Supplementary Material

Waste chicken eggshell as low-cost precursor for efficient synthesis of nitrogen-doped fluorescent carbon nanodots and their multi-functional applications

Yaotang Ke,[a] Bhaskar Garg,[a] and Yong-Chien Ling*[a,b]

[a]Department of Chemistry, National Tsing Hua University, 101, Section 2, Kuang-Fu Road, Hsinchu, 30013, Taiwan

[b]Institute of Nano Engineering and Microsystems, National Tsing Hua University, 101, Section 2, Kuang-Fu Road, Hsinchu, 30013, Taiwan

Fax: + 886 3572774 Tel: +886 35715131 ext.33394

E-mail: ycling@mx.nthu.edu.tw

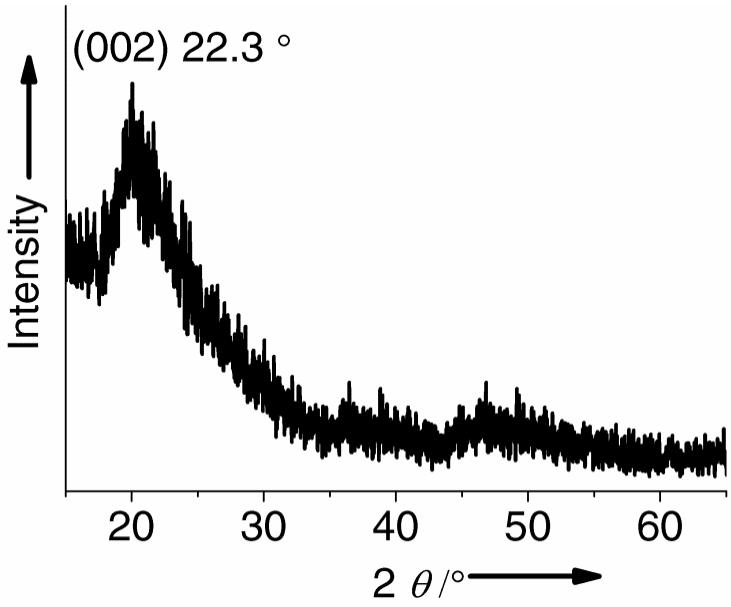

Fig. S1. The XRD spectrum of **NCND 2**.

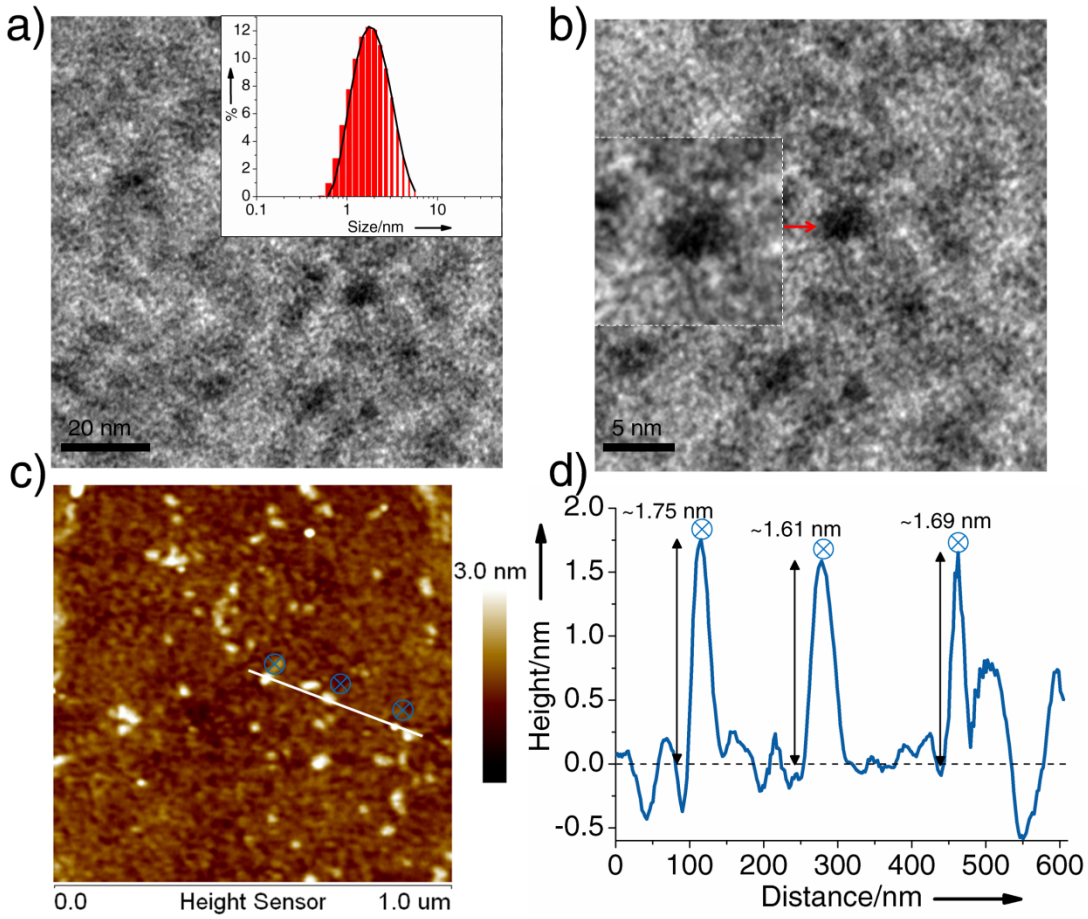

Fig. S2. (a) TEM image of as-prepared **NCND 1**; scale bar 20 nm (inset: the corresponding size distribution histograms. (b) HRTEM image of **NCND 1**; scale bar 5 nm. (c) AFM image of **NCND 1** on a silicon substrate. (d) The corresponding height-profile analysis along the line in (c).

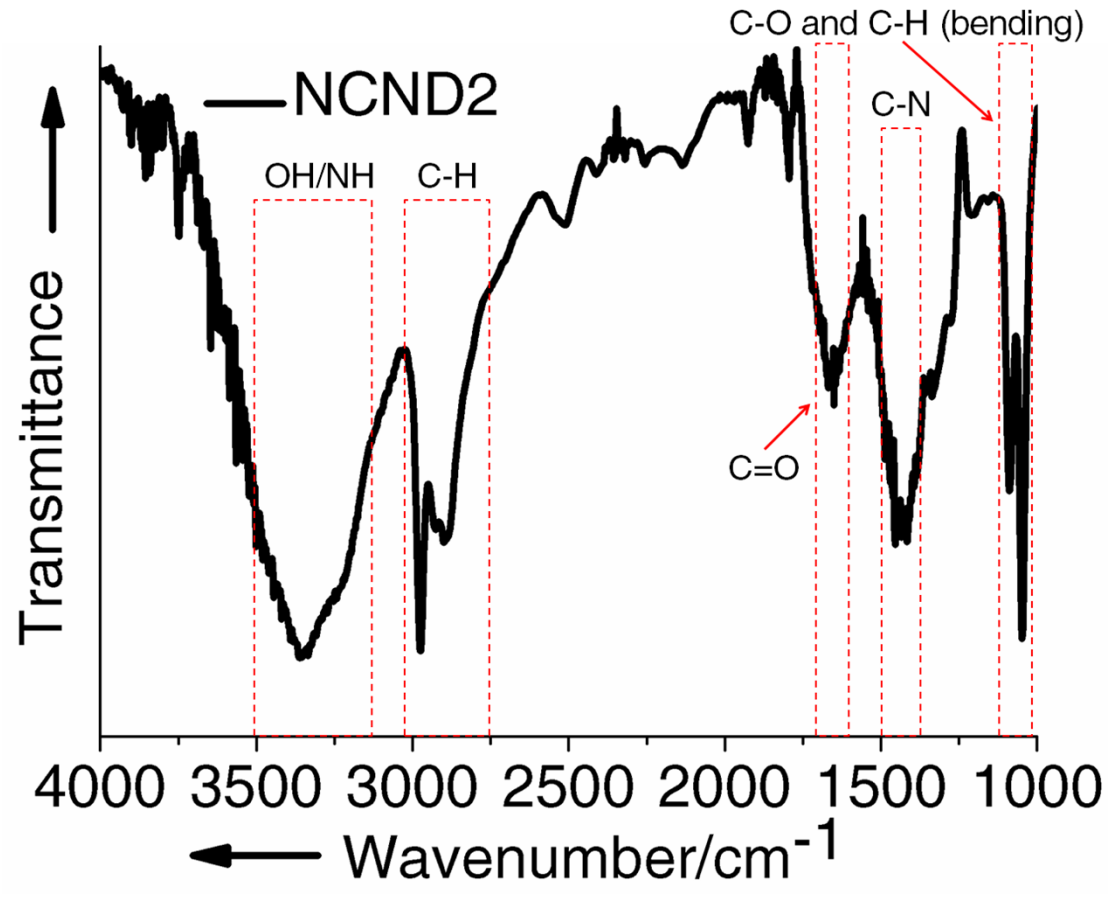

Fig. S3. The FTIR spectrum of **NCND 2**.

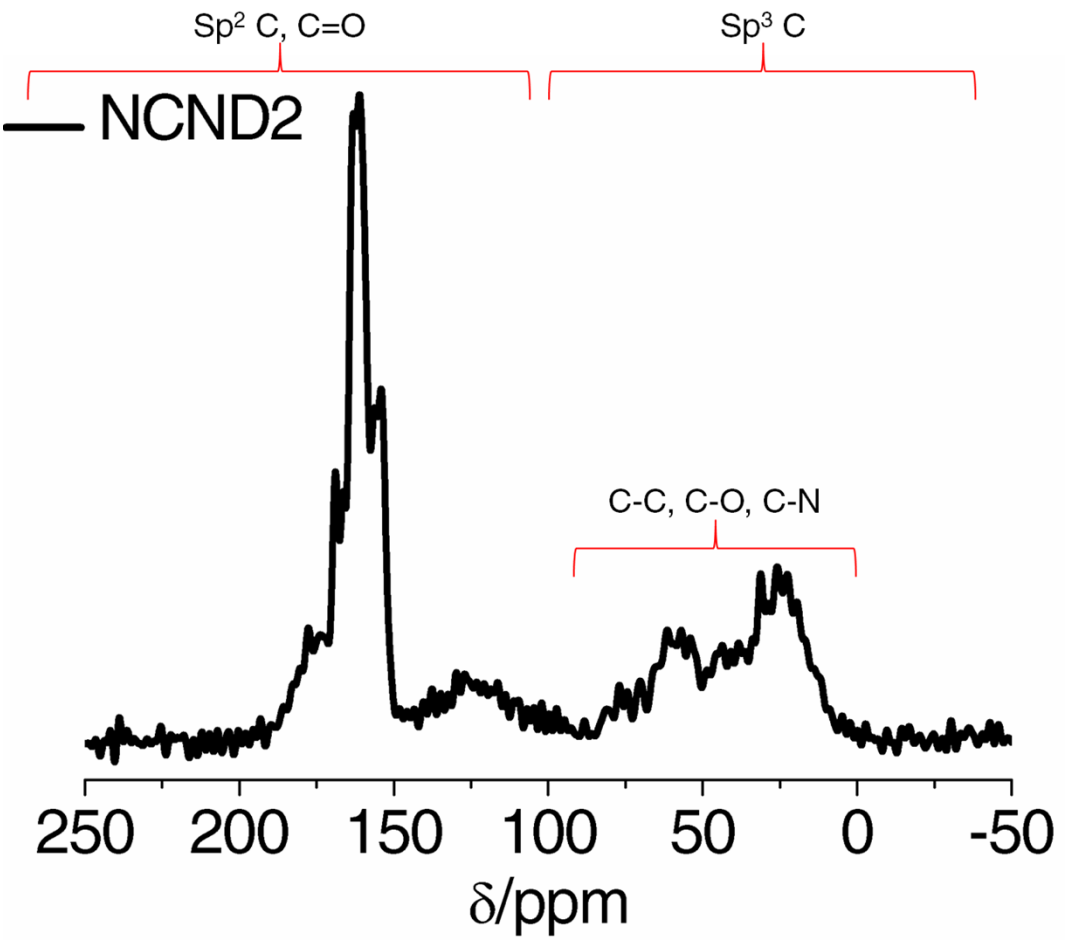

Fig. S4. The solid-state ^{13}C NMR spectrum of **NCND 2**.

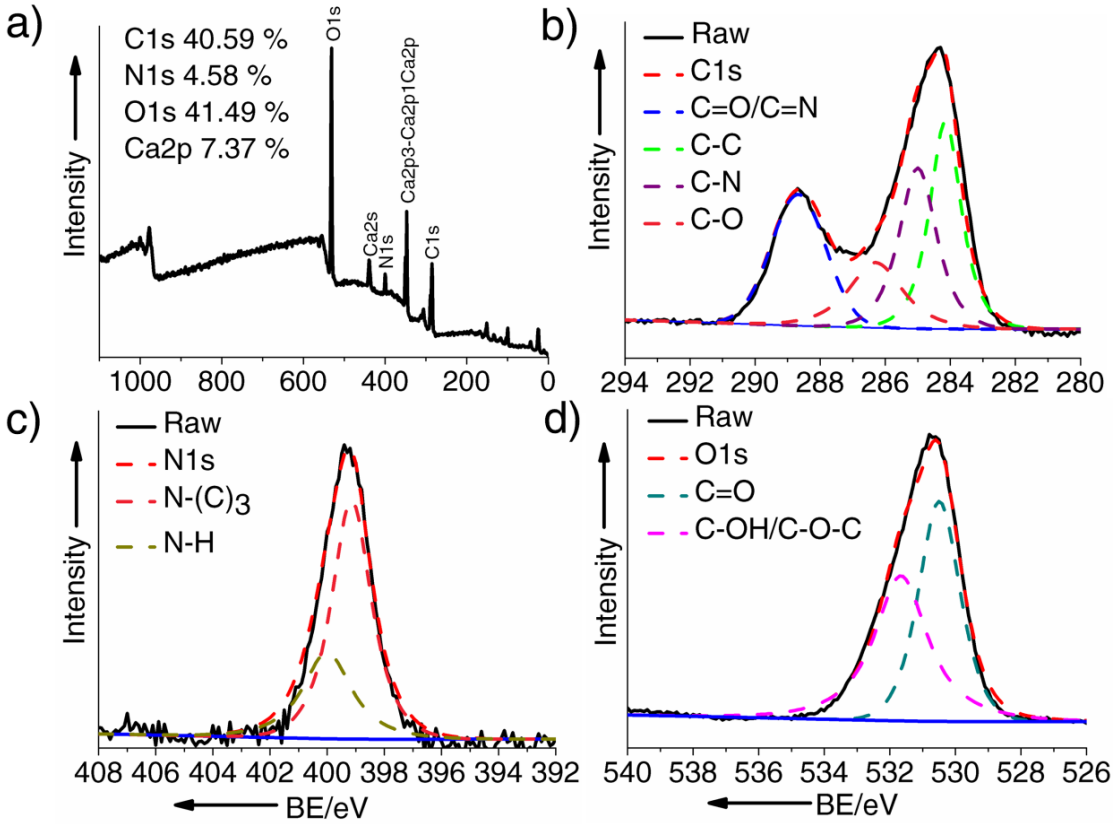

Fig. S5. XPS spectra of the eggshell powder. (a) Survey spectrum. (b)-(d) High resolution spectrum of (b) C1s, (c) N1s, and (d) O1s.

The XPS spectra of eggshell powder revealed that it mainly contains carbon, nitrogen, oxygen, and calcium, The atomic ratios of O1s, Ca2p, C1s and N1s were found to be 41.49, 7.37, 40.59, and 4.58%. The C1s spectrum can be deconvoluted into four peaks at 284.1, 285.1, 286.3, and 288.6 eV that corresponds to C-C, C-N, C-O and C=O/C=N functional groups, respectively. The O1s spectrum shows mainly two peaks at 530.49 and 531.66 eV corresponding to C=O, and C-OH/C-O-C groups, respectively. Further, the N1s spectrum shows only two peaks at 399.1 and 400.1 eV corresponding to N-$(C)_3$ and N-H groups respectively.

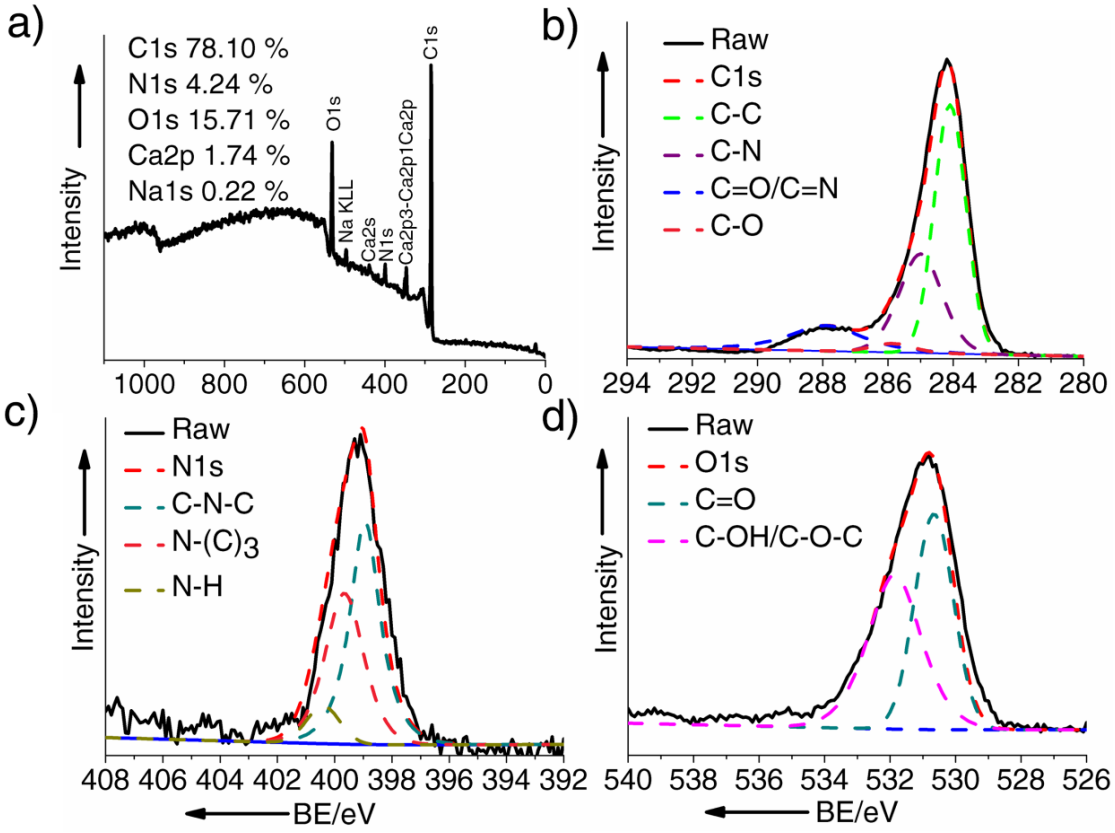

Fig. S6. XPS spectra of **NCND 1**. (a) Survey spectrum. (b)-(d) High resolution spectrum of (b) C1s, (c) N1s, and (d) O1s.

The XPS spectra of **NCND 1** revealed that it mainly contains carbon, nitrogen and oxygen together with a limited amount of calcium and sodium, which may come from the trace minerals in the eggshell powders. The atomic ratios of C1s, N1s, and O1s were found to be 78.10, 4.24 and 15.71%. In detail, the C1s can be deconvoluted into four peaks at 284.2, 284.9, 285.8, and 287.9 eV that corresponds to C-C, C-N, C-O and C=O/C=N functional groups, respectively. The similar features with O1s spectrum can be attributed to C=O (530.49 eV) and C-OH/C-O-C (531.66 eV) groups, respectively. However, after calcination, the N1s spectrum of **NCND 1** exhibited three main peaks at 398.9, 399.6 and 400.3 eV, which can be attributed to C-N-C, N-$(C)_3$ and N-H groups, respectively.

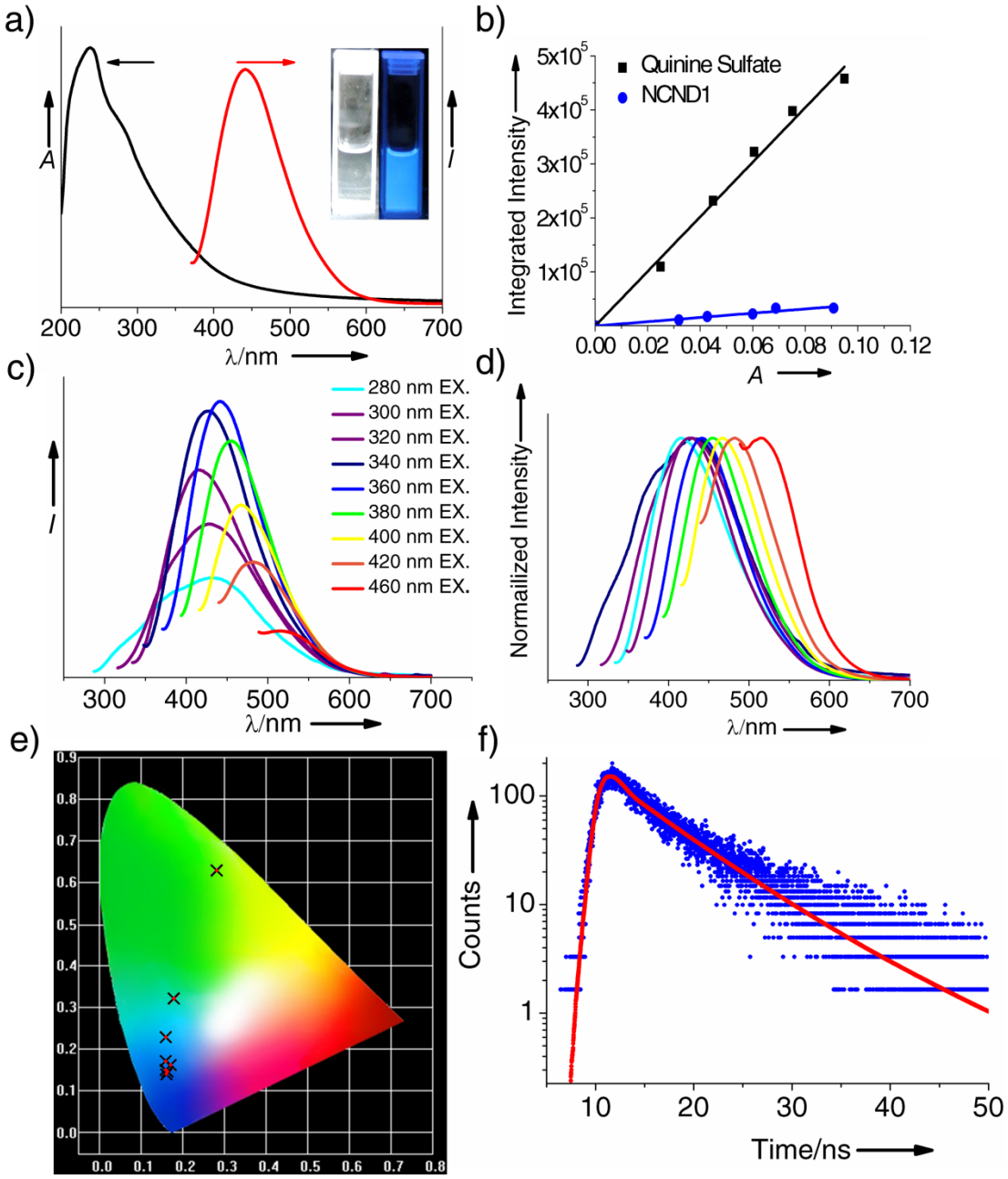

Fig. S7. Characteristic optical properties of **NCND 1**. (a) The UV-Vis absorption and FE spectra of **NCND 1** in aqueous solution (λ_{ex} = 360 nm); inset: digital photographs of **NCND 1** solutions under daylight (left) and UV light (right). (b) Determination of fluorescence QY (4.2%) of **NCND 1**. (c) FE spectra of **NCND 1** solution at various excitation wavelengths. (d) The corresponding normalized FE spectra of **NCND 1**. (e) The corresponding colour coordinate of **NCND 1** excited from 280 to 460 nm. (f) A typical time-resolved fluorescence-decay curve of **NCND 1** (λ_{ex} = 350 nm) measured at 450 nm showed an average lifetime of 9.4 ns.

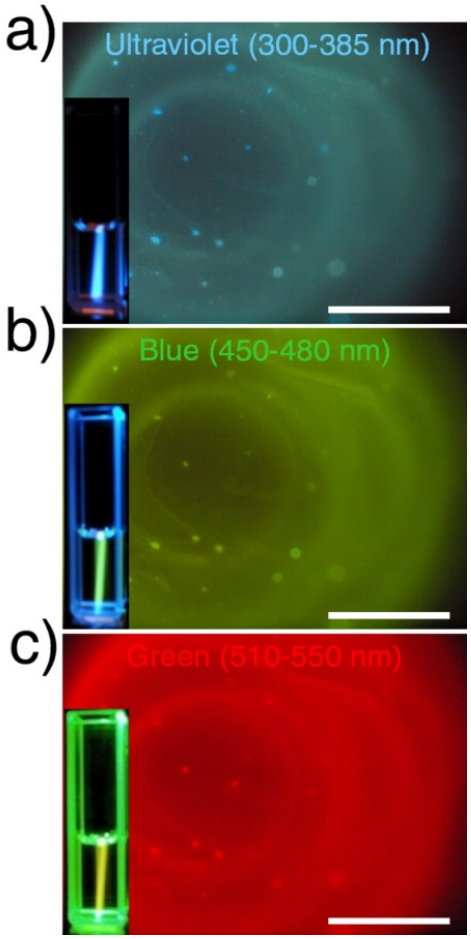

Fig. S8. Multicolor fluorescence images of **NCND 2** on glass plate under excitation at UV (300-385 nm), blue (450-480 nm), and green (510-550 nm) light; inset shows the corresponding fluorescence images of **NCND 2** in aqueous solution.

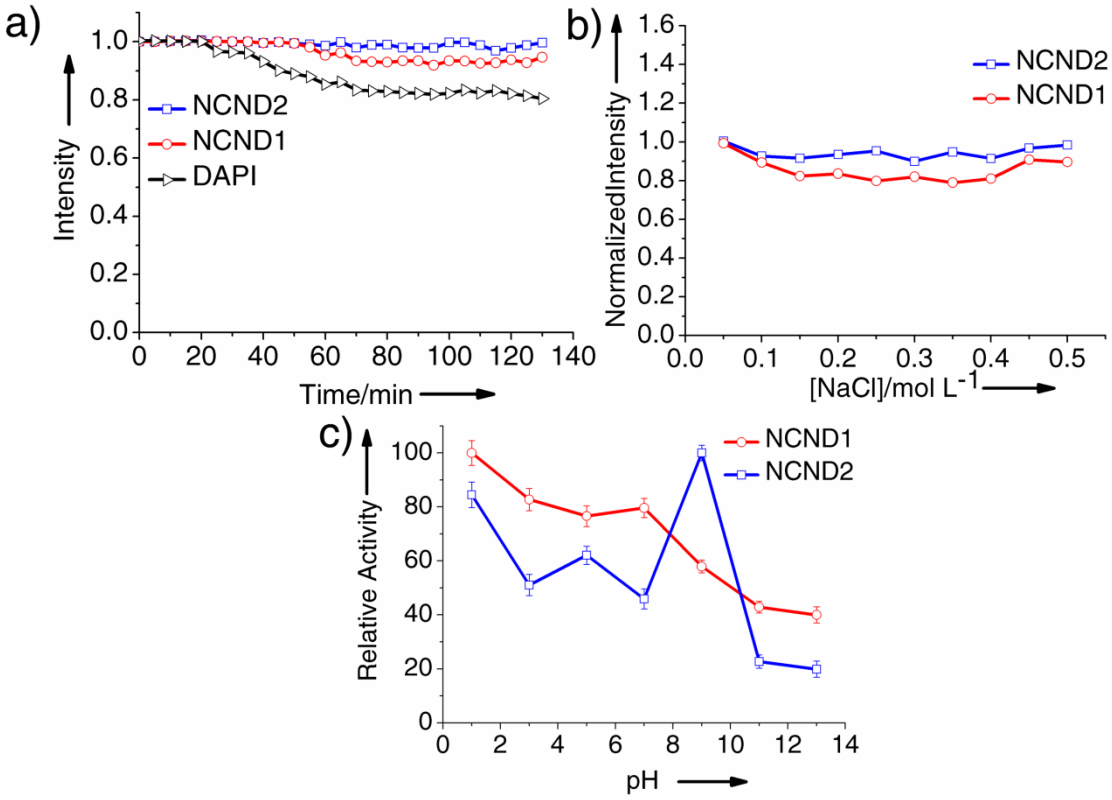

Fig. S9. The photostabilities of **NCND 1** and **NCND 2**. (a) Effects of irradiation time on thefluorescence intensity of **NCND 1** (red), **NCND 2** (blue), and an organic fluorophore, DAPI (black). (b) Effect of ionic strengths on the fluorescence intensity of **NCND 1** (red) and **NCND 2** (blue); the ionic strength were controlled by various concentrations of NaCl. (c) Effect of pH on the fluorescence intensity of **NCND 1** (red) and **NCND 2** (blue).

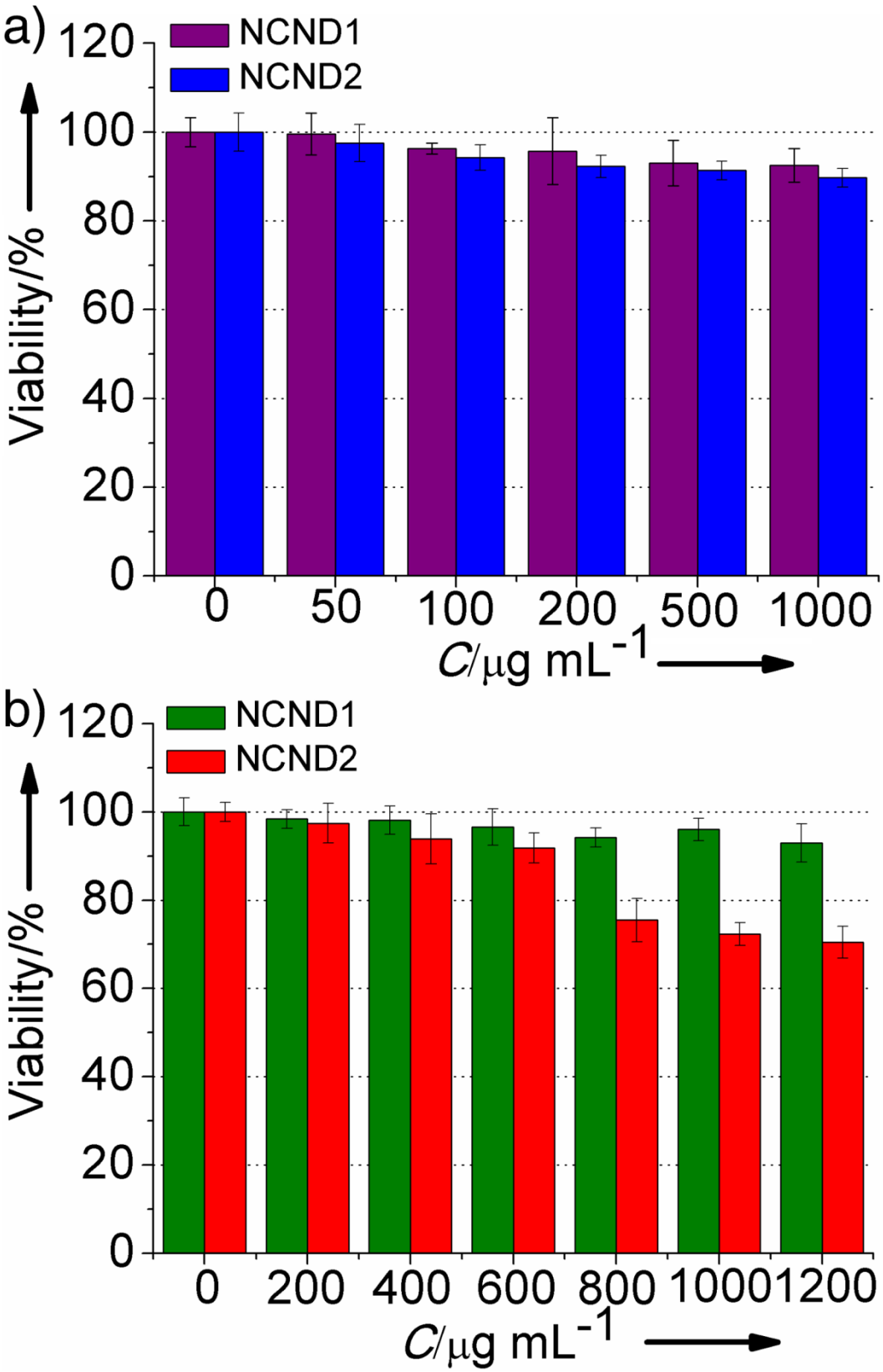

Fig. S10. Cellular toxicity of **NCND 1** and **NCND 2** in (a) HeLa and (b) CCRF-CEM cells (Cell viability by MTT assay).

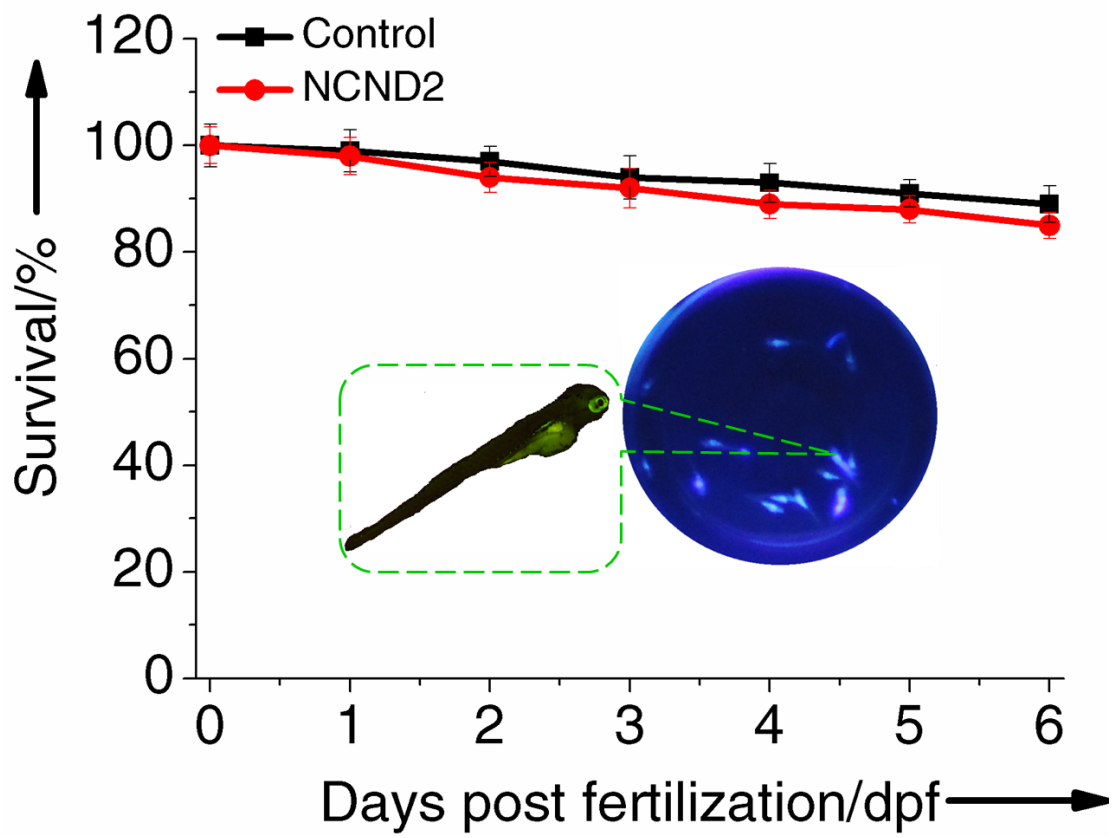

Fig. S11. *In vivo* (Zebrafish) cytotoxicity of **NCND 2** (1000 μg mL^{-1}) until complete development (0-6 dpf). Control: normal development (black line); triplicate experiments (n = 3, control and **NCND 2**).

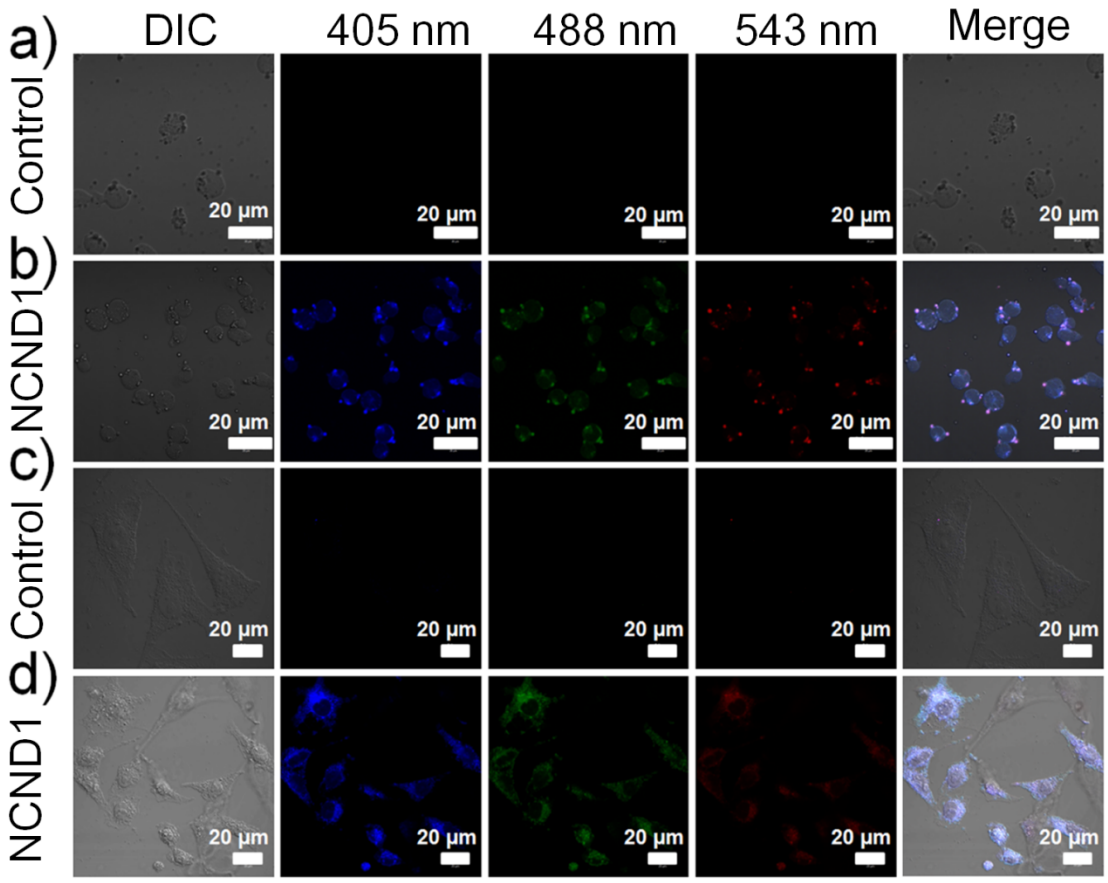

Fig. S12. Confocal differential inteference contrast / fluorescence images (all scale bars 20 µm) of CCRF-CEM (a, b) and HeLa cells (c,d). The images correspond to the control experiments (a, c) where no fluorescence appeared. The cells were incubated with (b) 1200 µg mL^{-1} and (d) 1000 µg mL^{-1} of **NCND 1** in PBS (pH = 7.4) at 37 °C for 6 h and were imaged under DIC and excited at 405, 488, and 543 nm wavelengths, respectively.

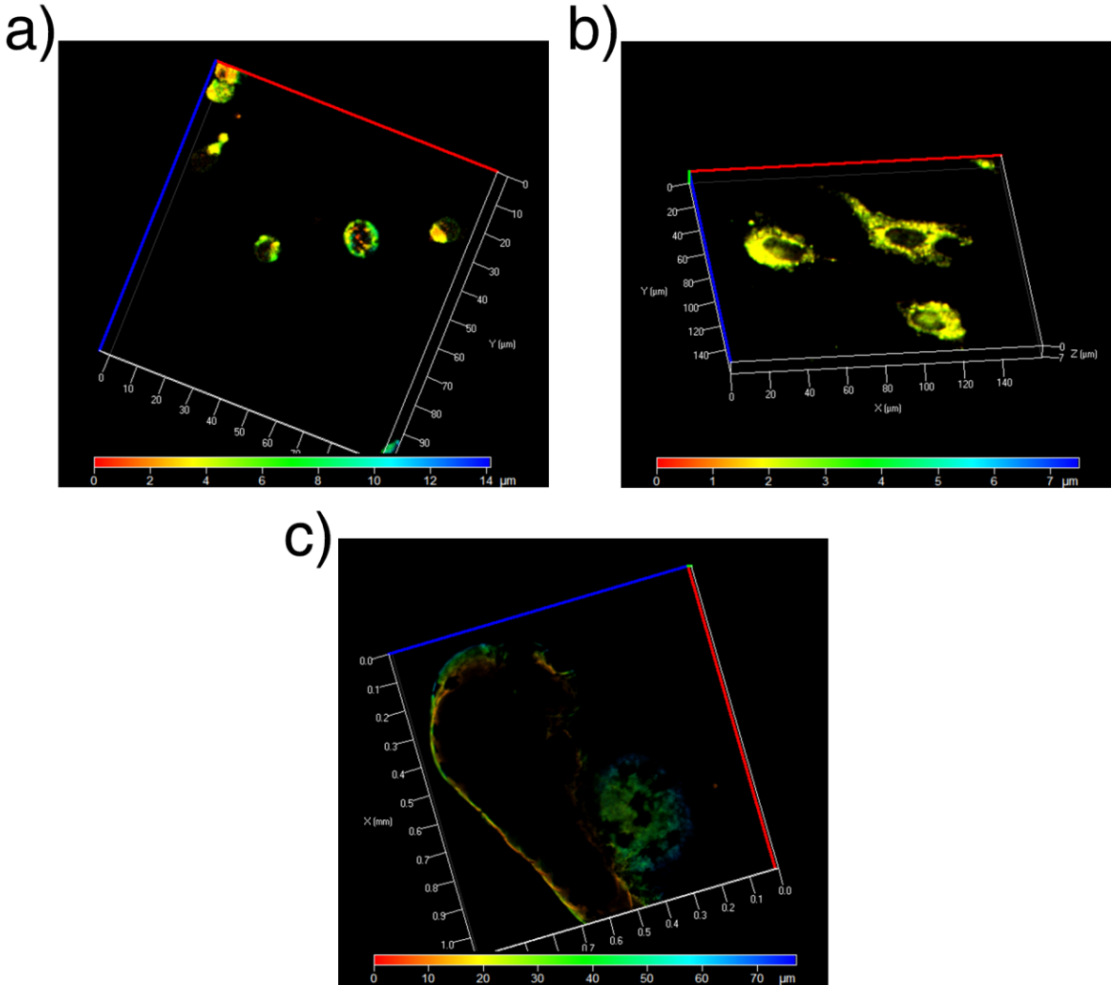

Fig. S13. The reconstructed 3D fluorescence images of CCRF-CEM cells (a), HeLa cells (b) and Zebrafish (c) incubated with **NCND 2**.

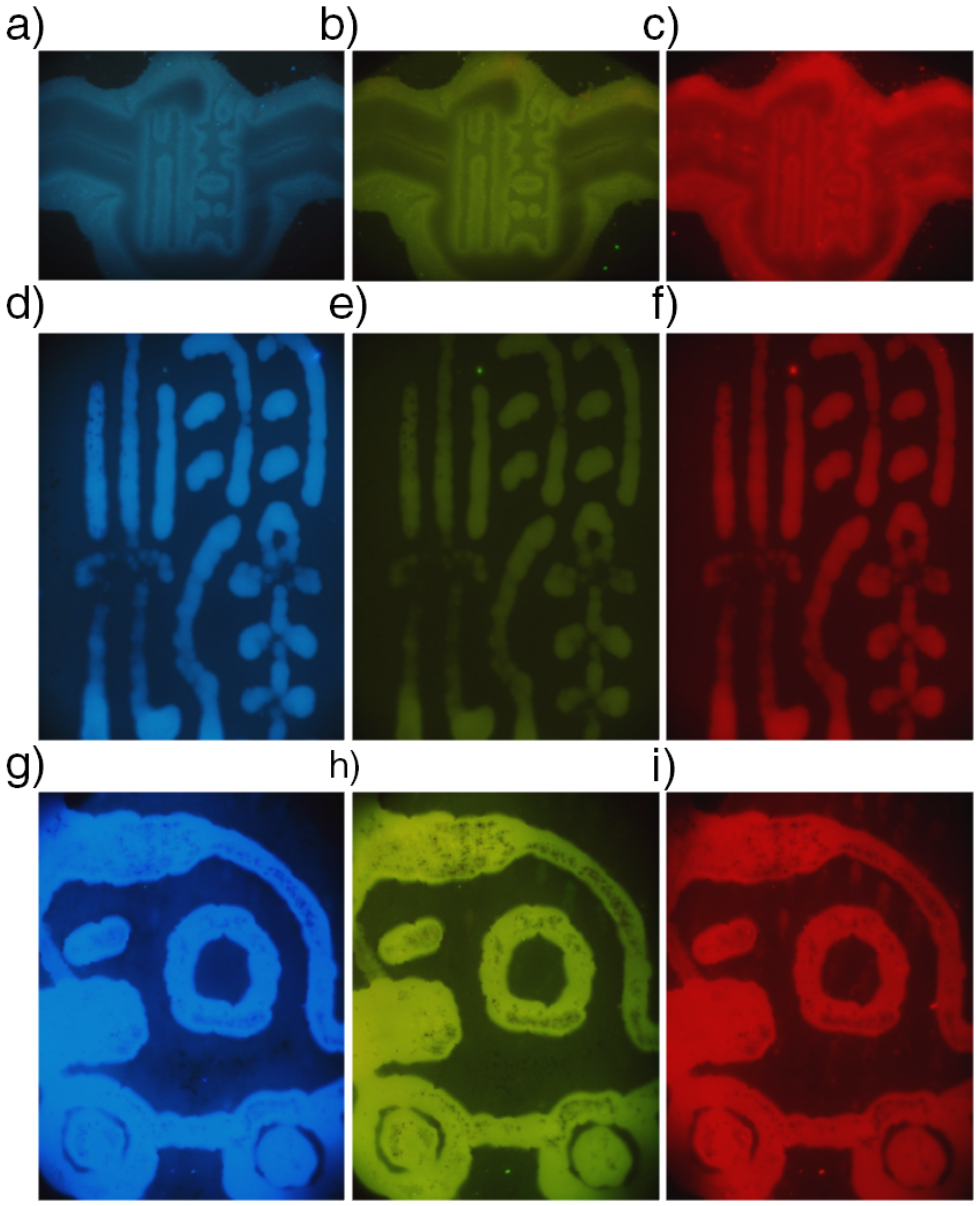

Fig. S14. Multicolour rubber stamping fluorescent images on commercial paper from **NCND 2**-derived fluorescent ink under UV (300-385 nm), blue (450-480 nm), and green (510-550 nm) light excitation. (a-c) The Logo of Tsing Hua University. (d-f) Traditional Chinese character. (g-i) Cartoon pattern.

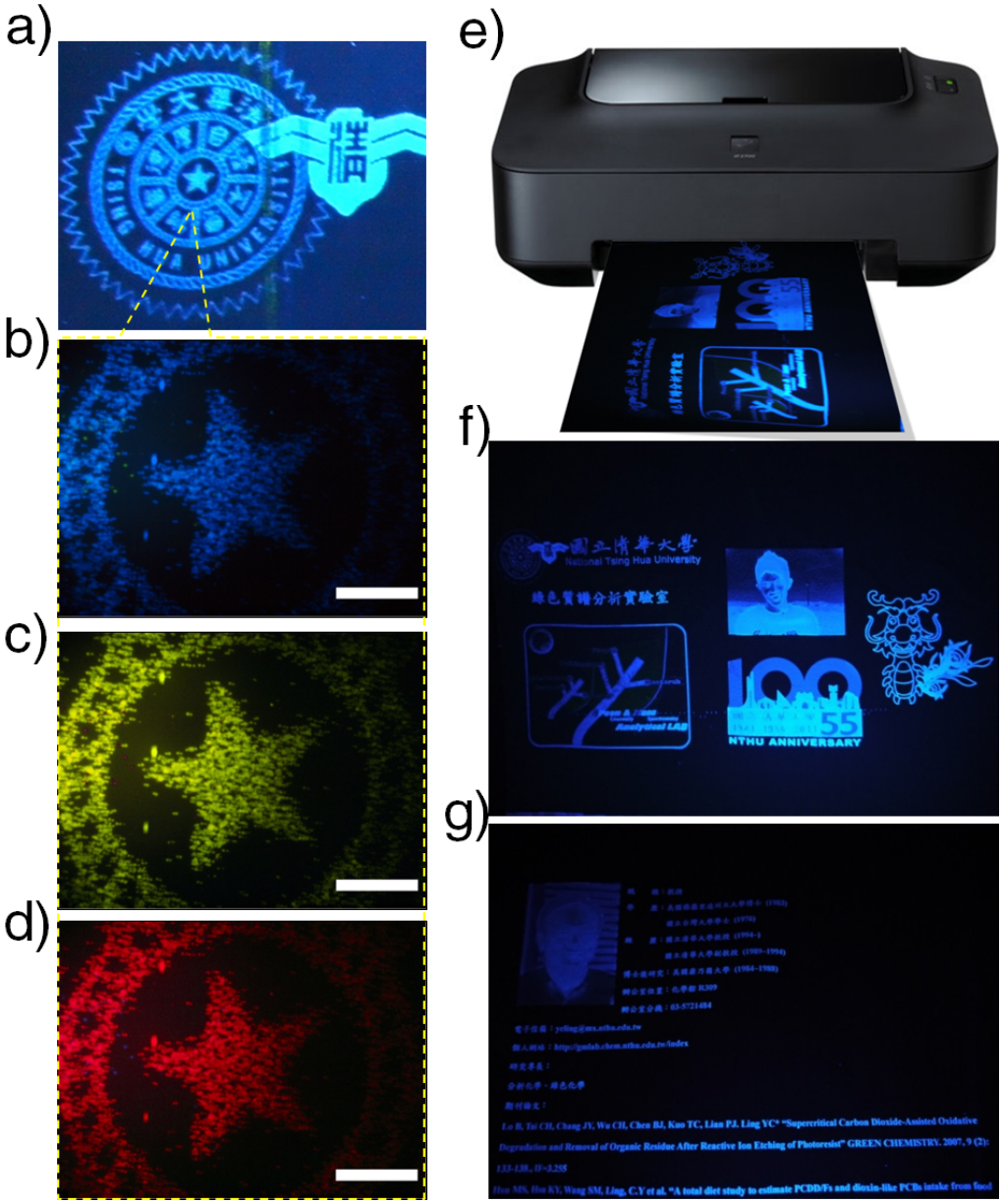

Fig. S15. Different graphic patterns (a, e, and f) and resume (g) obtained by **NCND 2** ink under the UV light excitation. Fluorescent images (b-d) captured under UV (300-385 nm), blue (450-480 nm) and green (510-550 nm) light excitation.

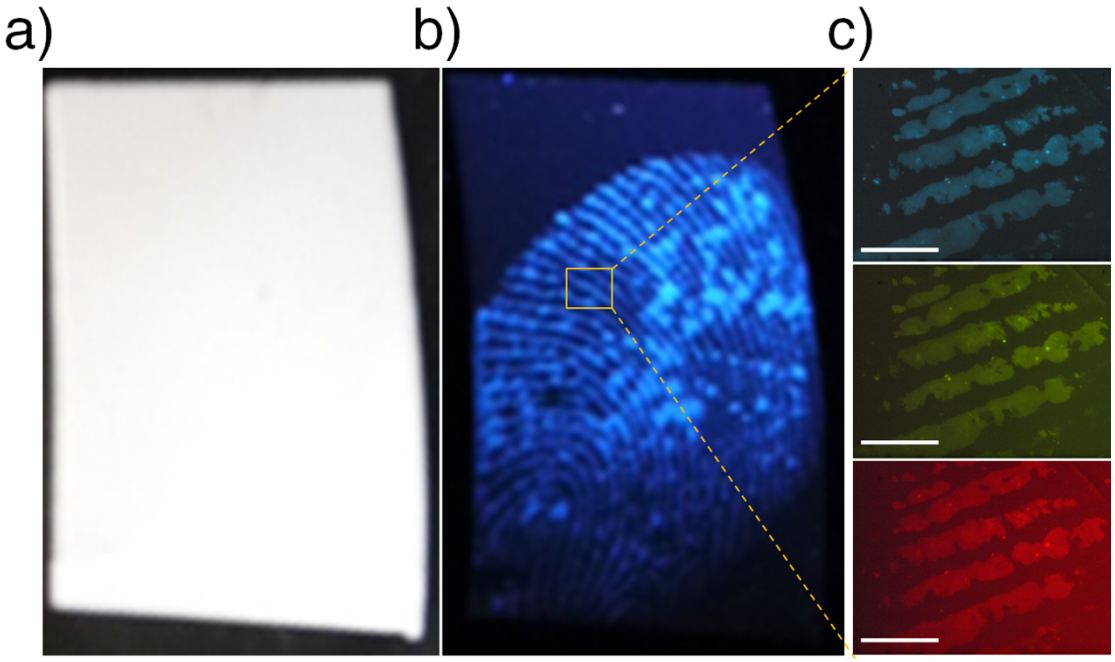

Fig. S16. An **NCND 2** formed fluorescent fingerprint on commercially available filter paper captured under (a) daylight (b) UV light (λ_{ex} =350 nm) and (c) UV (300-385 nm), blue (450-480 nm), and green (510-550 nm) light excitation, respectively.

Table S1. The results of absorption (max.), PL emission, XPS analysis, QY, PL lifetime and product yield of **NCND 1** and **NCND 2**.

Samples	Absorption max.	PL emission (λ_{ex} = 360 nm)	C1s (%)	N1s (%)	O1s (%)	QY (%)	τ (ns)	Yield (%)
NCND 1	227 nm	450 nm	78.10	4.24	15.71	4.2	9.4	85.23
NCND 2	243 nm	469 nm	60.06	15.35	19.41	7.8	11.3	80.65