

Supplementary Information

Surface molecular-imprinting engineering of novel cellulose nanofibril/conjugated polymer film sensors towards highly selective recognition and responsiveness of nitroaromatic vapors

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Experimental sections

1. Materials

9,9-dihexylfluorene-2,7-bis(trimethyleneborate), 3,5-dibromobenzamide, and tetrakis(triphenylphosphine) palladium (Pd(PPh₃)₄) were obtained from Synwit Technology Co., Ltd. 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), N-hydroxysuccinimide (NHS), 4-bromoaniline, 2-(N-Morpholino) ethanesulfonic acid (MES), glutaraldehyde and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) were purchased from Aladdin-Reagent Co., Ltd. Other reagents and solvents were obtained from commercial suppliers and used without further purification.

2. Characterization

FT-IR spectra were obtained using a Bruker TENSOR 27 spectrometer, and the samples were prepared as KBr disk pellets. UV-Vis absorption and photoluminescence (PL) spectra of samples were recorded using a Shimadzu UV-1700 Ultraviolet Spectrophotometer and a Hitachi F-4500 Fluorescence Spectrophotometer, respectively. X-ray photoelectron spectroscopy (XPS) data were

obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al K α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. Gel permeation chromatography (GPC) was carried out on a Waters GPC515-2410 System with THF as an eluant. ^1H NMR spectra were recorded with a Bruker Avance III 600 NMR spectrometer (DMSO- d_6 , 600 MHz).

3. Preparation of TOCN-COONa dispersions

TOCN-COONa dispersions were prepared according to the literature published by Akira et al. and described in brief as follows:¹ Cellulose fibers (2 g) were suspended in water (200 mL) containing TEMPO (0.033 g) and sodium bromide (0.33 g). The oxidation reaction was conducted by adding the predetermined amount of the NaClO solution (15 mmol/g cellulose). The pH value of the reaction solution was maintained 10 at 25 °C by adding 0.5 M NaOH for 4 h. The oxidized cellulose was thoroughly washed with water by filtration. 2 mg/mL oxidized cellulose/water slurries was sonicated for 5 min using an ultrasonic generator with a probe tip of 6 cm in diameter at an output power of 300 W in an ice bath. Cellulose nanofibrils dispersion was centrifuged at 10000 g for 10 min to remove the unfibrilated cellulose. The transparent cellulose nanofibrils dispersion was stored at 4 °C before used. The TEM of cellulose nanofibrils is shown in Fig. S6.

4. Preparation of TOCN films

The aqueous TOCN-COONa dispersions were poured into poly(styrene) petri dishes, and dried in a ventilated oven at 45 °C for 2 days without forced air-flow to obtain self-standing TOCN-COONa films. The TOCN films were obtained by the conversion of the sodium carboxylate groups to free carboxyl groups on the surface of films in HCL for 2 h (pH ~ 2.0), and then washed with water to neutral.

5. Surface modification of creating Br-containing reactive sites on TOCN films (Br-g-TOCN film)

Grafting of 4-bromoaniline onto the TOCN film surfaces with EDC and NHS was performed according to published literature.² A brief example is given here. First, the TOCN films (~2 cm², 64 mg) were added to MES buffer (20 mL, pH 5.0). Then EDC (226 mg) and NHS (38 mg) were added to this mixture with slowly stirring at 4 °C. After 30 min, the solution of 4-bromoaniline (177 mg) and DMF (5 mL) was added and stirred for another 24 h. The final TOCN films were rinsed twice each with solvent following sequence of DMF, water and methanol. The samples were used soxhlet extraction with THF and dried in vacuo.

6. Synthesis of grafted polymer chains (PFB)

The grafted polymer was performed according to the literature.^{3,4} To a 100-mL flask were added reagents consisting of 9,9- dihexylfluorene-2,7-bis(trimethyleneborate) (502 mg, 1 mmol), 3,5-dibromobenzamide (279 mg, 1 mmol), THF (15 mL) and 2M aqueous solution of K₂CO₃ (10 mL). The reaction mixture was stirred and degassed by bubbling N₂ for 30 min, then Pd(PPh₃)₄ (24 mg, 2.0 mol%) was added in one portion under N₂. After refluxing (about 69 °C) for 48 h, the end groups were capped by heating the mixture under reflux with 9,9- dihexylfluorene-2,7-bis(trimethyleneborate) (200 mg, 0.4 mmol) for another 6 h. The mixture was cooled and poured into methanol. The precipitates were collected by filtration and washed with abundant methanol and water several times, respectively. After removal of organic solvents and water, the solid was extracted with acetone for 48 h using Soxhlet apparatus to remove oligomers and catalyst residues. Finally, the PFBs were obtained after being dried at 40 °C under vacuum for 3 days. The ¹H NMR spectrum of PFB polymer is shown in Fig. S7.

7. Synthesis of PFB-g-TOCN films

The PFBs (800 mg) were dissolved in THF (30 mL) and 2 M aqueous solution of K_2CO_3 (20 mL), and the modified TOCN films ($\sim 2\text{ cm}^2$, 300 mg) were added. The mixture was stirred and degassed with nitrogen for 30 min, and a catalytic amount of $Pd(PPh_3)_4$ (24 mg) was added quickly. The reaction was then performed at $69\text{ }^\circ\text{C}$ for 12 h. After cooling to room temperature, the PFB-g-TOCN films were rinsed twice with THF, DCM, methanol, water and THF. The samples were then soxhlet extracted for 12 h in THF before being dried in vacuo.

8. Preparation of TNT/DNT-imprinted PFB-g-TOCN films

The PFB-g-TOCN films ($\sim 2\text{ cm}^2$, 0.5 g) were added into the DNT aqueous solution (1 mmol/L). The mixture was interacted at room temperature for 5 h until the adsorption reached equilibrium. Then, the PFB-g-TOCN films, which have adsorbed DNT in a saturation state, were dried under vacuum. The DNT-adsorbed PFB-g-TOCN film ($\sim 2\text{ cm}^2$, 0.1 g) was placed in a mixed solution (100 mL) of water and DNT, in which DNT with a concentration of 1 mmol/L was contained. After adding the crosslinking agent glutaraldehyde (1 mL), the crosslinking reaction was performed at $50\text{ }^\circ\text{C}$ for 8 h. The films were washed repeatedly with ethanol and acetic acid solution containing NaCl, THF, methanol and water to remove the residual glutaraldehyde and template DNT. Then the DNT-imprinted PFB-g-TOCN film was obtained.

The TNT-imprinted PFB-g-TOCN film was obtained in the the same way. The non-imprinted PFB-g-TOCN film was prepared following the same procedure as for the imprinted film except not having a template added.

9. Synthesis of PFB(SC) film

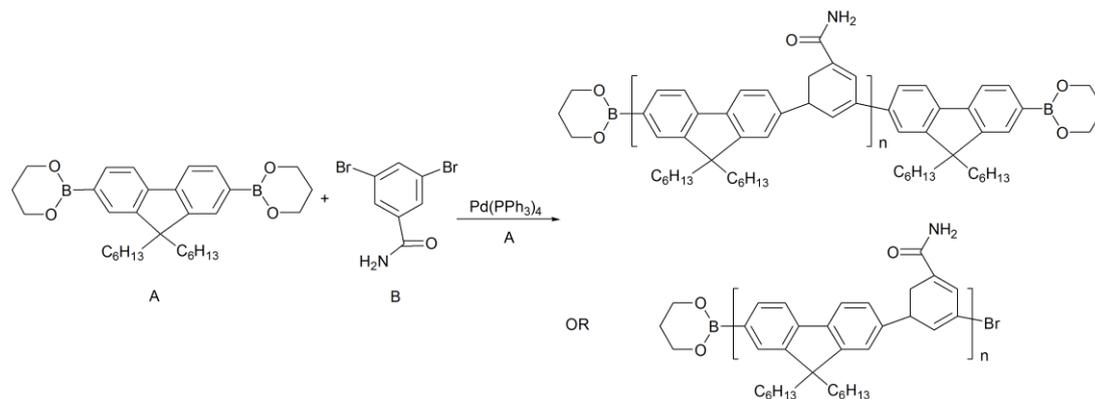
The PFB(SC) films were prepared by a conventional spin-coating technique. In brief, the PFBs

solution (0.45 mg in 1.0 mL THF) was spin-coated onto a quartz substrate (microscope slide, length: 24 mm, width: 24 mm and thickness: 1 mm) at a spin rate of 1000 rpm. Then, the films were dried at 30 °C under vacuum for 1 day to remove any residue in the films.

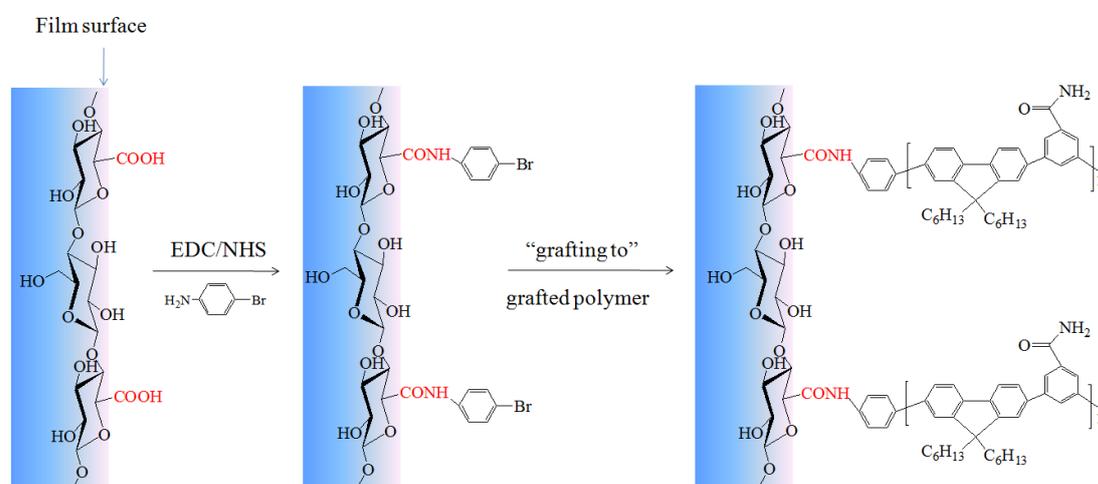
References

1. T. Saito, S. Kimura, Y. Nishiyama and A. Isogai, *Biomacromolecules*, 2007, 8, 2485-2491.
2. N. Dhar, S. P. Akhlaghi and K. C. Tam, *Carbohydrate Polymers*, 2012, 87, 101-109.
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4. Q. Zhao and W. Wu, *Synthetic Metals*, 2009, 159, 1153-1157.

1) Synthetic routes of PFB



2) Grafting PFB onto the TOCN film surface



Scheme S1 Schematics of synthetic routes of PFB and its coupling onto the TOCN film surface

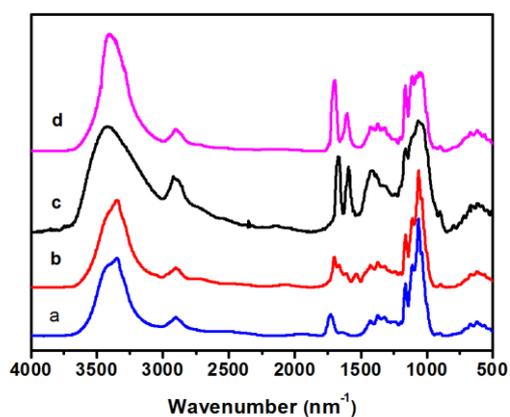


Fig. S1 Infrared spectra of a) TOCN film, b) Br-g-TOCN film, c) PFB-g-TOCN film, and d) "DNT-imprinted" PFB-g-TOCN film

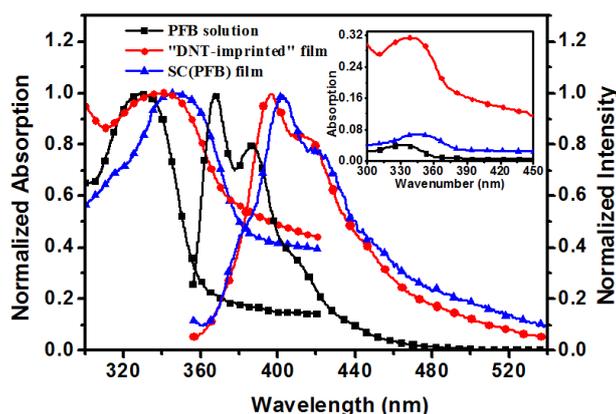


Fig. S2 Absorption (*left*) and fluorescence (*right*) spectra of PFB solution, PFB(SC) film, and “DNT-imprinted” PFB-g-TOCN film; Inset: the original non-normalized absorption spectra of PFB solution, PFB(SC) film, and “DNT-imprinted” PFB-g-TOCN film.

Table S1 Photophysical data of PFB solution, “DNT-imprinted” PFB-g-TOCN film, and PFB(SC) film

Samples	$\lambda_{\text{abs}}^{[a]}$ (nm)	$\lambda_{\text{em}}^{[b]}$ (nm)	Stokes shift ^[c] (nm)	$\phi_{\text{PL}}^{[d]}$
PFB solution ^[e]	330	368	38	0.59
PFB(SC) film	344	403	59	0.35
“DNT-imprinted” film	338	397	59	0.33

[a] Absorption maximum; [b] Emission maximum; [c] Stroke shift = $\lambda_{\text{em}} - \lambda_{\text{abs}}$; [d] Fluorescence quantum yield (ϕ_{PL}) determined using 9,10-diphenylanthracene ($\phi_{\text{PL}}=0.90$ in cyclohexane) as standard (for solution sample) or measured by $\sim 10^{-3}$ M 9,10-diphenylanthracene in Poly(methyl methacrylate) (PMMA) spin-cast film (for solid films, $\phi_{\text{PL}}=0.83$); [e] In dilute THF solution (4.7 mg/L).

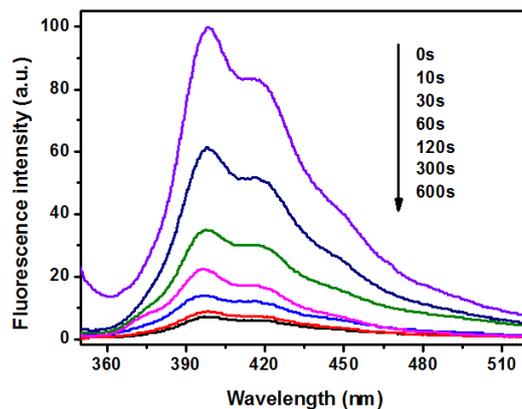


Fig. S3 Time-dependent fluorescence intensities of “TNT-imprinted” PFB-g-TOCN film upon exposure to TNT vapor at excitation wavelength of 338 nm

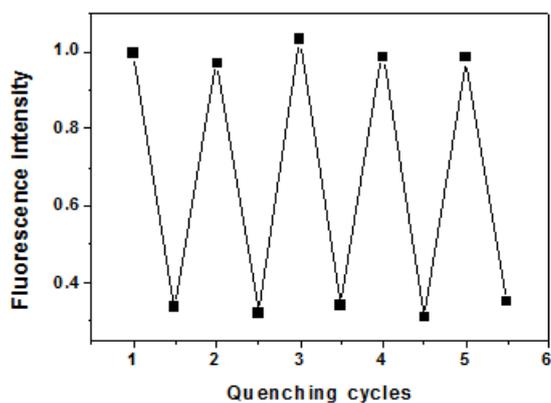


Fig. S4 The fluorescence quenching-recovery cycles test after the “DNT-imprinted” PFB-g-TOCN film exposing to DNT for 60 s

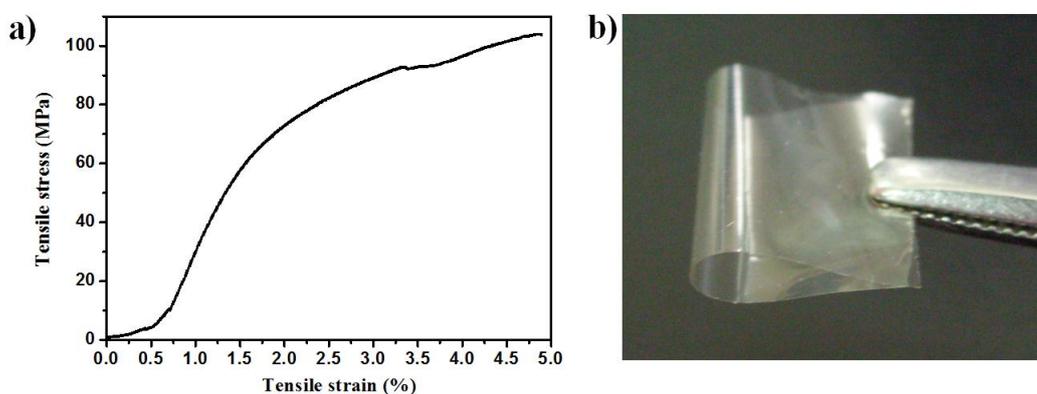


Fig. S5 a) Stress-strain curve of “DNT-imprinted” PFB-g-TOCN film; b) Digital pictures of “DNT-imprinted” PFB-g-TOCN film

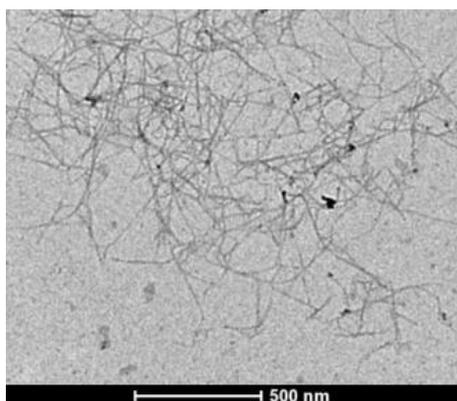


Fig. S6 TEM of cellulose nanofibrils

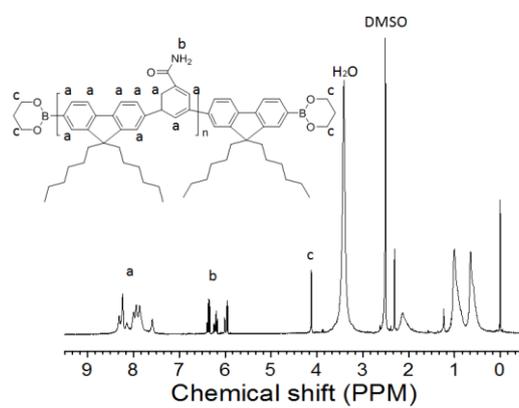


Fig. S7 The ¹H NMR spectrum of PFB polymer