Electronic Supplementary Information (ESI)

Stimuli-responsive fluorophores with aggregation-induced emission: implication for dual-channel optical data storage

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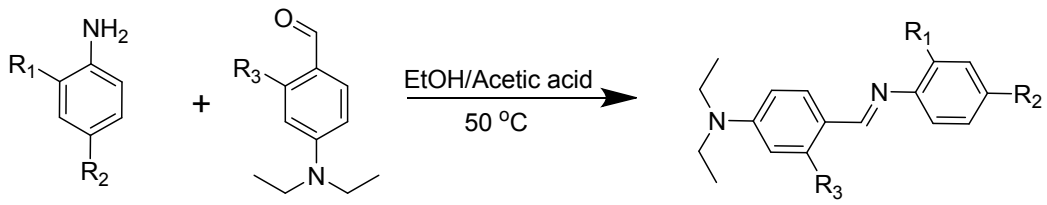
Experimental section

Materials and methods

Chemicals involved in this study were purchased from Aldrich or Alfa Aesar and used as received without further purification. ESI-mass spectra were recorded on a Bruker APEXII FT-ICR mass spectrometer. ^{1}H NMR spectra were recorded on a Varian VNMRS 600 MHz spectrometer using tetramethylsilane (TMS; $\delta = 0$) as an internal reference. UV-vis spectra were measured on a SHIMADZU UV 2550 spectrophotometer. Emission spectra were measured on a HITACHI F-7000 FL spectrophotometer. The ground-state geometries were optimized using density functional theory (DFT) with the B3LYP hybrid functional at the basis set level of 6-31G. The calculations were performed using the Gaussian 05 package. The fluorescence quantum yields (Φ_F) were determined using HORIBA FluoroMax-4 equipped with a calibrated integrating sphere. Wavelength accuracy: 0.5 nm. Absorption error: 0.097, relative error: 0.017.[1]

Synthesis and structural characterization

The fluorophores were prepared by a simple one-step reaction shown in Scheme S1. Synthesis and structural characterization of PBBA can be found in our previous publications.[2] Detailed synthetic process of PHBBA, OBBA and OHBBA is given as follows:



PBBA: R_1 = H R_2 = COOH R_3 = H

PHBBA: R_1 = H R_2 = COOH R_3 = OH

OBBA: R_1 = COOH R_2 = H R_3 = H

OHBBA: R_1 = COOH R_2 = H R_3 = OH

Scheme S1 Synthetic route to PBBA, PHBBA, OBBA and OHBBA.

Synthesis of PHBBA. To 250 ml round-bottom flask were added 4-(diethylamino)-2-hydroxybenzaldehyde (2.00 g, 10.35 mmol), 4-aminobenzoic acid (1.42 g, 10.35 mmol), 150 ml dehydrated ethanol and two drops of acetic acid. The reaction mixture was stirred at 50 °C for 5 h. After cooling to room temperature, the formed precipitate was filtered and washed several times by ethanol and hexane, respectively. No further purification was needed. Yield: 58%.

^{1}H NMR (400 MHz, DMSO-d6), δ (ppm): 13.42 (s, 1H), 12.83 (s, 1H), 8.75 (s, 1H), 7.98-7.95 (m, 2H), 7.41-7.35 (m, 3H), 6.36-6.33 (q, 1H), 6.09-6.08 (d, 1H), 3.43-3.38 (q, 4H), 1.15-1.11 (t, 6H).

ESI-MS: m/z: 313.10 ($[M + H]^+$ calcd 313.15).

Synthesis of OBBA. 4-(diethylamino)benzaldehyde (2.00 g, 11.28 mmol) was dissolved in dehydrated ethanol (130 ml) in a 250 ml round-bottom flask. Then dissolving 2-aminobenzoic acid (1.55 g, 17.06 mmol) in small amount of N,N-Dimethylformamide (DMF). The DMF solution and two drops of acetic acid were added to the flask. The mixture was stirred at 50

^{o}C for 5 h. It was then cooled to room temperature before being filtered. The solid product was washed several times by ethanol and hexane. No further purification was needed. Yield: 53%.

^{1}H NMR (400 MHz, DMSO-d6), δ (ppm): δ 8.64 (s, 1H), 8.04-8.02 (d, 1H), 7.72-7.61 (m, 5H), 7.32-7.30 (t, 1H), 7.21-7.18 (t, 1H), 6.82-6.81 (d, 2H), 6.72-6.71 (d, 1H), 6.49-6.46 (t, 1H), 3.45-3.41 (q, 4H), 1.12-1.10 (t, 6H).

ESI-MS: m/z: 297.15 ($[M + H]^{+}$ calcd 297.15).

Synthesis of OHBBA. An ethanol solution (130 ml) of 4-(diethylamino)-2-hydroxybenzaldehyde (2.00 g, 10.35 mmol) and a DMF solution (20 ml) of 4-aminobenzoic acid (1.42 g, 10.35 mmol) were mixed in a 250 ml round-bottom flask. Two drops of acetic acid were added and the reaction was stirred at 50 ^{o}C for 6 h. The precipitation was filtered and washed several times by ethanol and hexane, respectively. No further purification was needed. Yield: 57%.

^{1}H NMR (400 MHz, DMSO-d6), δ (ppm): 8.73 (s, 1H), 7.96-7.94 (d, 1H), 7.64-7.63 (d, 1H), 7.58-7.56 (t, 1H), 7.44-7.42 (d, 1H), 7.29-7.27 (t, 3H), 6.64 (s, 1H), 6.42-6.40 (d, 1H), 3.47-3.43 (q, 4H), 1.14-1.12 (t, 6H).

ESI-MS: m/z: 313.15 ($[M + H]^{+}$ calcd 313.15)

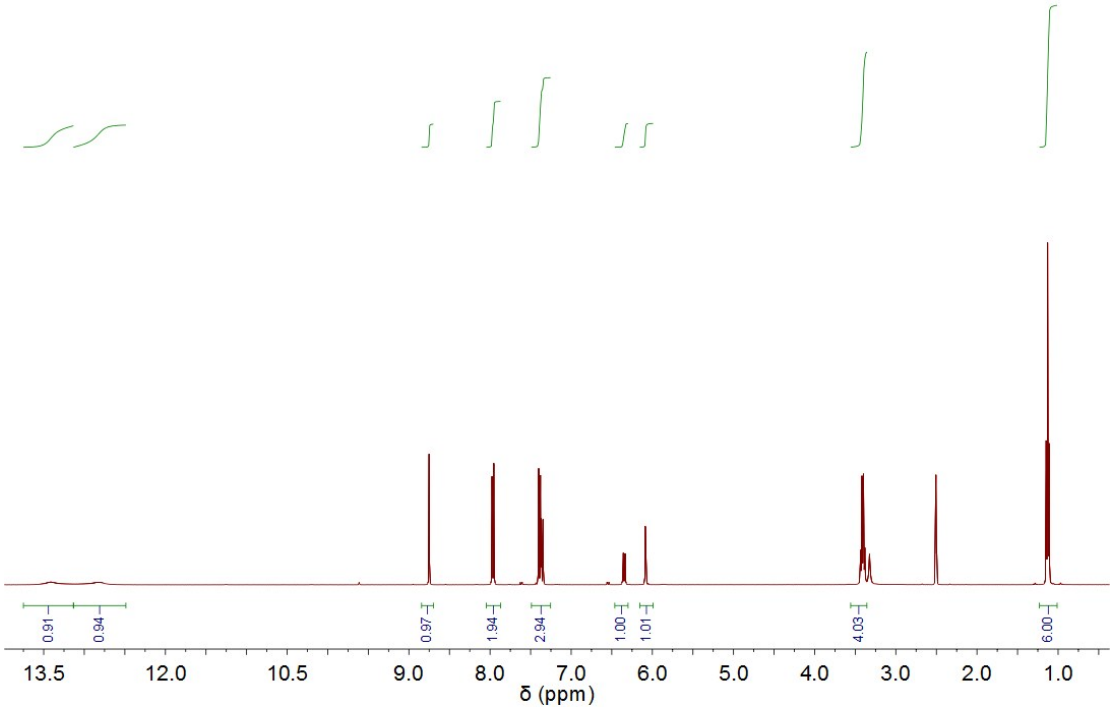


Fig. S1 ^{1}H NMR (600 MHz, 298 K) spectrum of PHBBA in DMSO-d_6.

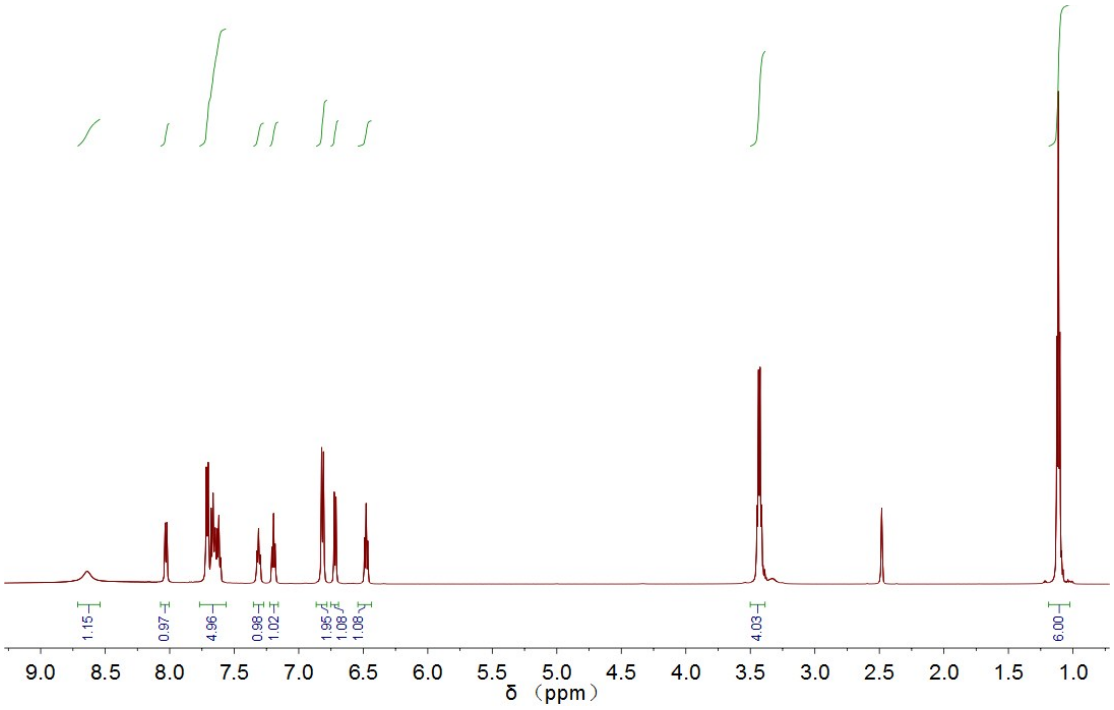


Fig. S2 ^{1}H NMR (600 MHz, 298 K) spectrum of OBBA in DMSO-d_6.

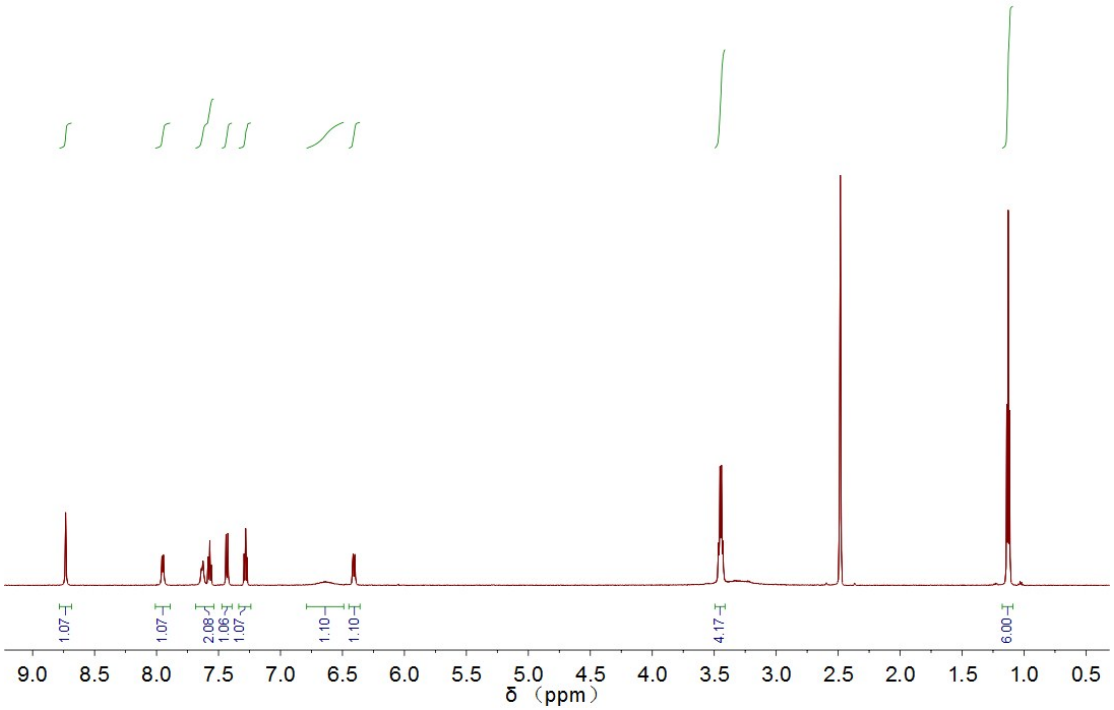


Fig. S3 ^{1}H NMR (600 MHz, 298 K) spectrum of OHBBA in DMSO-d_6.

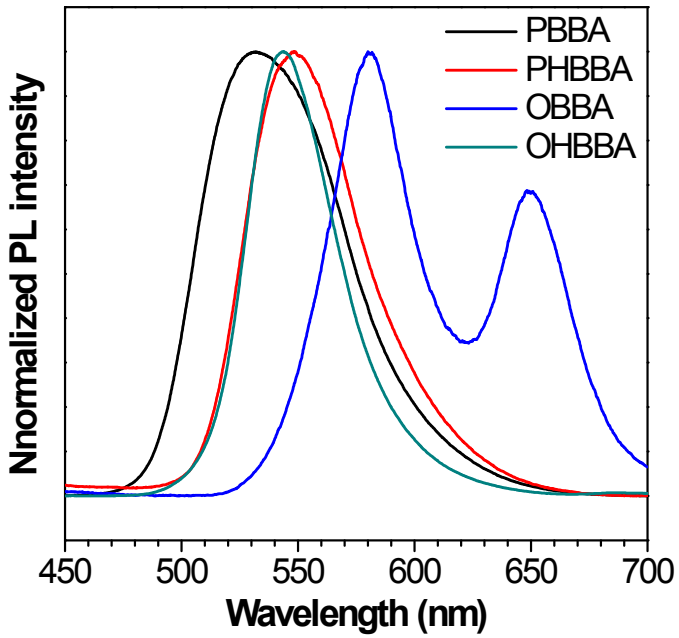


Fig. S4 Normalized emission spectra of PBBA, PHBBA, OBBA and OHBBA at solid state. Excitation wavelength: 360 nm (PBBA), 380 nm (PHBBA) and 370 nm (OBBA and OHBBA).

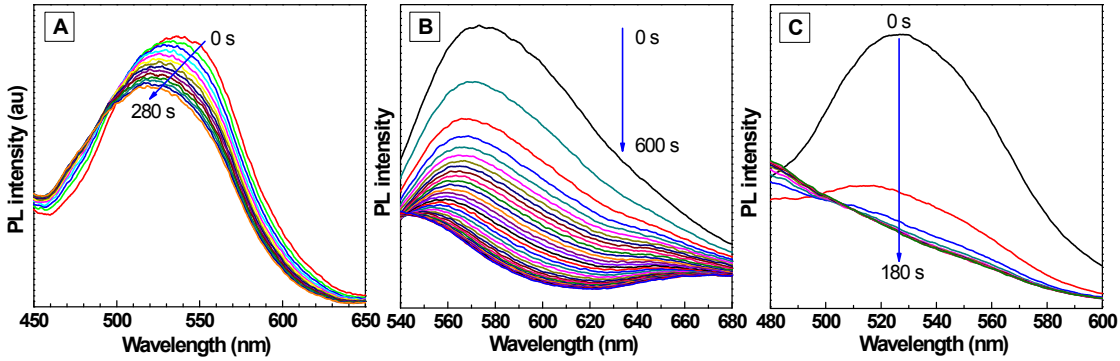


Fig. S5 Emission spectra of PHBBA (A), OBBA (B) and OHBBA (C) loaded on paper strip at every 20 s upon fuming by ammonia water. Excitation wavelength: 360 nm (PBBA), 380 nm (PHBBA) and 370 nm (OBBA and OHBBA).

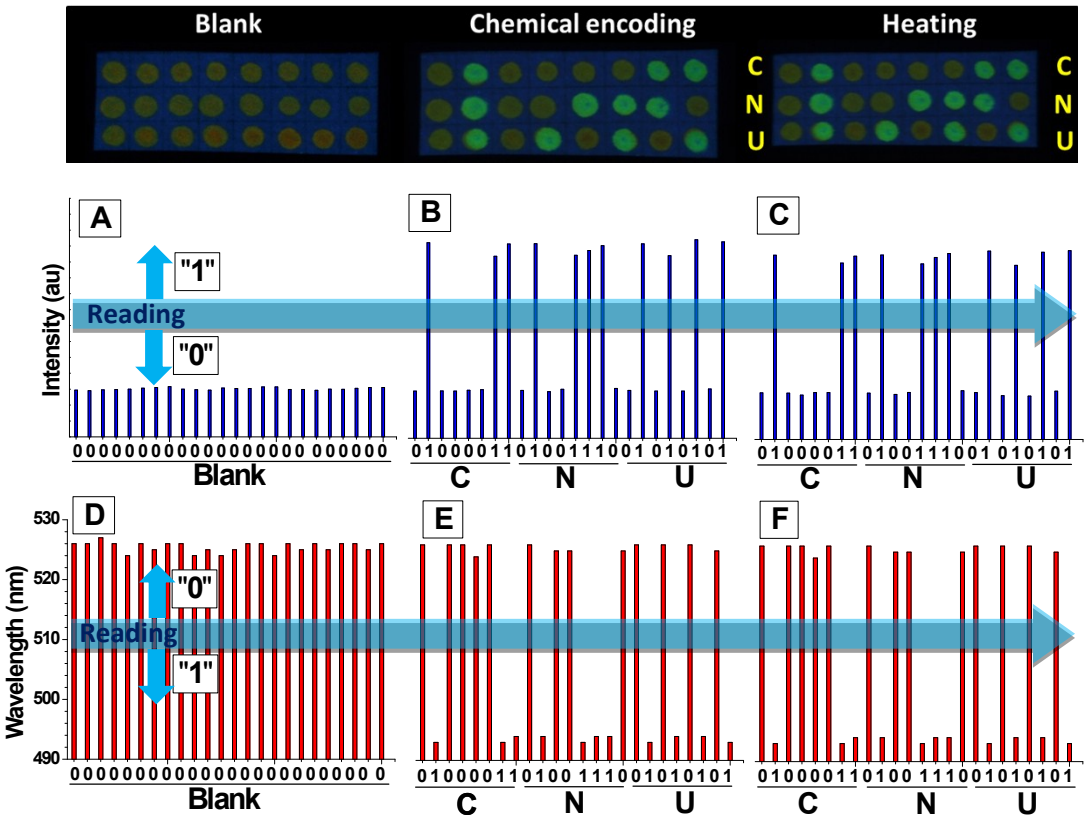


Fig. S6 Intensity histogram of the blank (A), Na_2CO_3-encoded (B) and thermally treated (C) dot matrix fabricated by PHBBA solution (THF, 5 mM). Threshold value: 1476; wavelength histogram of the blank (D), Na_2CO_3-encoded (E) and thermally treated (F) dot matrix. Threshold value: 509 nm. Excitation wavelength: 380 nm.

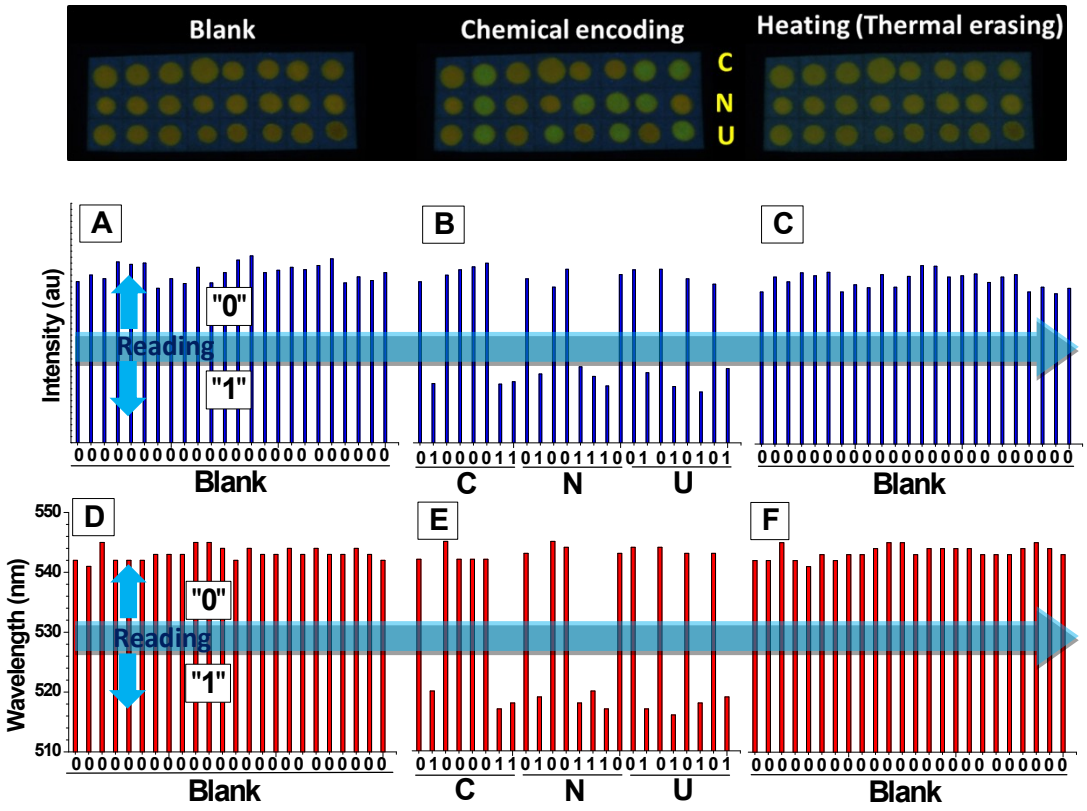


Fig. S7 Intensity histogram of the blank (A), NH_3-encoded (B) and thermally treated (C) dot matrix fabricated by PHBBA solution (THF, 5 mM). Threshold value: 492; wavelength histogram of the blank (D), NH_3-encoded (E) and thermally treated (F) dot matrix. Threshold value: 531 nm. Excitation wavelength: 380 nm.

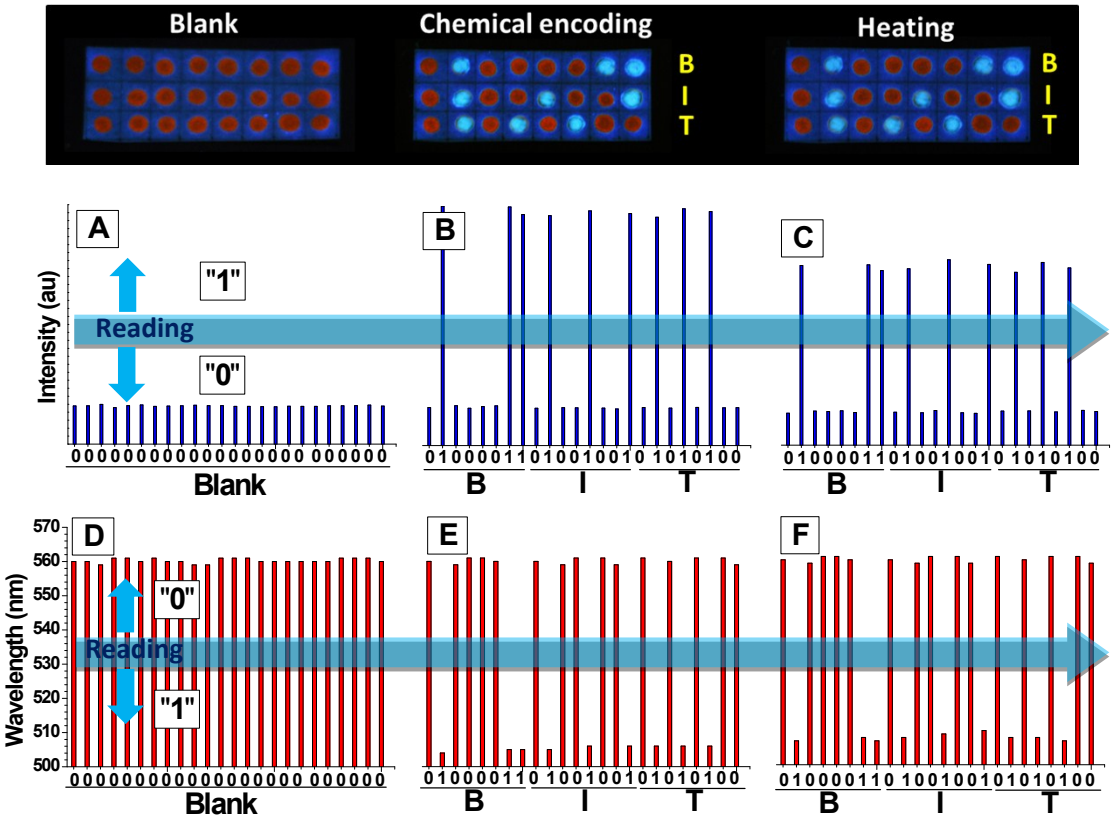


Fig. S8 Intensity histogram of the blank (A), Na_2CO_3-encoded (B) and thermally treated (C) dot matrix fabricated by OBBA solution (THF, 50 mM). Threshold value: 1700; wavelength histogram of the blank (D), Na_2CO_3-encoded encoded (E) and thermally treated (F) dot matrix. Threshold value: 532 nm. Excitation wavelength: 370 nm.

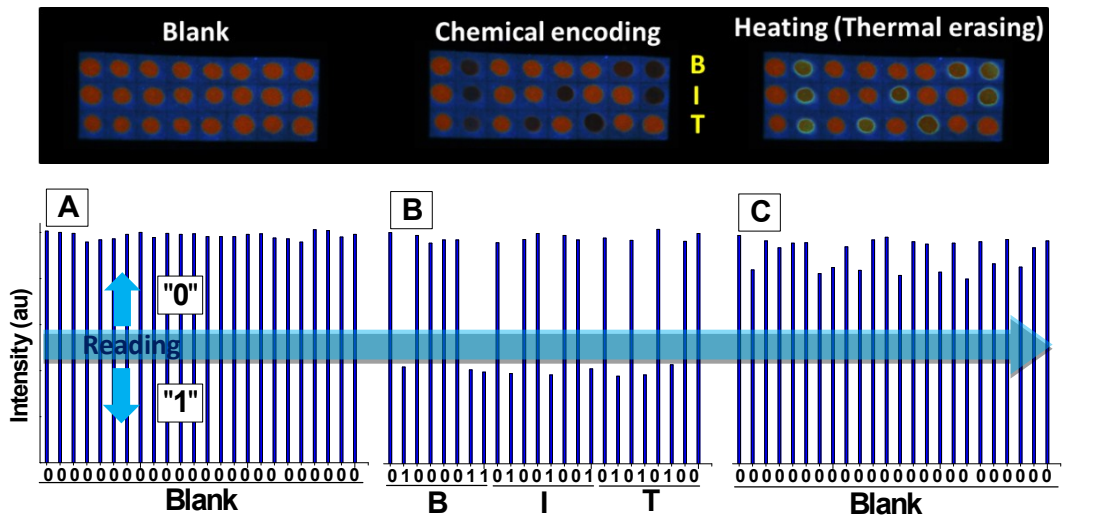


Fig. S9 Intensity histogram of the blank (A), NH_3-encoded (B) and thermally treated (C) dot matrix fabricated by OBBA solution (THF, 50 mM). Threshold value: 345. Excitation wavelength: 370 nm.

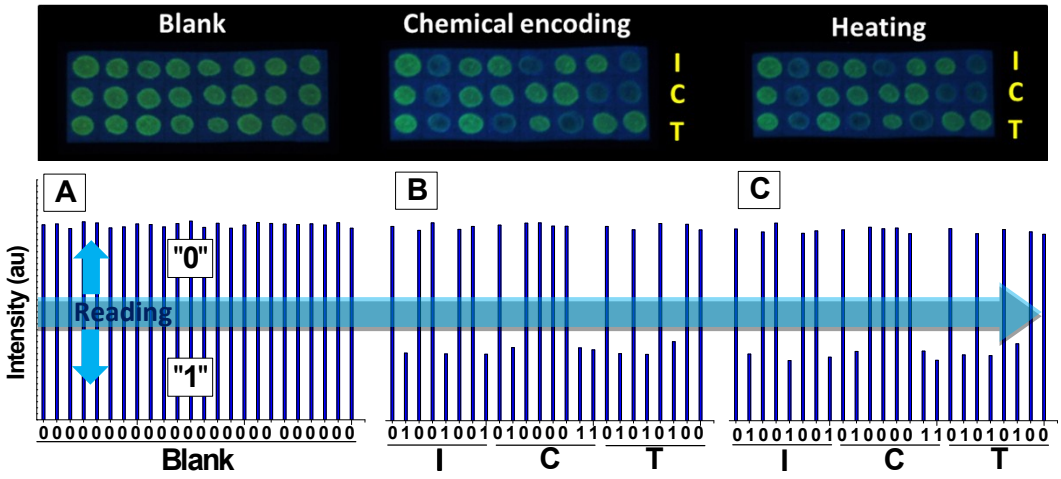


Fig. S10 Intensity histogram of the blank (A), Na_2CO_3-encoded (B) and thermally treated (C) dot matrix fabricated by OHBBA solution (THF, 5 mM). Threshold value: 2191. Excitation wavelength: 370 nm.

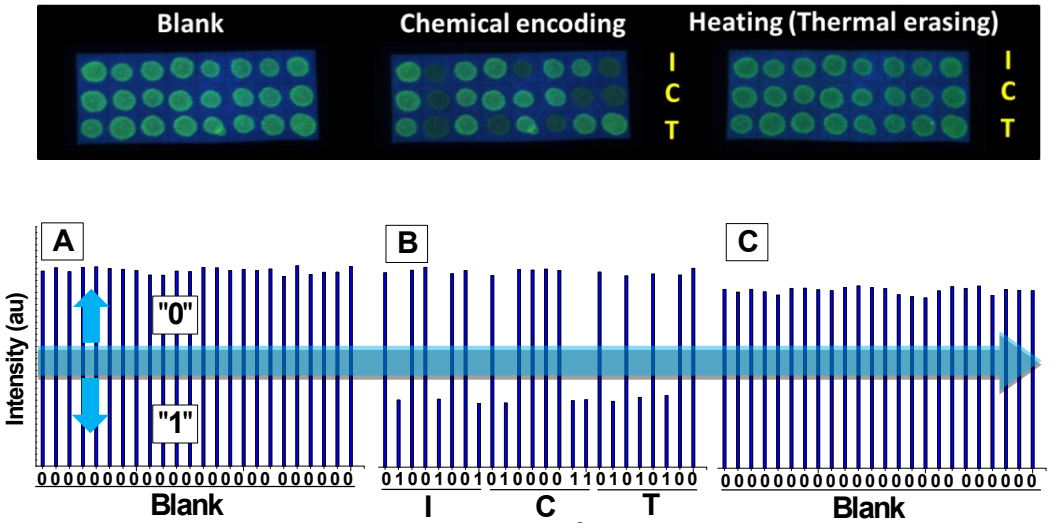


Fig. S11 Intensity histogram of the blank (A), NH_3-encoded (B) and thermally treated (C) dot matrix fabricated by OHBBA solution (THF, 5 mM). Threshold value: 2183. Excitation wavelength: 370 nm.

Reference

1 http://www.horiba.com/scientific/products/fluorescence-spectroscopy/

2 T. Han, W. Wei, J. Yuan, Y. Duan, Y. Li, L. Hu and Y. Dong, *Talanta*, 2016, **150**, 104.