Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

Synthesis of Urchin-like Metal-phenolic Coordination Crystals as a Sensing Platform for Sequence-Specific Detection of Nucleic Acid

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Experiment

Chemicals

Tannic acid (TA, analytical regent), $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were purchased from Macklin Biochemical Co., Ltd. Ammonia solution (25-28 wt%) were purchased Tianjin Zhiyuan Chemical Co., Ltd. Pluronic® F127 was purchased from Sigma-Aldrich. Probe DNA (5'-TCAACATCAGTCTGATAAGCTA-3'), target DNA (5'-TAGCTTATCAGACTGATGTTGA-3'), single-base mismatched DNA (sm-DNA, 5'-TAGCTTATCAGACTAATGTTGA-3'), double-base mismatched DNA (dm-DNA, 5'-TAGCTTAGCAGACTAATGTTGA-3') and triple-base mismatched DNA (tm-DNA, 5'-TAGATTAGCAGACTAATGTTGA-3') were purchased from Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China). High-purity water was used in all the experiments.

Synthesis of metal-TA coordination crystals

Urchin-like Cu-TA coordination crystals were synthesized via metal-ligand coordination driven self-assembly process. F127 (0.2 g) was dissolved in the mixture of water (37 mL) and ethanol (8 mL). Different amount of ammonia solution (0.4-0.8 ml) was then added followed by the addition of tannic acid (0.2 g). After stirring 12 h, $Cu(NO_3)_2 \cdot$(0.1 g of $Cu(NO_3)_2 \cdot 3H_2O$ dissolved in 2 mL of water) solution was added to the above solution. After further stirring for 12 hours, the product was transferred into an autoclave (100 mL) for hydrothermal treatment at 100 ºC for 12 h. The obtained Cu-TA coordination crystals were collected by centrifugation, washing and drying. Zn-TA coordination crystals were synthesized using the same procedure

except $Zn(NO_3)_2 \cdot 6H_2O$ was used as the metal source.

Characterizations

Scanning electron microscopy (SEM) images were taken with a field-emission scanning electron microscope (Hitachi S-4800). The thermogravimetry analysis was performed by using TG 209 F3 thermal gravimetric analyzer (NETZSCH, Germany) with a heating rate of 10 °C·min^{-1}. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Kratos AXIS Ultra DLD system with Al K_α radiation as an X-ray source for radiation. The charge compensation (C 1s, 284.6 eV), contents of elements, relative sensitivity factor and element-binding configuration from XPS results were analyzed using CasaXPS (one kind of software). Powder X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5-80 ° at room temperature using a PANalytical X'pertPRO diffractometer (Netherlands) in a transmission geometry using Cu K_α radiation (40 mA and 40 kV). The scan rate was 2 °/min and step size was 0.02 °.

DNA detection

The fluorescence quenching ability of urchin-like Cu-TA coordination crystals was investigated by mixing 6-carboxyfluorescein (FAM)-labeled single-strand DNA (20 nM) with urchin-like Cu-TA (500 μg/ml) in Tris-HCl buffer (0.1 M, pH 7.4) in a total volume of 150 μL. After 30 min of incubation, the fluorescence spectrum was measured by a FluoroMax-4 fluorescence spectrophotometer (Horiba Jobin Yvon, Kyoto, Japan). To test the recovery ability, target DNA (50 nM) was added in the mixture of FAM-labeled DNA and urchin-like Cu-TA coordination crystals followed

by fluorescence spectrum test 1 hour later. The fluorescence spectrum of free FAM-labeled DNA solution (20 nM) as a reference was also recorded. Excitation and emission wavelengths were set at 490 and 520 nm respectively. The emission spectra were obtained by scanning the emission from 510 to 570 nm in steps of 1 nm.

To detect the target DNA (DNA analogue of miRNA-21), nanoprobes were prepared by mixing FAM-labeled DNA (20 nM) with Cu-TA coordination crystals (2000 μg/ml) in Tris-HCl buffer (0.1 M, pH 7.4). After 30 min of incubation, different concentrations of target DNA (0, 5, 10, 20, 30, 40, 50, 60, 80 and 100 nM) were added. Their fluorescence spectra were measured after 1 hour of hybridization. To investigate the selectivity of the nanoprobe, 50 nM of target DNA, single-, double, and triple-base mismatched DNA (sm-DNA, dm-DNA and tm-DNA) were introduced respectively into the nanoprobes in Tris-HCl buffer (0.1 M, pH 7.4) and allowed to hybridize for 1 h. Fluorescence measurements were performed.

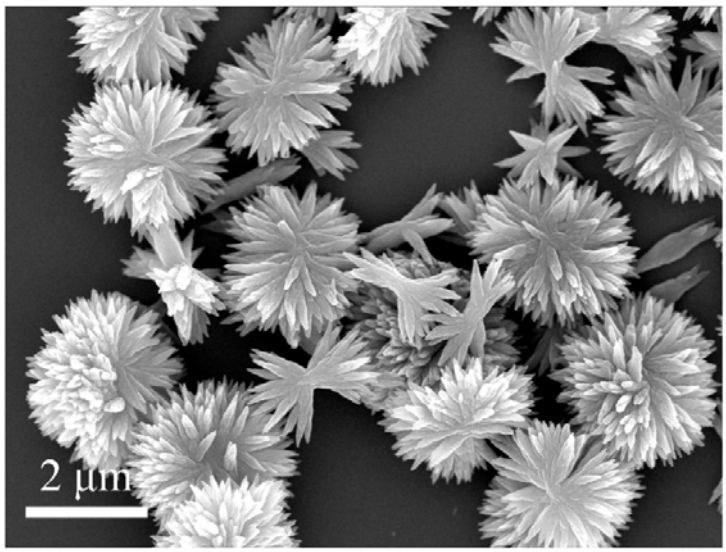

Figure S1 SEM image for urchin-like Cu-TA synthesized when the amounts of ammonia is 0.8 mL.

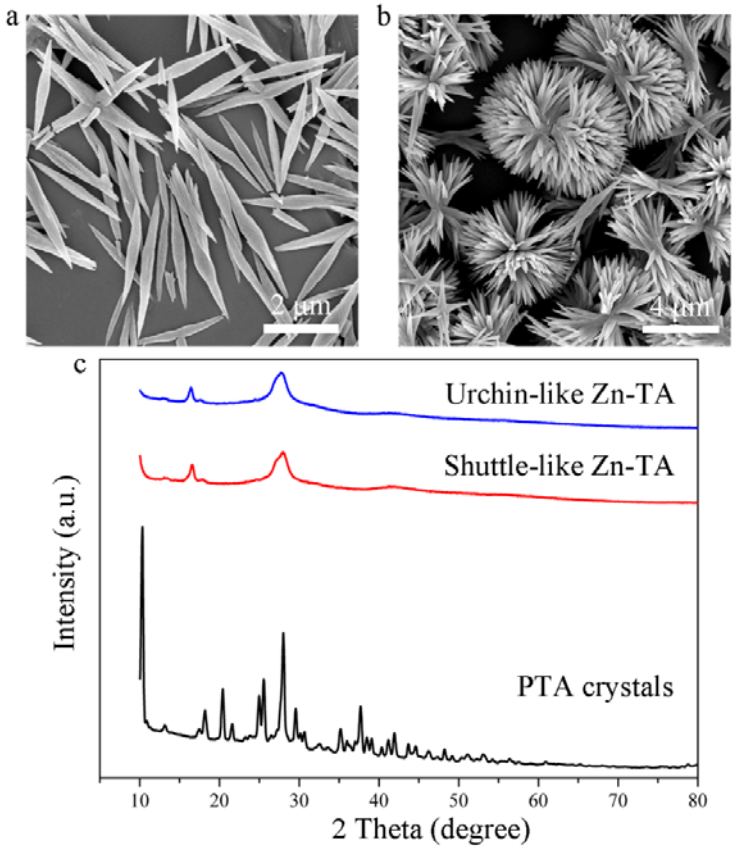

Figure S2 SEM images for (a) shuttle-like and (b) urchin-like Zn-TA crystals. (c) XRD patterns of shuttle-like, urchin-like Zn-TA crystals, and PTA crystals synthesized without using any metal ions.

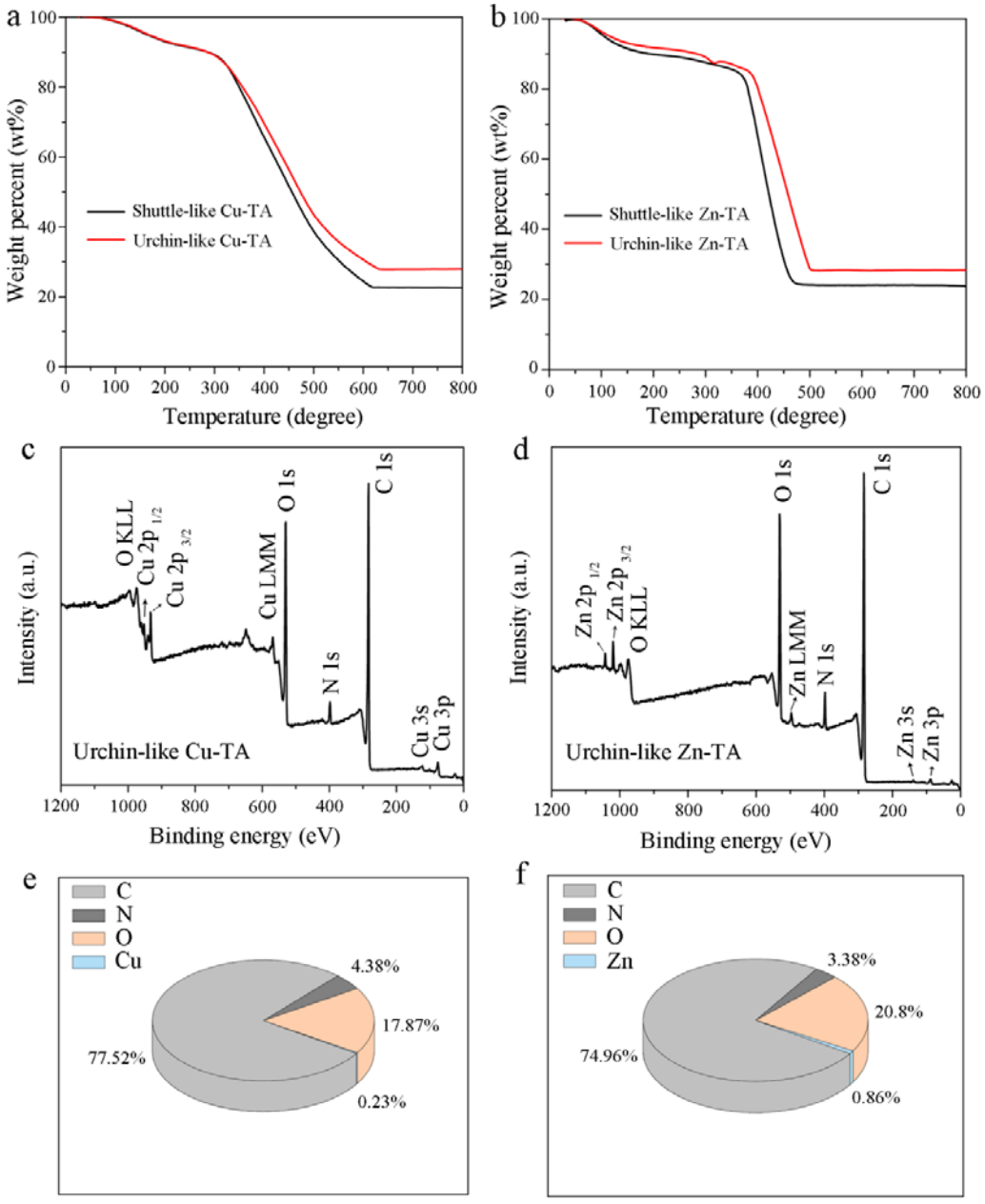

Figure S3 TG curves for (a) Cu-TA crystals and (b) Zn-TA crystals. XPS spectra for (c) urchin-like Cu-TA and (d) Zn-TA crystals. The element contents in (e) urchin-like Cu-TA and (f) Zn-TA crystals calculated from XPS results.

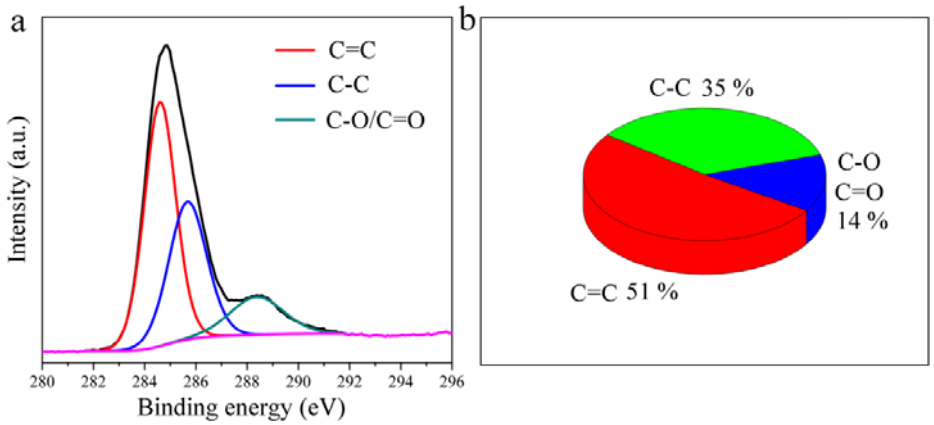

Figure S4 (a) High resolution XPS spectra for C 1s. (b) The content (at %) of different kinds of carbon atoms.

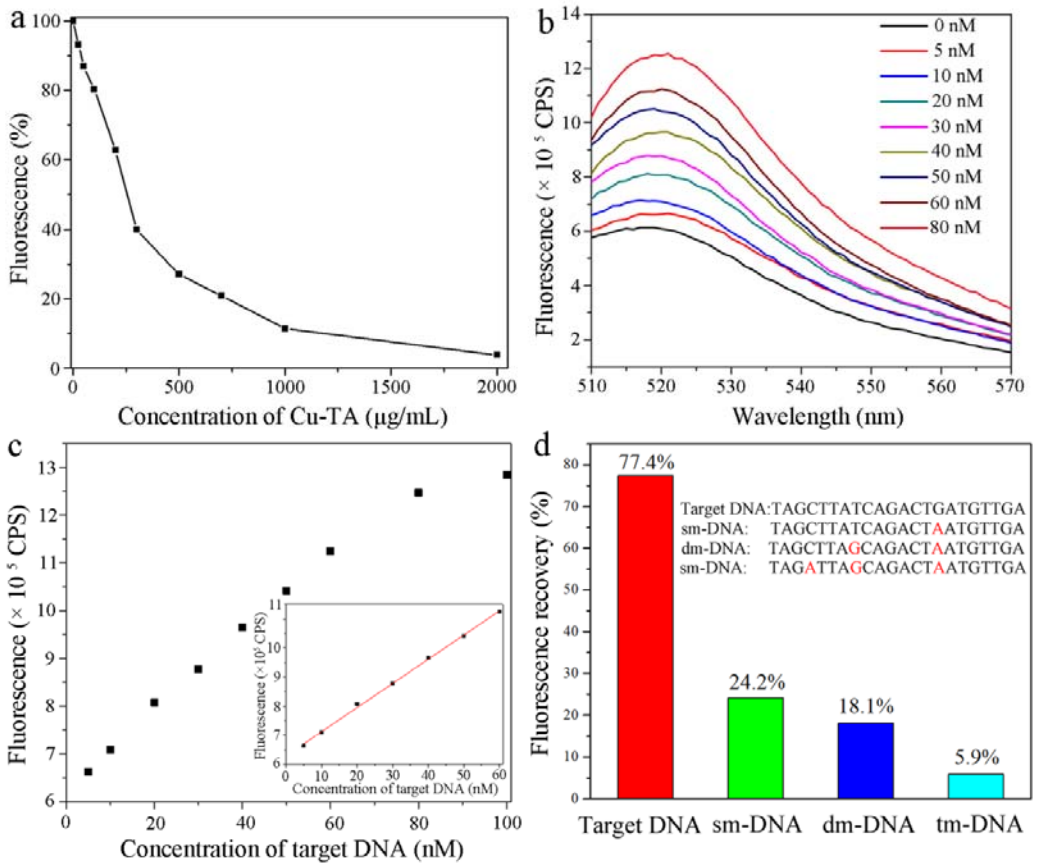

Figure S5 (a) Fluorescence intensities of probe DNA at 520 nm versus different concentrations of shuttle-like Cu-TA crystals. (b) Fluorescent recovery in different concentrations of target DNA solution (0-80.0 nM). (c) Fluorescence intensities versus different concentrations of target DNA (0.5-100 nM). Insets are corresponding calibration curve for target DNA detection. (d) Selectivity for the detection of DNA.

Table S1 Fluorescence quenching and recovery for different metal-phenolic coordination polymers

Materials	Fluorescence quenching (at 500 μg/mL) (%)	Fluorescence quenching (at 2000 μg/mL) (%)	Fluorescence recovery (at 50 nM)	Fluorescence recovery (at 80 nM)
Urchin-like Cu-TA	75.8	96.5	0.892	1.223
Shuttle-like Cu-TA	72.9	96.2	0.711	1.047

Table S2 The selectivity for different metal-phenolic coordination polymers

Materials	Fluorescence recovery (T-DNA)	Fluorescence recovery (sm-DNA)	Fluorescence recovery (dm-DNA)	Fluorescence recovery (tm-DNA)
Urchin-like Cu-TA	1.0238	0.3823	0.2947	0.2098
Shuttle-like Cu-TA	0.7736	0.2418	0.1806	0.0593

Table S3 Comparison the performance of fluorescent DNA sensors

Materials	Fluorescent reporter	Sensitivity (detection limit)	Detection time	Reference
MOF	FAM	0.16 nM	2 h	*Chem. Commun.* **2016**, *52*, 132
Cu(H_2dtoa)	FAM	1.3 nM	N. A	*Chem. Commun.* **2013**, *49*, 1276
Cu(H_2dtoa)	TFO	1.3 nM	3 h	*Analyst.* ***2013***, *138*, 3490
Cu-TA crystals	FAM	0.74 nM	1 h	***This work***