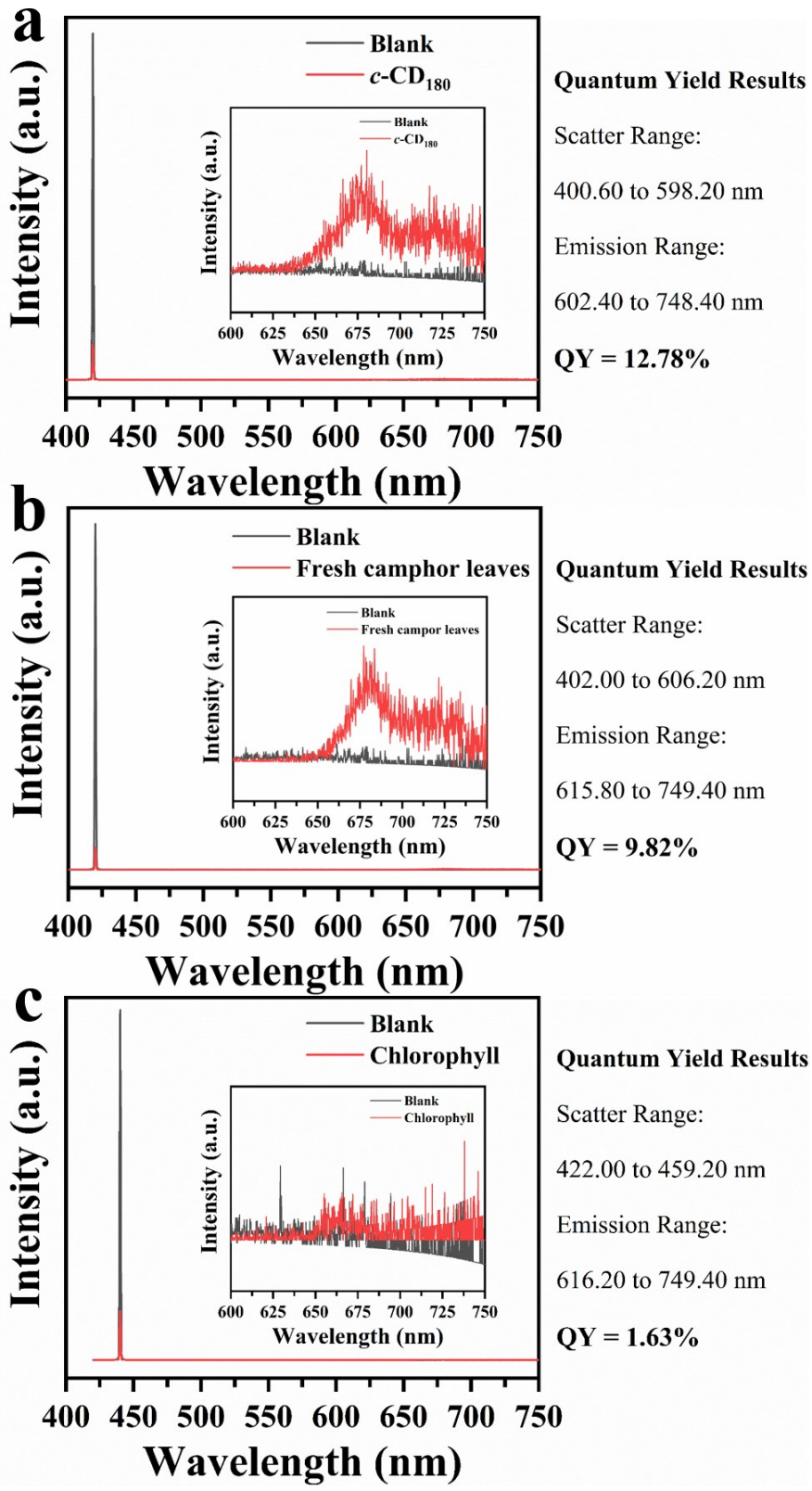


**Fig. S8** The absolute PLQY of (a) *c*-$CD_{180}$ and (b) fresh camphor leaves in ethanol solution under the excitation wavelength of 420 nm. (c) The absolute PLQY of chlorophyll in ethanol solution under the excitation wavelength of 440 nm.

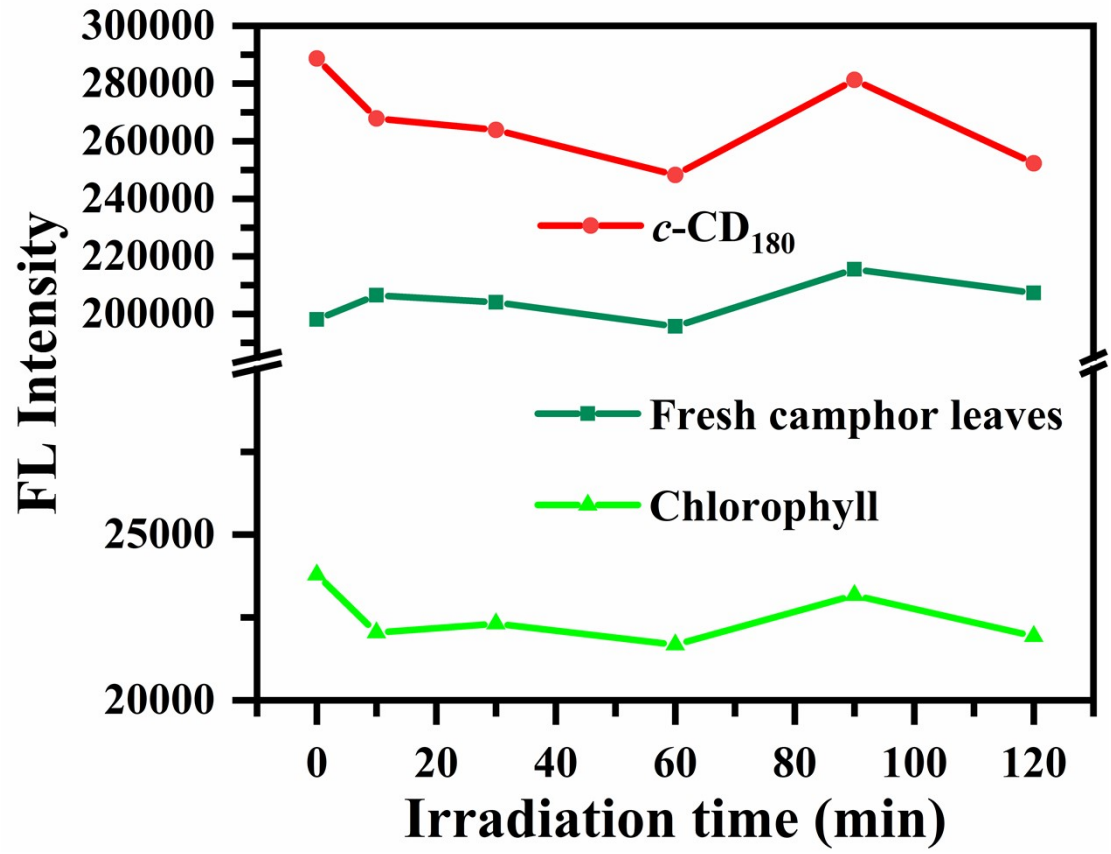


**Fig. S9** Effect of the irradiation time with a 365 nm UV-lamp on the fluorescence intensity of the *c*-$CD_{180}$, fresh camphor leaves and chlorophyll ethanol solution.

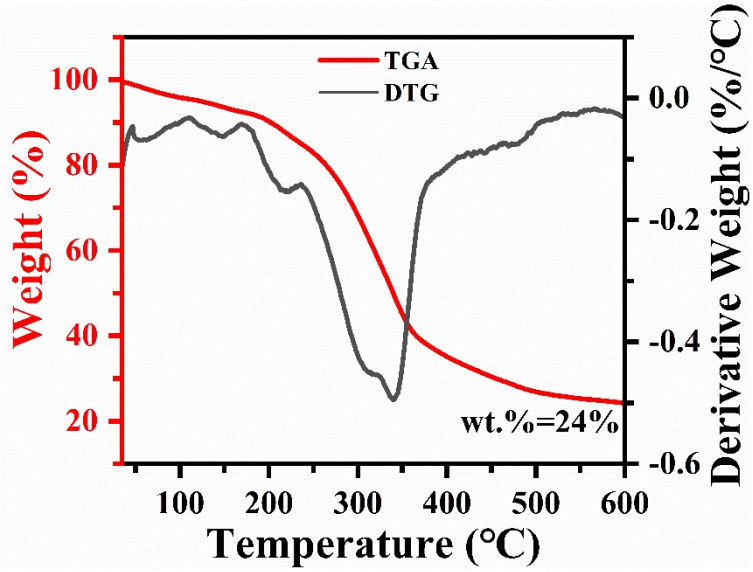


**Fig. S10** Thermogravimetric analysis (TGA; red line) and derivative thermogravimetric analysis (DTG; black line) thermograms of camphor leaves powder with the heating rate of 10 °C $min^{-1}$ under $N_2$ atmosphere.

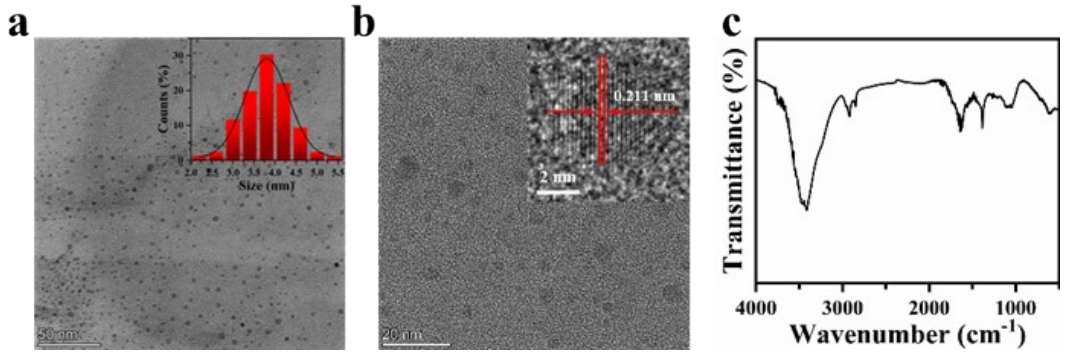


**Fig. S11** (a) TEM image and corresponding dots diameter distribution histogram from *c*-$CD_{200}$. (b) HRTEM image of *c*-$CD_{200}$. (c) FT-IR spectrum of *c*-$CD_{200}$.

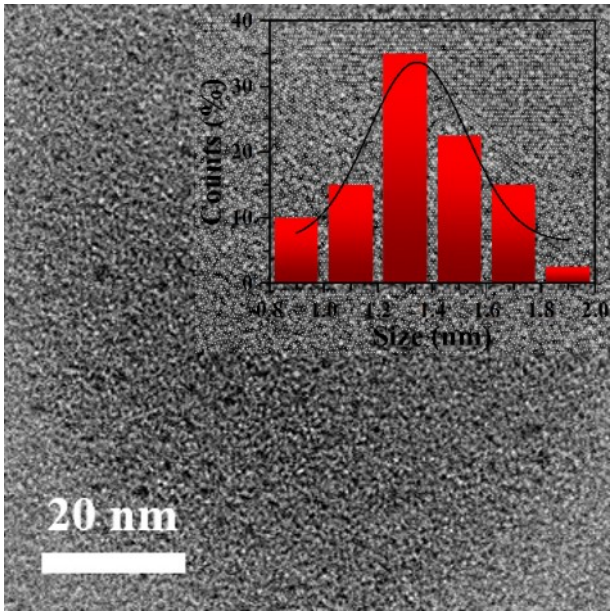


**Fig. S12** TEM image and corresponding dots diameter distribution histogram from *c*-$CD_{280}$.

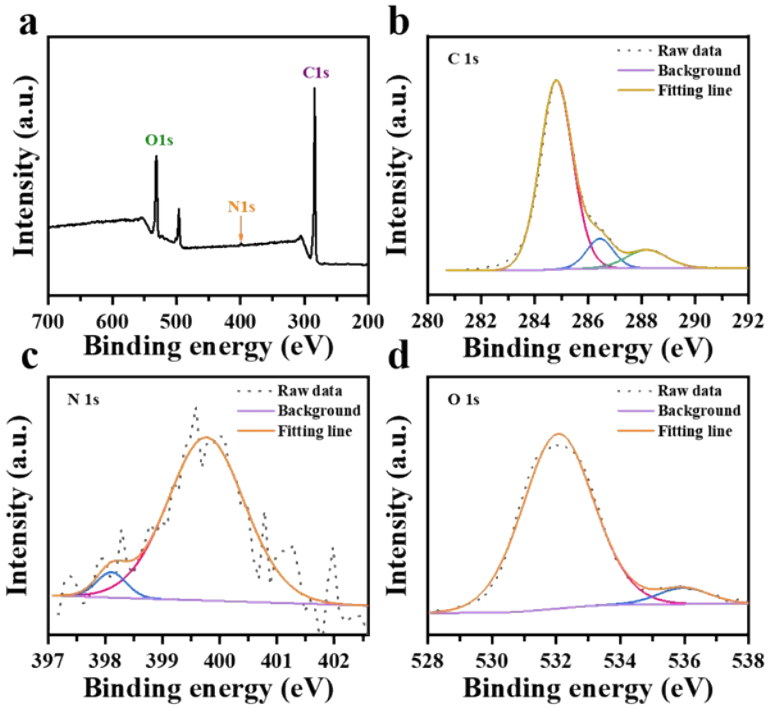


**Fig. S13** The full XPS spectrum (a), high-resolution (b) C 1s, (c) N 1s and (d) O 1s spectra of *c*-$CD_{280}$.

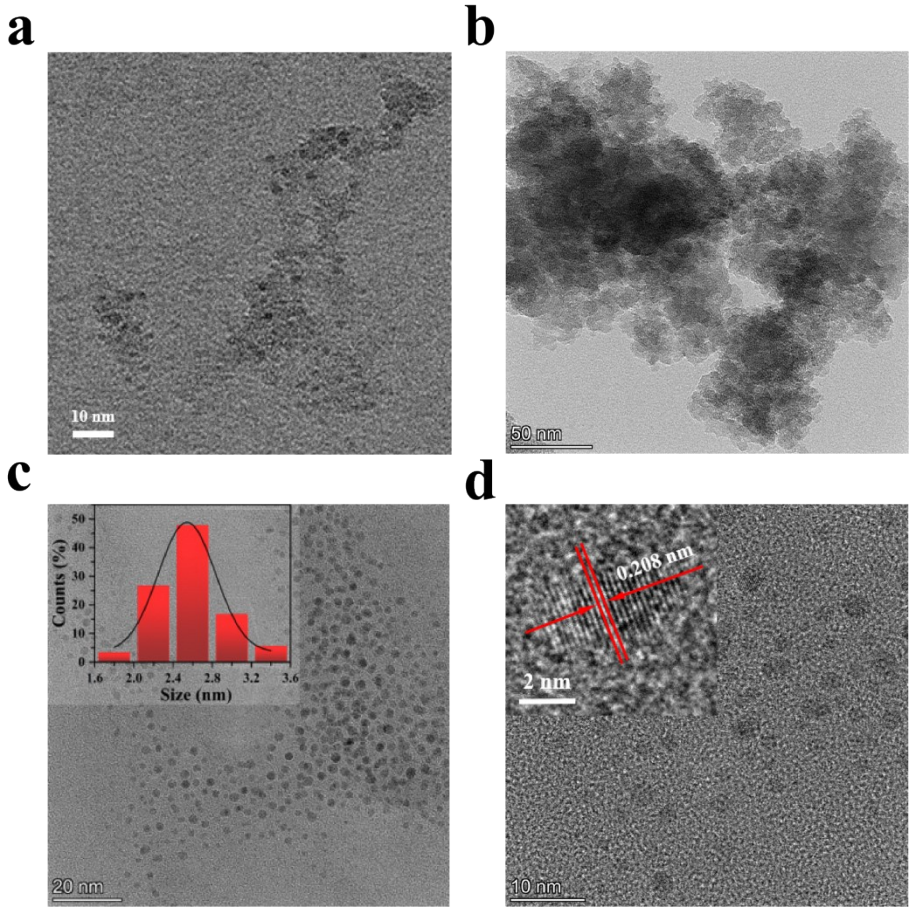


**Fig. S14** (a) TEM image of *chlorophyll*-$CD_{180}$. (b) TEM image of *chlorophyll*-$CD_{200}$. (c) TEM image and corresponding dots diameter distribution histogram from *chlorophyll*-$CD_{280}$. (d) HRTEM image of *chlorophyll*-$CD_{280}$.

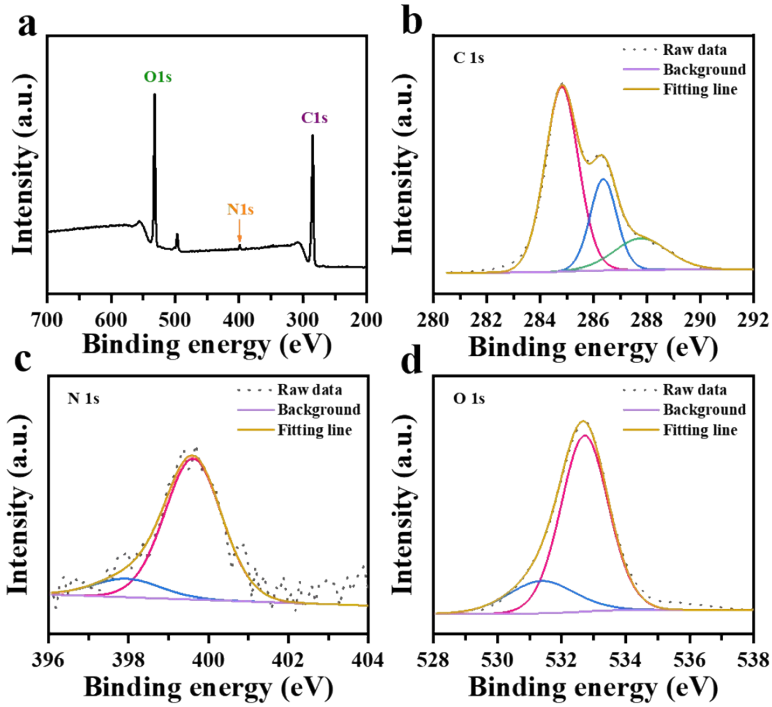


**Fig. S15** The full XPS spectrum (a), high-resolution (b) C 1s, (c) N 1s and (d) O 1s spectra of *chlorophyll*-$CD_{180}$.

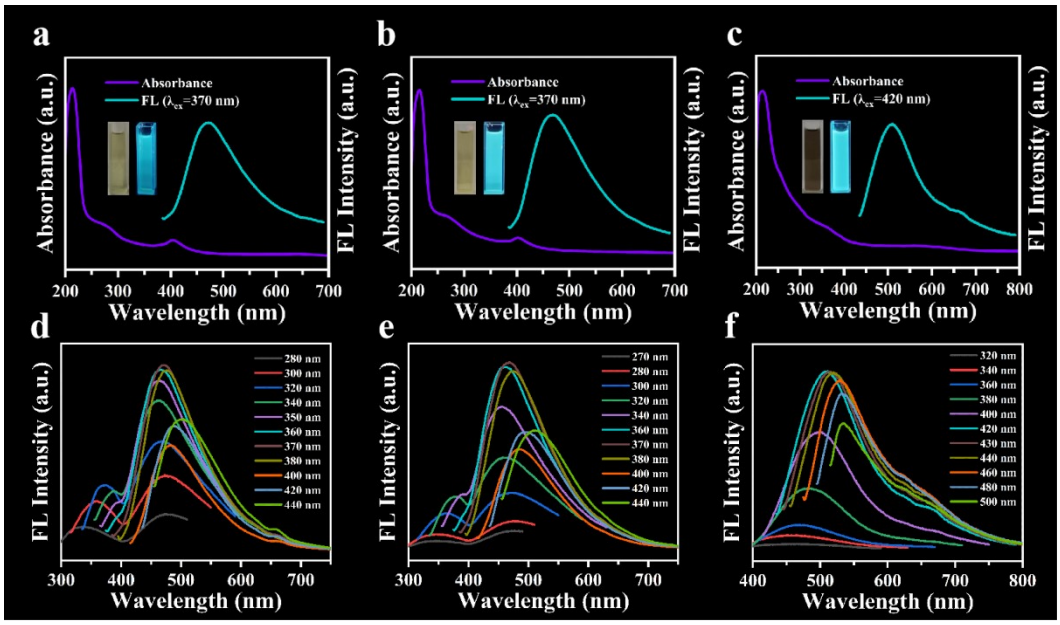


**Fig. S16** (a)-(c) UV/vis absorption (purple line) and FL emission (blue-green line) spectra of *chlorophyll*-$CD_{180}$, *chlorophyll*-$CD_{200}$ and *chlorophyll*-$CD_{280}$, respectively. And inset photographs of corresponding solution under day light (left) and UV light (365 nm) (right), respectively. (d)-(f) FL spectra of *chlorophyll*-$CD_{180}$, *chlorophyll*-$CD_{200}$ and *chlorophyll*-$CD_{280}$ solution at different excitation wavelengths.