Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Support Information

An ultrasensitive PVDF-based molecularly imprinted fluorescent test strip for rapid and off-line detection of 4-NP with improved anti-coffee ring effect

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Drugs and reagents

4-nitrophenol (4-NP), polyethyleneimine (PEI), dopamine hydrochloride (DA), Thioglycolic acid (TGA), γ-methacryloxypropyl trimethoxysilane (KH570), $CdCl_2 \cdot 2.5H_2O$, $NaBH_4$, methacrylic acid (MAA), tellurium powder, tetraethyl orthosilicate (TEOS), ammonium hydroxide ($NH_3 \cdot H_2O$), ethylene glycol dimethacrylate (EGDMA), Allyl glycidyl ether (AGE), 2,2-azobis (2-methylpropionitrile) (AIBN), o-nitrophenol (o-NP), m-nitrophenol (m-NP), catechol (CA) and 2, 6-dichlorophenol (2, 6-DP) were purchased from Aladdin reagent Company (Shanghai, China). HCl, NaOH, ethyl alcohol, toluene, acetic acid, methyl alcohol and methanol (chromatographically pure) were bought from Guoyao Chemical Reagent (Shanghai, China). All chemicals were of analytical grade reagents, and the water used in the whole experiment was double distilled water (DDW).

Instrument

The model of heating magnetic stirrer is RET basic (IKA, Germany). The electronic balance model is TE124S (Sartorius, Germany). The structure and composition analysis of nanomaterial was investigated by Nicolet NEXUS-470 apparatus fourier transform infrared (FT-IR, U.S.A), The laser confocal microscope (LCSM), TCS SP5 II, brookhaven instruments companies in the United States. F98 fluorescence spectrophotometer (Shanghai Leng Light Technology Co. LTD, China) was used to measure the FL spectrum of fluorescent probes. The laser confocal microscope (LCSM), TCS SP5 II, brookhaven instruments companies in the United States. The scanning electron microscope (SEM, JEOL, JSM-7001F) and transmission electron microscope (TEM, JEOL, JEM-2100) were employed to observe the morphologies. The contact angles were detected by OSA60 (LAUDA Scientific, Germany). HPLC (Agilent 1260 Infinity II) was used to detect 4-NP in actual samples.

Preparation of CdTe QDs

The thiol modified CdTe QDs was synthesized with reflux method referring to previous reported work [1, 2].

First, precursors are prepared. Typically, tellurium powder (51 mg), $NaBH_4$ (100 mg) and DDW (1.5 mL) turned into the centrifuge tube in turn. After removal of hydrogen, the precursor NaHTe was obtained by ultrasonic reaction for 1.0 h. Then $CdCl_2 \cdot 2.5H_2O$ and TGA solutions were dispersed in DDW (100 mL) and set pH to 11.2 by NaOH (1.0 mol/L). Nitrogen gas was purged to intermixture under continuous

stirring for half an hour. Then, the above NaHTe was rapidly added in the mixture. The mixture was allowed to reflux react for 3.0 d at 120 ^{o}C under nitrogen condition. The green-emission CdTe QDs was the same operation with red-emission CdTe QDs except the reaction time, green-emission CdTe QDs were obtained by the reflux react for 1.0 h. The green-emission and red-emission CdTe QDs was collected by centrifuge.

Preparation of F-PDA

The synthesis of F-PDA referred to the previous synthesis method with some modifications[3], firstly, the PEI was dissolved in DDW, the concentration of PEI solution was 1.0 g/L, next, 20 mg DA was added into the PEI solution, the reaction was sit for a while without stirring, the PEI solution was alkaline, which provided the conditions for the oxidation of dopamine, after sitting for 6.0 h, the color of the reaction turning into brown and the color of the reaction under 365 nm UV lamp was green, then the F-PDA was stirred in DDW with a 3500 Da dialysis bag for 24 h to filter out unreacted reactants and impurities to obtain pure fluorescent polydopamine. Finally, all the solutions were freeze dried under -90 ^{o}C and were stored in low temperature for further use.

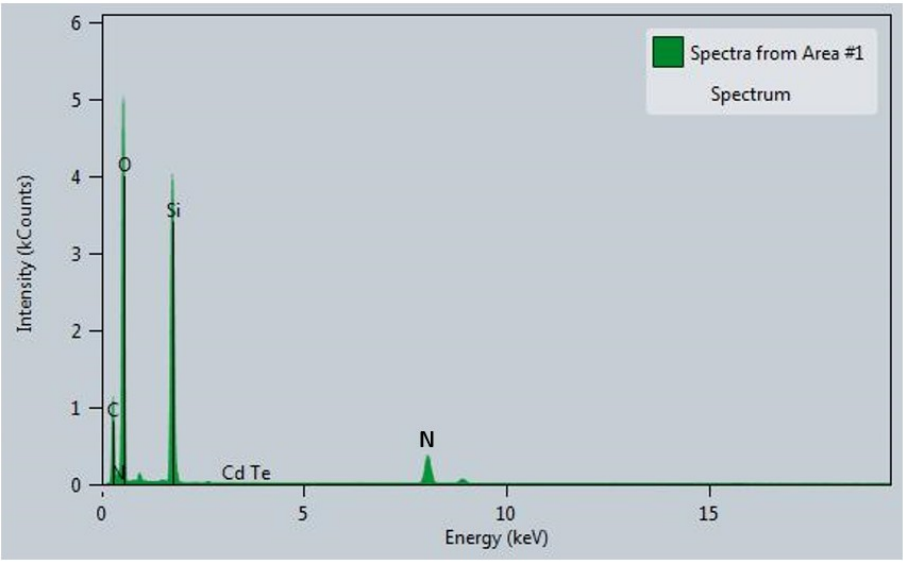


Figure S1. Energy spectrum analysis of CdTe@SiO_2@F-PDA/MIPs

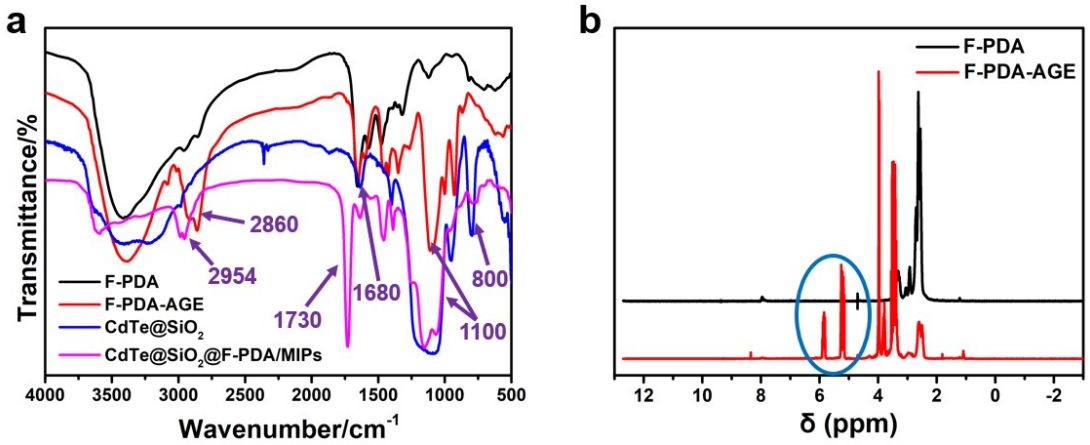


Figure S2. (a) FT-IR spectra of F-PDA (black line), F-PDA-AGE (red line), CdTe@SiO_2 (blue line) and CdTe@SiO_2@F-PDA/MIPs (pink line); (b) ^{1}HNMR spectra of F-PDA (black line) and F-PDA-AGE (red line)

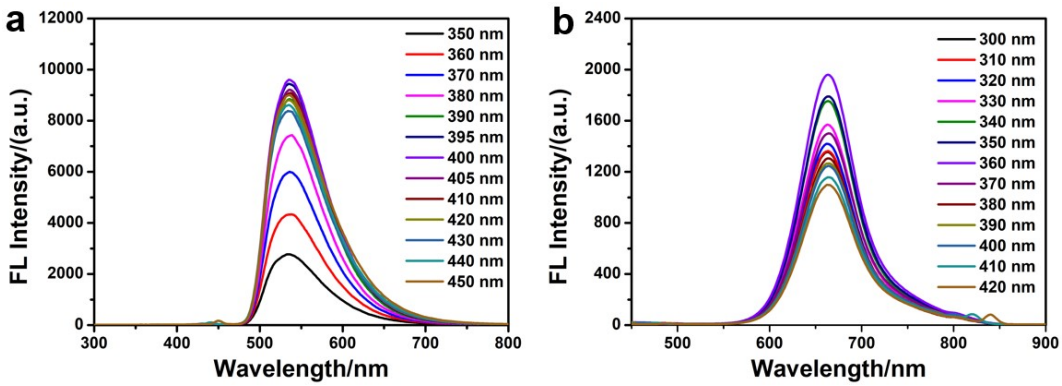


Figure S3 Fluorescence emission wavelengths and fluorescence intensities pictures of F-PDA (a) and CdTe QDs (b) as a function of different excitation wavelengths

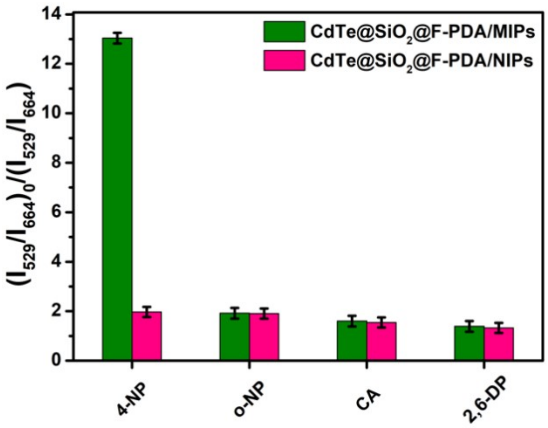


Figure S4 The $(I_{529}/I_{664})_0/(I_{529}/I_{664})$ value of CdTe@SiO_2@F-PDA/MIPs (green bars) and CdTe@SiO_2@F-PDA/NIPs (pink bars) exposed to 550 nM 4-NP, o-NP, CA and 2, 6-DP.

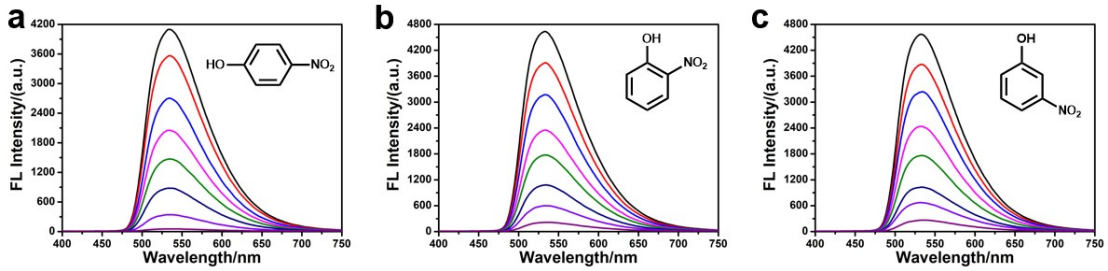


Figure S5 FL spectra of F-PDA exposed to the same concentrations (0-200 nM) of 4-NP (a), o-NP (b) and m-NP (c)

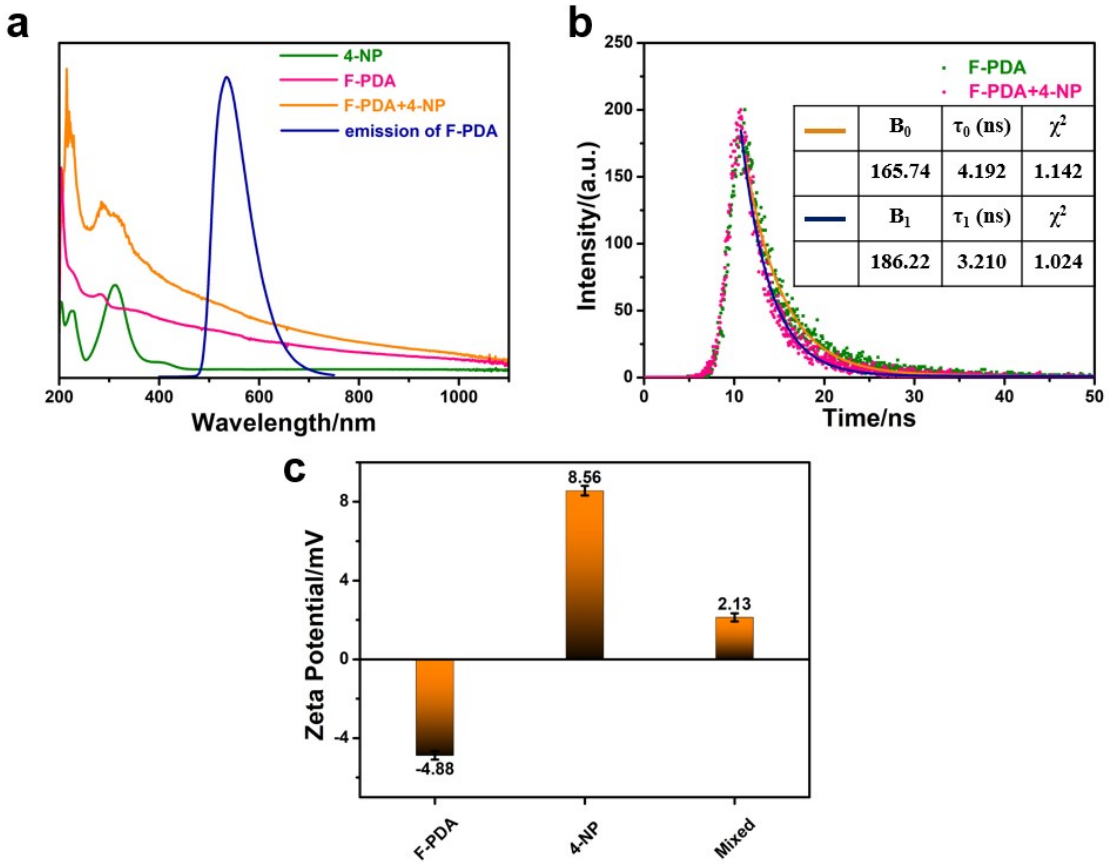


Figure S6 (a) Fluorescence emission spectrum of F-PDA (blue line), UV absorption spectra of 4-NP (green line), F-PDA (pink line) and F-PDA with 4-NP (orange line); (b) fluorescence lifetimes of F-PDA (green square) and F-PDA with 4-NP (pink diamond), the corresponding first-order fitting curves of F-PDA (orange line) and F-PDA with 4-NP (blue line); (c) zeta potential of F-PDA, 4-NP and the mixture of F-PDA with 4-NP

Table S1 List of surface roughness values of different hydrophobic membranes

Hydrophobic membrane	PE membrane	PTFE hydrophobic membrane	PVDF hydrophobic membrane
Rq/nm	45.1	84.1	197
Ra/nm	34.8	65.7	156

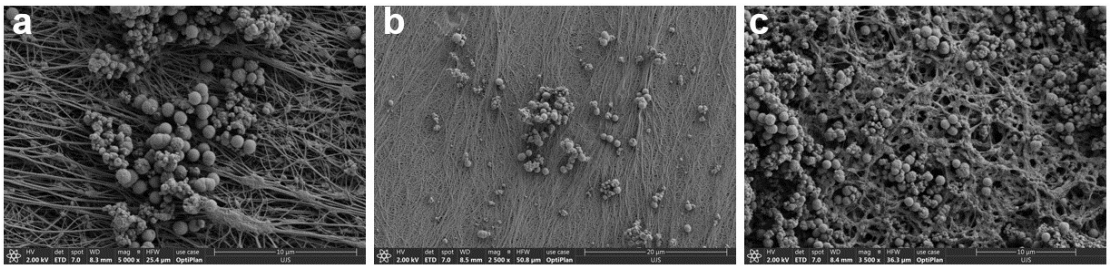


Figure S7 SEM images of the same amount of CdTe@SiO_2@F-PDA/MIPs on PTFE hydrophobic membrane (a), PE membrane (b) and PVDF hydrophobic membrane (c) after keeping for a week

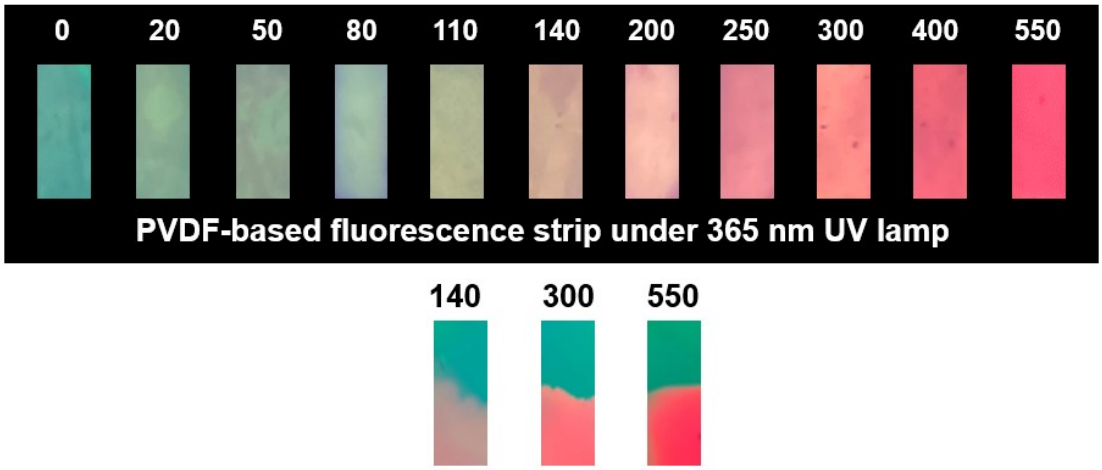
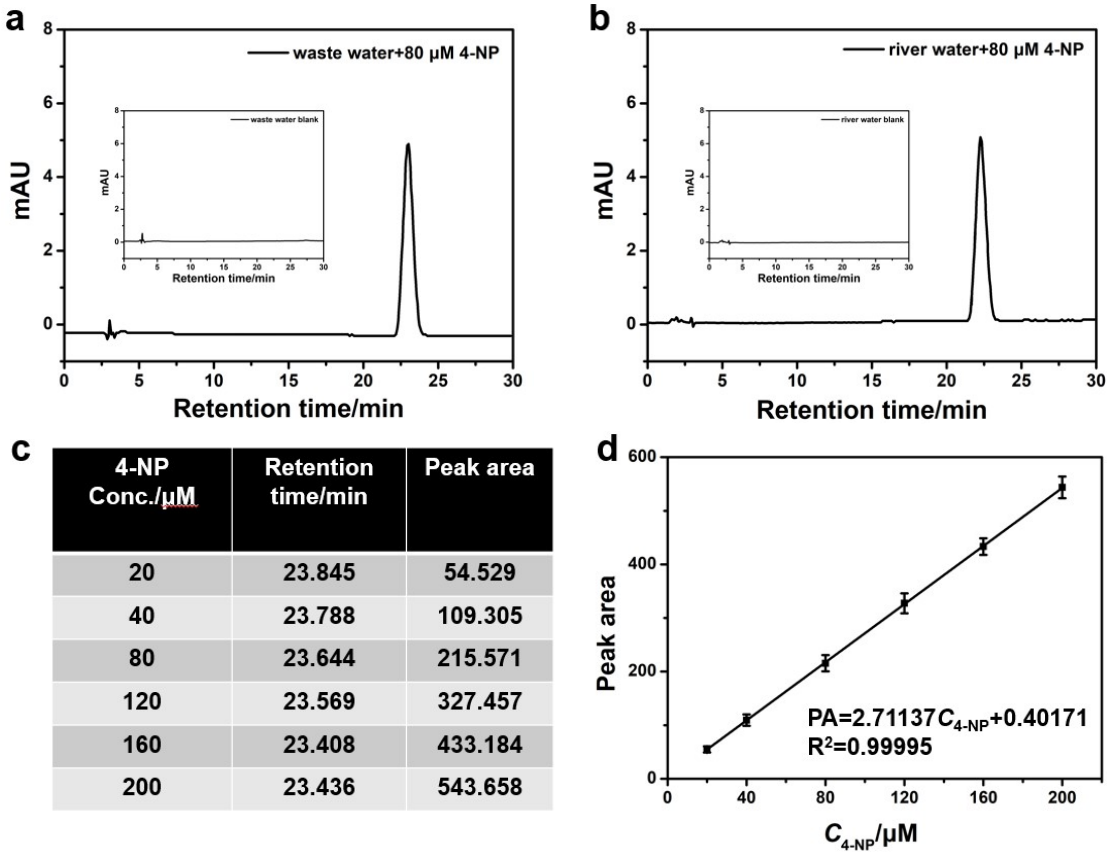


Figure S8 Pictures of PVDF fluorescent test strips under different 4-NP concentrations with fully addition (above) and with partly addition (bottom).



4-NP Conc./μM	Retention time/min	Peak area
20	23.845	54.529
40	23.788	109.305
80	23.644	215.571
120	23.569	327.457
160	23.408	433.184
200	23.436	543.658

Figure S9 (a) and (b) The HPLC profiles of waste water and river water spiked with 80 μM 4-NP, (the insets were the HPLC profiles of waste water and river water), the actual concentrations of 4-NP in waste water and river water were 0.443 μM and 0.268 μM respectively; (c) and (d) The paramaters of HPLC results and corresponding calibration curve for 4-NP.

Reference:

[1] X. Wei, T. Hao, Y. Xu, K. Lu, H. Li, Y. Yan, Z. Zhou, Facile polymerizable surfactant inspired synthesis of fluorescent molecularly imprinted composite sensor via aqueous CdTe quantum dots for highly selective detection of lambda-cyhalothrin, Sensors and Actuators B-Chemical, 224 (2016) 315-324.

[2] X. Wei, Z. Zhou, T. Hao, Y. Xu, H. Li, K. Lu, J. Dai, X. Zheng, L. Gao, J. Wang, Y. Yan, Y. Zhu, Specific recognition and fluorescent determination of aspirin by using core-shell CdTe quantum dot-imprinted polymers, Microchimica Acta, 182 (2015) 1527-1534.

[3] M.Y. Liu, J.Z. Ji, X.Y. Zhang, X.Q. Zhang, B. Yang, F.J. Deng, Z. Li, K. Wang, Y. Yang, Y. Wei, Self-polymerization of dopamine and polyethyleneimine: novel fluorescent organic nanoprobes for biological imaging applications, Journal of Materials Chemistry B, 3 (2015) 3476-3482.