Electronic Supplementary Information

A versatile covalent organic framework-based platform for sensing biomolecules

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EXPERIMENTAL SECTION

Reagents. All chemicals and reagents used are at least of analytical grade. Ultrapure water was purchased from Wahaha Foods Co. (Tianjin, China). 1,3,5-Triformylphloroglucinol (Tp), 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (Tta), 1,3,5-Tris(4'-aminophenyl)benzene (Tab) was obtained from Chengdu Tongchuangyuan Pharmaceutical Technology Co. (Chengdu, China), p-phenylenediamine (Pa-1), benzidine (BD), Tris(hydroxymethyl)aminomethane (Tris), KCl, NaCl and $MgCl_2$ were obtained from Aladdin Chemistry Co. (Shanghai, China). Hydrochloric acid (HCl), 1,4-dioxane, mesitylene, acetic acid, dichloromethane (DCM), and N,N-dimethylformamide (DMF) were purchased from Concord Fine Chemical Research Institute (Tianjin, China). Adenosine 5'-triphosphate (ATP), uridine 5'-triphosphate (UTP), guanosine 5'-triphosphate (GTP) and all oligonucleotides used in this work were synthesized by Shanghai Sangon Biotechnology Co., Ltd. (Shanghai, China), single-base mismatched DNA (T1) 5'-CTA CGA TGA ACA TGT TAG CGA-3' and dual-base mismatched DNA (T2) 5'-CTA CGA TGA ACA TTT TAG CGA-3'.

Instrumentation and Characterization. X-ray diffraction spectrometry (XRD) patterns were recorded on a D/max-2500 diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 1.5418 Å) over the angular range from 2° to 80°. The morphology of the COF was characterized on a Shimadzu SS-550 scanning electron microscope at 15.0 kV and high-resolution transmission electron micrograph on a JEM-2100F field emission transmission electron microscope (JEOL, Japan) operating at a 200 kV accelerating voltage. A Magna-560 spectrometer (Nicolet, Madison, WI) was used to record the Fourier transform infrared spectra in KBr plate. All fluorescence measurements were carried out on an F-7000 spectrofluorometer (Hitachi, Japan). The excitation

wavelength was set to 493 nm, and the 24 photomultiplier tube voltage was set to 700 V. The emission spectra from 505 to 620 nm were collected, with the maximum emission observed at 528 nm. The slits for excitation and emission were both set at 5 nm.

Synthesis of TpTta / TpTab. TpTta / TpTab were synthesized via solvothermal method. Briefly, Tp (0.15 mmol), Tta / Tab (0.15 mmol), 3 mL of dioxane, 0.25 mL of 6 M aqueous acetic acid was mixed in Schlenk tube. After flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles, the tube was sealed off and heated at 120 °C for 3 days. The precipitate was collected by centrifugation and washed with DMF thrice and DCM twice. The collected powder was dried in vacuum overnight. TpPa-1 and TpBD were synthesized according to the previous report.[1, 2]

COF-based fluorescent platform for sensing biomolecules. The DNA assay was performed in 100 μL of reaction buffer (10 mM Tris-HCl, 50 mM NaCl, 10 mM $MgCl_2$, PH=7.4) containing 10 μg TpTta, 50 nM FAM-labeled probe and the target DNA with different concentrations, and the reaction solution was incubated at 37 ^{o}C for 2 h before the fluorescence measurements. The ATP assay was performed in 100 μL of reaction buffer (20 mM Tris-HCl, 140 mM NaCl, 5 mM KCl, PH=7.4) containing 10 μg TpTta, 50 nM FAM-labeled aptamer and the ATP with different concentrations, and the reaction solution was incubated at 37 ^{o}C for 1 h before the fluorescence measurements.

Serum sample assay. 0.4 mL serum sample was mixed with 0.6 mL acetonitrile. After vigorous shaking for 2 min, the mixture was centrifuged at 10,000 rpm for 10 min. The obtained supernatant was diluted at a 1:100 ratio with the buffer solution for DNA assay.

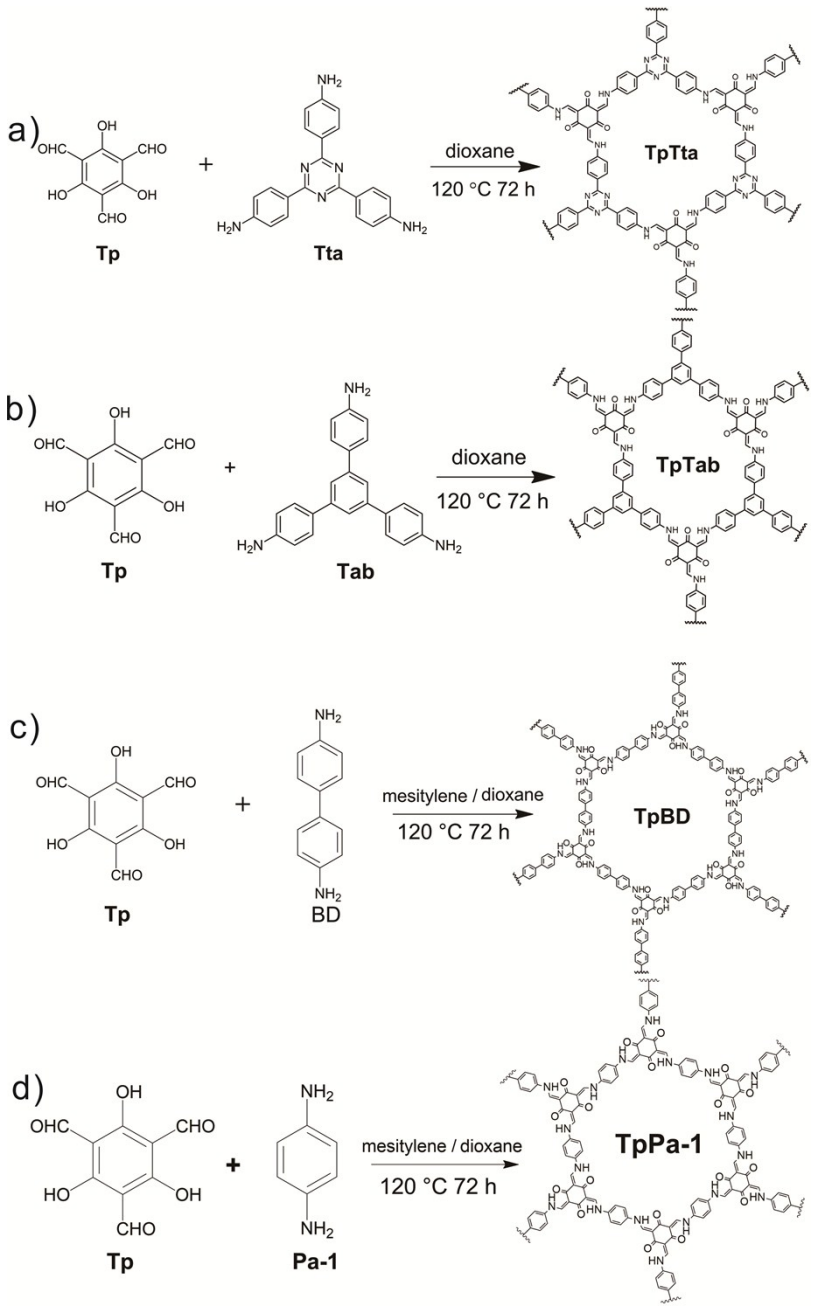

Fig. S1 Solvothermal synthesis reactions: (a) TpTta, (b) TpTab, (c) TpBD, (d) TpPa-1. These COFs are all stable in aqueous solution due to the irreversible reaction of the enol-to-keto tautomerism. The Brunauer−Emmett−Teller (BET) surface areas of TpTta, TpTab, TpBD and TpPa-1 are 609, 567, 537and 535 m^2 / g, respectively.[1-4]

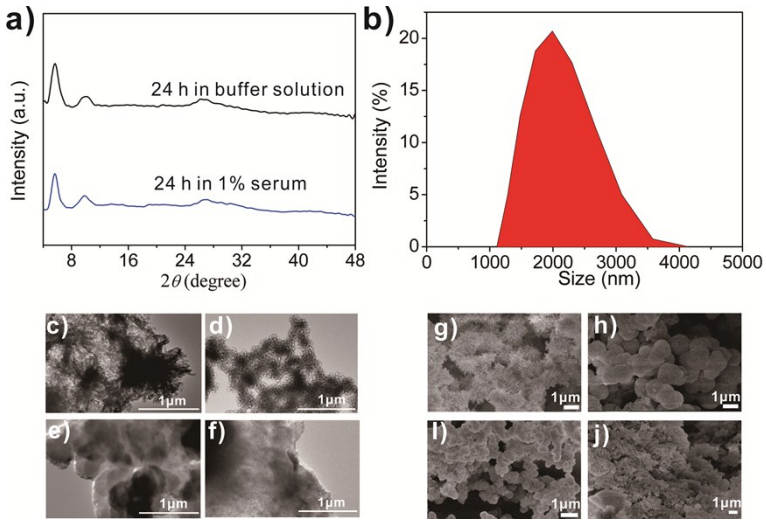

Fig. S2 (a) Stability of TpTta in the buffer solution and serum. (b) Dynamic light scattering spectra of TpTta. TEM images: (c) TpTta, (d) TpTab, (e) TpBD, (f) TpPa-1. SEM images: (g) TpTta, (h) TpTab, (i) TpBD, (j) TpPa-1.

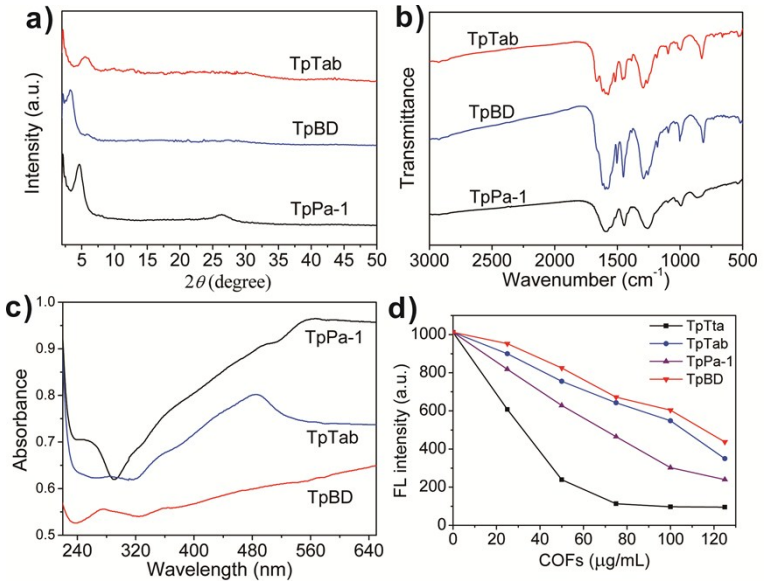

Fig. S3 (a) PXRD patterns of TpTab, TpBD, TpPa-1. (b) FT-IR spectra of TpTab, TpBD, TpPa-1. (c) UV–vis spectra of TpTab, TpBD, TpPa-1. (d) Effect of COF type on the fluorescence quenching of the probe 5´-FAM-TCG CTA ACC TGT TCA TCG TAG-3´.

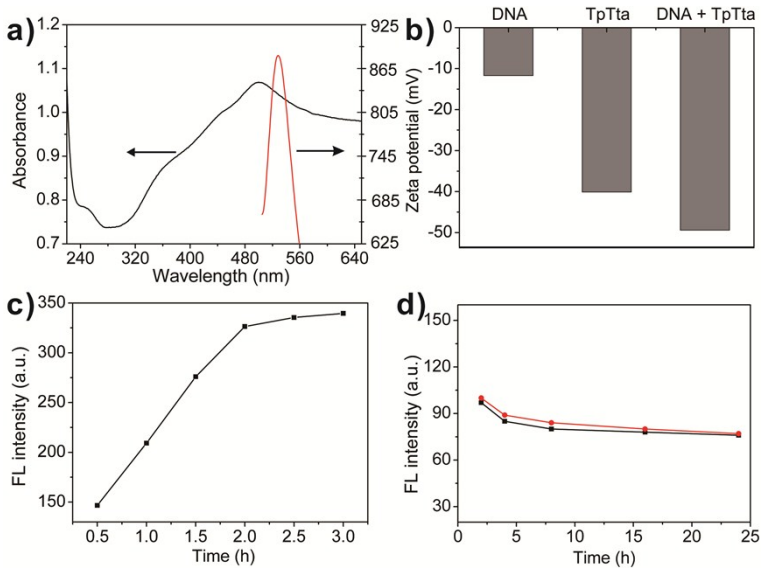

Fig. S4 (a) UV-vis spectra (black curve) of TpTta and the fluorescent spectra (red curve) of FAM. (b) Zeta potential of DNA, TpTta, DNA-TpTta complex. (c) Fluorescence intensity versus the reaction time in the presence of 100 nM DNA. (d) Fluorescence intensity of TpTta-DNA complex in the buffer solution (black) and 1% serum (red) against incubation time.

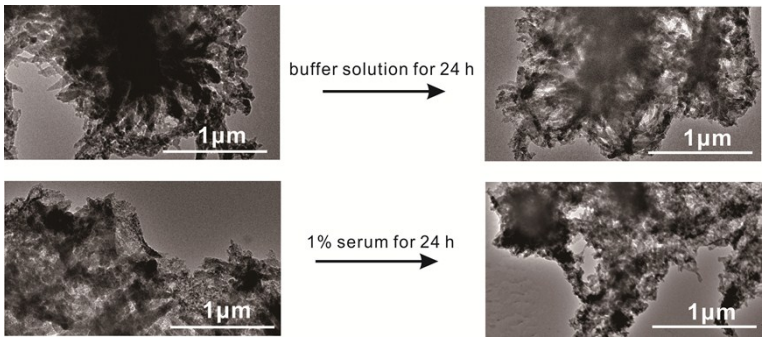

Fig. S5 TEM image of DNA-TpTta complex in the buffer solution and serum for 24 h.

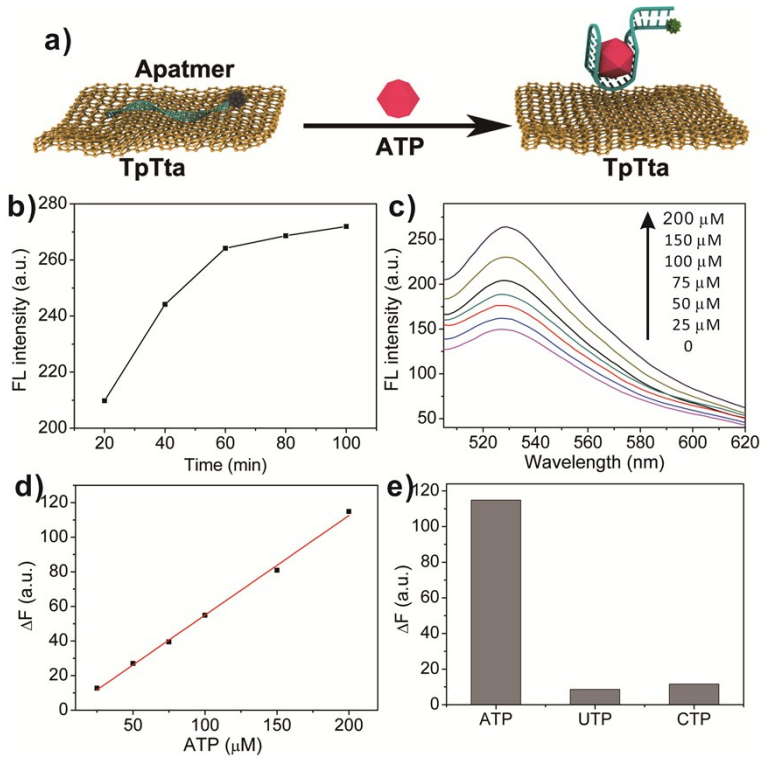

Fig. S6 (a) Illustration for fluorescence detection of ATP by using TpTta as sensing platform. (b) Fluorescence intensity versus the reaction time in the presence of 200 μM ATP. (c) Dependence of the fluorescence of the probe (50 nM) on the concentration of ATP (0, 25, 50, 75, 100, 150 and 200 μM). (d) Plot of the recovered fluorescence intensity (ΔF) against the target concentration. (e) Selectivity of this ATP assay.

Table S1. Analytical Results for the Determination of DNA in human serum samples

		Concentration (mean ± s, n = 3) / nM
Samples	Spiked DNA / nM	Present method
Serum 1	0	Not detected
	80.0 nM	77.3 ± 3.8
Serum 2	0	Not detected
	60.0 nM	60.4 ± 2.0
Serum 3	0	Not detected
	40.0 nM	39.5 ± 2.0

References

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4 R. Gomes and A. Bhaumik, *RSC Adv.*, 2016, 6, 28047.