

Water-Triggered Luminescent “Nano-bombs” Based on Supra-(Carbon Nanodots)

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Fluorescence imaging is regarded as a powerful technique for data recording, security, and clinical diagnosis; it greatly depends on the development of smart luminescent materials.^[1] Although some smart luminescent materials (e.g., transition-metal complexes, fluorescent crystals, and dyes) have been reported for optical data recording, protection devices, and sensor matrices using external mechanical, vapor, or thermal stimuli,^[2] most of them are held back from actual applications owing to their low photostability, potential biotoxicity, high cost, or poor compatibility with traditional inkjet printing technology.^[3] In addition, from a green perspective, it is essential to develop a fluorescence imaging technique that is friendly to the environment. Carbon nanomaterials – such as carbon nanotubes, fullerenes, and graphene, with the advantages of being cheap, being environmentally friendly, and having abundant sources – play important roles in every aspect of science and technology.^[4] Developing new smart luminescent materials from carbon-based nanomaterials to overcome those deficiencies would be very promising.

Luminescent carbon nanodots (CDs) are an emerging fascinating carbon nanomaterials because they can make non-luminescent carbon materials strongly luminescent at the nanoscale.^[5] Luminescent CDs are regarded as potential candidates for the advancement of bioimaging,^[6] sensors,^[7] optoelectronics,^[8] and energy conversion/storage devices,^[9] owing to their superior physical, chemical, and optical properties, such as resistance to photobleaching, chemical inertness, water solubility, high biocompatibility, and low cost,^[10] when compared with organic dyes and transition-metal complexes. In recent years, luminescent CDs have been used as low-toxicity

and eco-friendly fluorescent ink aiming at luminescent printing patterns, multicolor patterning, and information encryption because they adhere well to printing paper, have stable photo-physical properties, and have excitation-wavelength-dependent photoluminescence (PL).^[11–13] However, ink-based printing has some drawbacks, such as potential safety issues and the frequent replacement of ink cartridges that would likely occur as a result of their on-going usage as fluorescent inks. It is well known that self-assembly technology is a powerful tool for modulating the optical properties of functional molecules or nanoparticles because of the ability to control their self-assembly behavior.^[14] It is highly relevant to develop a new type of smart CD-based system, whose optical properties can be modulated by controlling their self-assembly behavior; such a system would fully display the merits of CDs and find various practical applications.

In this work, we broadened the scope of CDs to smart supra-CD system, leading to the development of CDs that are partially functionalized with alkyl chains (CD-Ps); CD-Ps can self-assemble into supra-CDs in toluene. The supra-CDs exhibit water-induced enhancement of the photoluminescent behavior owing to the decomposition of the supra-CDs that was induced by water. On the basis of the “turn-on” phenomenon, in which water-induced rapid luminescence is observed in the supra-CD-coated paper, ink-free printing luminescent paper, which is compatible with the water-jet printing technique, is fabricated for information storage and encrypted devices. This novel CD-based nanomaterial also has potential application in medicine and forensics. The power of precisely mapping the active sweat pores on a human fingerprint is also demonstrated via the deposition of a fingerprint on the supra-CD-coated paper.

The CD-Ps were prepared through the partial functionalization of the surfaces of the raw CDs (CD-R) with alkyl chains; this preparation was according to our previous work, involving the starting materials of citric acid (3 g) and urea (6 g).^[11,15] The prepared CD-Rs were processed in water, followed by centrifugation (10 000 rpm, 20 min) to remove any large or agglomerated particles. The synthesis process of CD-Ps is illustrated in **Figure 1b**. The surface functionalization agent was 1-bromododecane. CD-Rs contain amide groups on the surface, as indicated by ¹H NMR (**Figure 1a**); the amide groups can react with the bromine group of 1-bromododecane. More experimental details are given in the Supporting Information. Partially dodecyl-functionalized CDs and their completely functionalized counterparts can co-exist in the reaction solution. The amide groups are hydrophilic, while the dodecyl chains are hydrophobic. The partially dodecyl-functionalized CDs (CD-Ps) are amphiphathic carbon nanodots, which can self-assemble into a supra-CD system in

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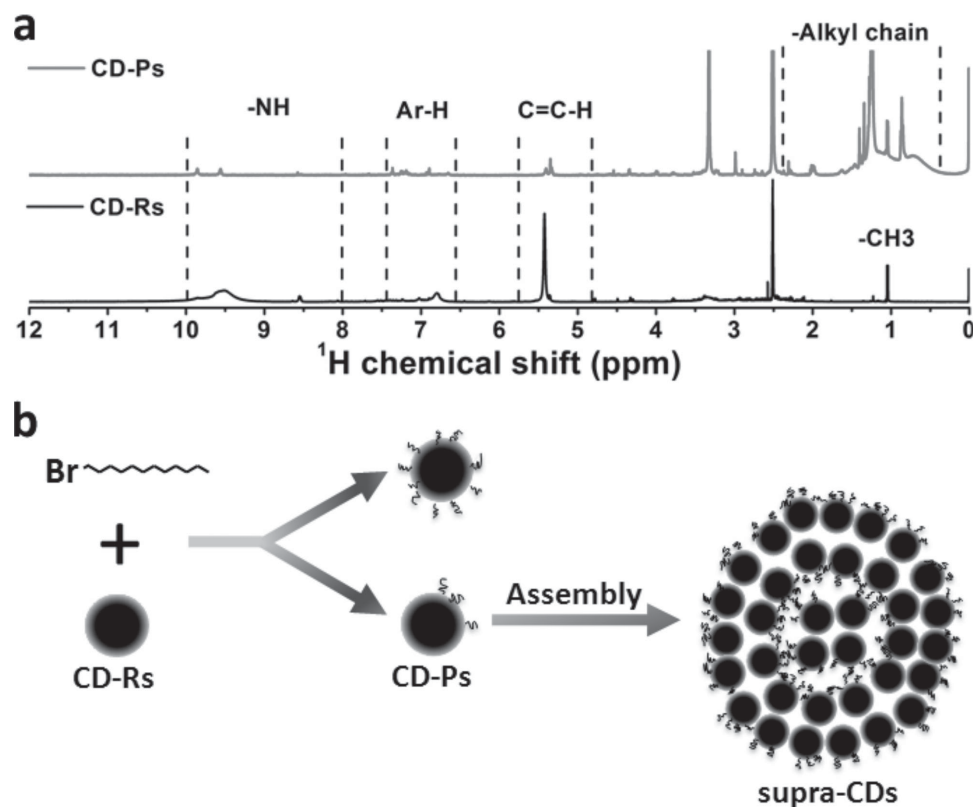


Figure 1. a) ^1H NMR spectroscopy of CD-Rs and CD-Ps in $\text{DMSO}-d_6$. b) Schematic for the formation of supra-CDs from CD-Ps.

the form of agglomerates through amphiphilic interaction in toluene. The supra-CDs can thus be separated by centrifugation (8000 rpm, 20 min) for further investigation.

^1H NMR spectroscopy was employed to demonstrate the changes of the functional groups on the surface of the CD-Rs and CD-Ps (Figure 1a). The functionalization of the surface of the CDs with dodecyl chains is confirmed by the ^1H NMR spectrum, in which intense signals in the range of 0.5–2.4 ppm emerge; they correspond to the protons of dodecyl groups. The signals at 8.0–10.0 ppm correspond to the protons of the amino groups. It can be seen that the amino groups did not completely react with 1-bromododecane, and residual amino groups (hydrophilic groups) still exist on the surface of the CD-Ps, indicating that the surface of the CD-Ps is only partially alkyl-chain-functionalized and that the CD-Ps are amphiphilic carbon nanodots.

CD-Ps do not dissolve well in water, but they can be dispersed in dimethyl sulfoxide (DMSO), resulting in a strong green luminescence under UV excitation (Figure 2a). The supra-CDs, however, have very weak luminescence in toluene due to the luminescent quenching effect caused by the aggregations of the CD-Ps. The solvent-induced aggregation of CD-Ps is reflected in UV–vis absorption spectra. The obvious broadened and weakened absorption band centered around 415 nm and the enhanced level-off tails in the visible spectral region due to increased scattering intensity illustrate how CD-Ps self-assemble into supra-CDs in toluene. The transmission electron microscopy (TEM) and atomic force microscopy (AFM) images indicate CD-Ps in DMSO are dispersive particles ranging in the size from 1 to 5 nm (Figure 2e and Figure. S1, Supporting Information).

Well-resolved lattice fringes with an interplanar spacing of 0.21 nm in the CD-Ps (Figure 2e, inset) are close to the (100) facet of graphitic carbon.^[12,16] The confocal microscopy image of CD-Ps on a glass substrate, as a result of depositing the CD-Ps from DMSO solution, exhibits dispersed green luminescent dots under 405 nm excitation (Figure 2d). In contrast, AFM, scanning electron microscopy (SEM), and TEM images (Figure 2f–g) show that the supra-CDs in toluene are particles ranging in size from 150 to 400 nm, indicating that the supra-CDs are aggregations of numerous CD-Ps.

After dropping the toluene solution of supra-CDs onto paper, the resulting supra-CD-coated paper exhibits weak luminescence, indicating that supra-CDs remain after the coating process. As shown in Figure 2b, the PL of the supra-CD-coated paper can be significantly enhanced after a water-spraying treatment. A high PL quantum yield (QY) of up to 40.6% is achieved for the water-sprayed paper (Table 1). The enhanced PL of the water-sprayed supra-CD-coated paper can be preserved after drying the paper in air, which means water, as a trigger, induced an irreversible change in the PL properties of the supra-CD-coated paper (Figure S6, Supporting Information). The PL decay trace (Figure 2c) of the supra-CD-coated paper without the water-spraying treatment could be fitted well using a triple-exponential function with an average lifetime of 10.29 ns (goodness of fit, $\chi^2 = 1.09$, under excitation of 405 nm). In contrast, the PL decay of the supra-CD-coated paper after the water-spraying treatment is fitted well to a bi-exponential function with an increased average lifetime of 12.74 ns ($\chi^2 = 1.06$), which is approximately the same as that of CD-coated

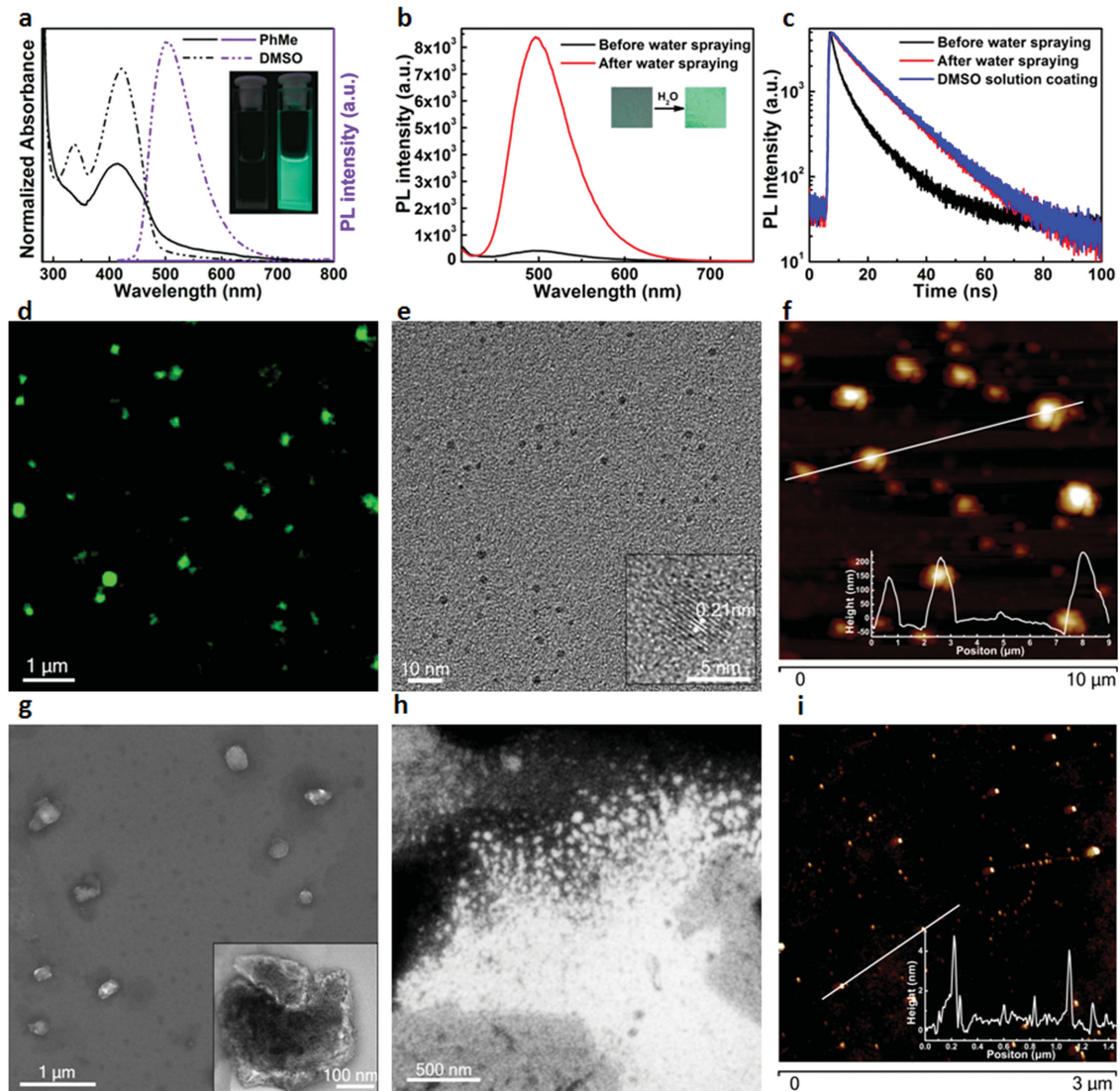


Figure 2. a) UV-vis absorption (black line) and photoluminescence spectra (violet line, excitation at 405 nm) of supra-CDs in toluene (PhMe) and CD-Ps in DMSO. Inset: a photograph of supra-CDs in PhMe (left) and CD-Ps in DMSO (right) under UV (365 nm) illumination. b) Water-induced changes in the emission spectra of paper coated by supra-CDs in PhMe solution (excitation at 405 nm). c) Water-induced PL decay in the dynamic spectra of supra-CD-coated paper made from a supra-CD PhMe solution, and PL decay in the dynamic spectrum of paper directly coated with CD-Ps from DMSO solution. d) Confocal microscopy image of CD-Ps deposited from DMSO solution onto a glass substrate under 405 nm excitation. e) TEM image of CD-Ps on a carbon-coated copper grid after deposition from DMSO solution. Inset: high-resolution TEM image of a CD-P. f,i) AFM images of supra-CDs on a silicon substrate before (f) and after (i) water-spraying. Insets: height profiles along the lines marked in the AFM images. g,h) SEM images of supra-CDs on a silicon substrate before (g) and after (h) water-spraying. Insets of g: corresponding TEM image of the supra-CDs.

paper arising from CD-P in DMSO solution, indicating that the enhanced luminescence is due to the decomposition of supra-CDs. The water-induced decomposition of the supra-CDs can be further demonstrated by SEM and AFM. After water-spraying,

the supra-CDs decompose into numerous small nanoparticles, as illustrated in the SEM image (Figure 2h). The AFM image shows the heights of the small nanoparticles in Figure 2i; they are distributed in the range of 1 to 5 nm, indicating the small

Table 1. Photophysical data for paper coated with supra-CDs (2.5 mg/mL in toluene) before and after water-spraying treatment.

States	$\lambda_{em}^a)$ [nm]	$\alpha_1^b)$ [%]	$\tau_1^c)$ [ns]	$\alpha_2^b)$ [%]	$\tau_2^c)$ [ns]	$\alpha_3^b)$ [%]	$\tau_3^c)$ [ns]	$\bar{\tau}^d)$ [ns]	$\chi^2 e)$	$\Phi_p^f)$
Before	500	20.0	1.10	42.2	4.54	37.8	12.9	10.29	1.09	0.06
After	500	9.0	4.08	91.0	13.00	–	–	12.74	1.06	0.41

^{a)}Emission wavelength; PL peak excited at 405 nm; ^{b)}Fractional contribution of PL decay; ^{c)}PL lifetime; ^{d)}Average lifetime; ^{e)}Goodness of fit; ^{f)}PL quantum yield.

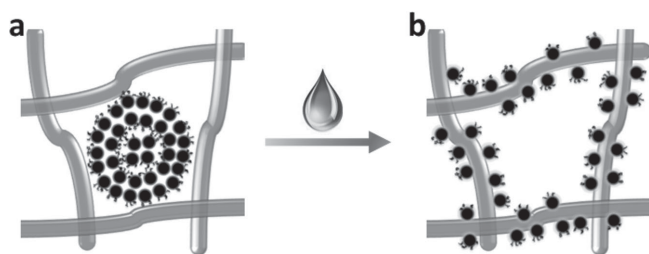


Figure 3. Schematic for the mechanism of the water-induced enhancement of the luminescence.

nanoparticles are dispersed CD-Ps (Figure 2e). Considering the similar PL decay curves of water-sprayed supra-CD-coated paper and the paper coated using CD-Ps in DMSO solution, it can be concluded that water can be a trigger to make supra-CDs decompose into dispersed CD-Ps in solid state.

A mechanism for the water-induced enhancement of the luminescence in the supra-CD-coated paper is illustrated in **Figure 3**. Supra-CDs of CD-Ps agglomerates with hydrophobic groups on the outer cores are attached to the fiber network of the paper after the toluene solution of the supra-CDs is dropped onto paper; at this point, the supra-CD-coated paper exhibits weak luminescence. During the water-spraying treatment, water molecules permeate into the supra-CDs, breaking the hydrogen bonds between the hydrophilic groups on the CD-Ps

and decomposing the supra-CDs. The hydrophilic groups of CD-Ps can effectively anchor on paper fibers, which contain an abundance of hydroxyl groups, and make the CD-Ps absorb on paper fibers in a dispersive manner.^[17] Therefore, the coupling interactions between CD-Ps become weak, which decreases the nonradiative recombination channels in the CD-Ps, leading to elongated luminescent lifetimes and a high yield of radiative recombination.^[18] These interesting phenomena indicate that the supra-CDs can act as water-triggered luminescent “nano-bombs”.

Water-jet printing is a novel technique using water as the trigger to generate high-resolution luminescent patterns on solid media such as papers.^[19] The supra-CD-coated paper, in which supra-CDs – acting as luminescent “nano-bombs” – are uniformly buried in the paper fibers and can be precisely exploded by water, provide an ideal medium for printing luminescent patterns. The supra-CD-coated paper is successfully utilized for printing luminescent patterns by water-jet printing using a commercially available ink-jet printer where the cartridge was filled with only water (Figure S7, Supporting Information). The printing papers were simply prepared by coating commercially available filter papers with the supra-CDs (see the Experimental Section in the Supporting Information); the papers exhibit very weak luminescence under UV illumination. An encrypted image was obtained by combining water-jet printing with color ink-jet printing (**Figure 4a,b**). In daylight,

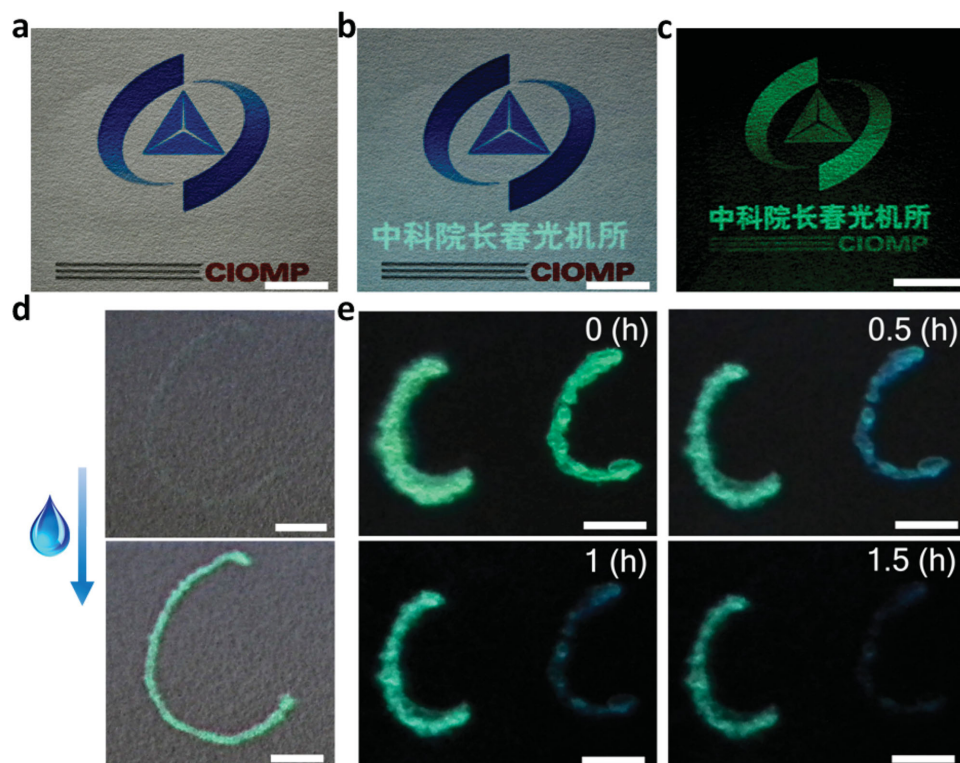


Figure 4. a,b) Photographs of printed image of supra-CD-coated paper using water-filled (3 mL) and HP 46 tricolor cartridges under daylight (a) and under UV and daylight (b) (scale bar = 1 cm). c) Photographs of printed image of supra-CD-coated paper using only purely water-filled (3 mL) cartridges under a UV lamp (scale bar = 1 cm). d) A handwritten image of “C” on commercially available filter paper using a fountain pen filled with a toluene solution of supra-CDs before and after water-spraying treatment under UV excitation (scale bar = 5 mm). e) Photostability of the water-induced luminescent image of “C” written using supra-CDs in toluene solution (left) and the luminescent image of “C” written using a commercially available highlighter pen (right) (scale bar = 1 mm).

only the colored-ink patterns are visible on the paper. The hiding characters on this sample are observable under UV light. A high-definition optical image containing both the icon and characters could be observed under UV and visible light (Figure 4c). In addition, a high-resolution image of the luminescent letters in point-size 5 can be observed under UV excitation with current water-jet printing (Figure S8, Supporting Information). It seems that the supra-CD-coated paper, which is compatible with water and commercially available inks, can be applied to information encryption and save fluorescent ink. Moreover, we also loaded the luminescent “nano-bombs” in patterns using a toluene solution of the supra-CDs on paper based on the pen-on-paper technique.^[20] Figure 4d shows the luminescent “nano-bombs” marked character C which is almost invisible under UV excitation. In contrast, a clear luminescent character C appears under UV excitation after water-spraying treatment. Meanwhile, the water-induced luminescent character C marked in the supra-CDs exhibits superior photostability compared to that marked in organic dyes from a commercially available highlighter pen (Figure 4h). The irradiating source was a 500 W mercury xenon lamp. The luminescent character marked in organic dyes was quickly quenched and nearly unobserved after 1.5 h irradiation. In contrast, the water-induced luminescent character C marked in supra-CDs can be clearly observed after 1.5 h irradiation. In addition, the water-induced enhancement of the luminescence in supra-CD-coated paper increased with an increase in the water-spraying treatment time and the concentration of the coated supra-CDs (Movie S1 and Figure S9

and S10, Supporting Information). These results indicate the supra-CD-coated paper can also be used as a new type of humidity sensor.

The collection and analysis of fingerprint information have played a very important role in the fields of forensic investigations, medical diagnostics, and social management owing to the uniqueness and stability of the friction ridge patterns for each individual.^[21] A single row of immutable and unique pores are distributed on each skin ridge, through which sweat is excreted and deposited on the surface of the skin. As the Level 3 fingerprint features (such as sweat-pores and ridge contours), sweat-pore analysis for personal identification has been mostly ignored because of the limitations in sweat-pore mapping technologies for obtaining fine, reliable, and straightforward sweat-pore patterns.^[22]

In view of the high sensitivity to trace amounts of water demonstrated in the process of printing the luminescent letters at high resolution, the supra-CD-coated paper has great potential for patterning sweat pores through the enhancement of luminescence induced by the water secreted from fingers. To verify this assumption, a fingerprint was deposited on a piece of supra-CD-coated paper by pressing a fingertip on the paper for 5 s. Compared to the reported fluorescent ink based on CD-Rs through which a fingerprint only contains the pattern of ridges and grooves (Figure S11, Supporting Information), the supra-CD-coated paper could form a clear fluorescent fingerprint in the form of green emitting dots under UV illumination (Figure 5a). This luminescent fingerprint in the form of emitting dots is

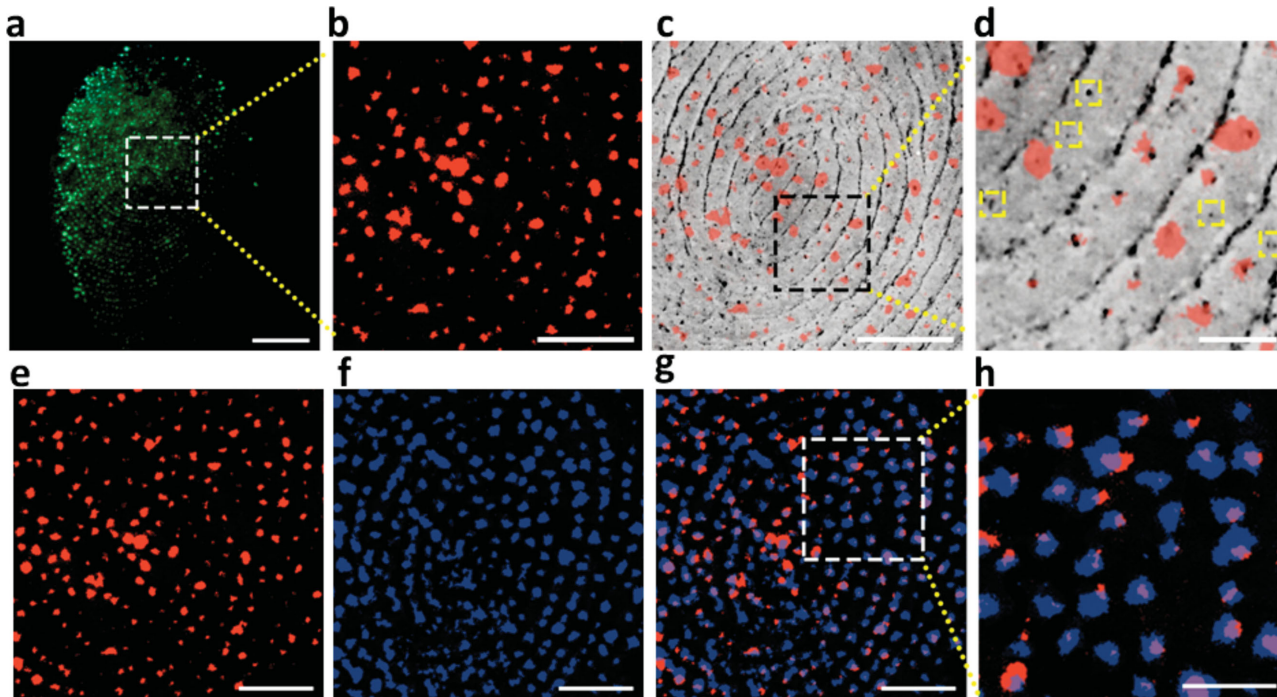


Figure 5. a) Photograph of a fingerprint image printed on supra-CD-coated paper (Scale bar = 5 mm). b) Fluorescence microscopy image of the magnified fingerprint area marked in (a) (Scale bar = 2 mm). c) Superimposed image of contrast-enhanced luminescent dots on a digital fingertip image (Scale bar = 2 mm); a “photoshop” program was used to improve the superimposed image. d) Magnified image of the marked area in (c) (Scale bar = 0.5 mm). e, f) Two independently printed contrast-enhanced luminescent microscopy fingerprint images deposited by the same donor. The red (e) and blue (f) images were intentionally generated using a “photoshop” program for comparison purposes (scale bar = 2 mm). g) Superimposition of the images displayed in (e) and (f) (Scale bar = 2 mm). h) Magnified image of the marked area in (g) (scale bar = 0.5 mm).

superimposed on a digital fingertip image (Figure 5b,c). These superimposed images demonstrate that the luminescent dots are distributed on the ridges of the fingerprint (Figure 5c,d). Meanwhile, the location of the black microdots in the digital fingertip image corresponding to sweat pores on the skin ridge matches well with the luminescent dots, confirming that these luminescent dots result from the explosion of the luminescent “nano-bombs” triggered by water in sweat secreted from sweat pores. In addition, luminescent dots do not appear in the yellow squares, indicating that sweat pores in these locations do not secrete sweat. To test the reproducibility of this mapping method, two independent fluorescent fingerprints were collected at different times (Figure 5e–h), which overlap with each other well. In order to investigate sweat pore functions, two superimposed fingerprint images from the same donor were deposited on the paper at different times (Figure S11, Supporting Information). Although most of the sweat pores are in the sweat-secreting state, some pores do not secrete sweat. Furthermore, the sweat-secreting active pores secreted different amounts of sweat during the observation period. This water-sensitive mapping method can be potentially applied to health monitoring and clinical diagnosis through the monitoring the sweat-secreting state.

In summary, water-induced luminescence is realized based on the supra-CD system. Following a facile route, partially dodecyl-functionalized CDs (CD-PS) are prepared; they self-assemble into supra-CDs with luminescence quenching in toluene. The weak luminescent supra-CD-coated paper exhibits enhanced luminescence after a water-spray treatment. This behavior is ascribed to the decomposition of the supra-CDs in the presence of water. Moreover, high-quality luminescent patterns and sweat-pore mapping of fingerprints are obtained on the supra-CD-coated paper by water-jet printing and simply pressing with a finger, respectively. These smart luminescent carbon nanomaterials hold great promise for applications in optical information storage, information security protection, and clinical diagnosis fields. The modulation of optical properties of CDs through self-assembly expands the scope of the research and applications of CDs, and will inspire further development of smart carbon-based nanomaterials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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