Supporting Information

Post-modification of a MOF through a fluorescent-labeling technology for the selective sensing and adsorption of Ag^+ in aqueous solution

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Contents

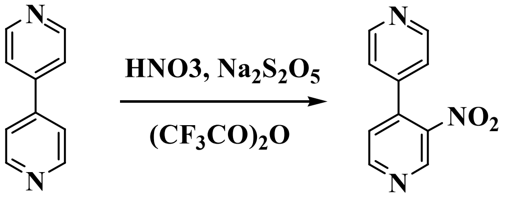
1. Materials and Methods.

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification unless otherwise noted. ^1H NMR spectra were measured on a Varian INOVA 400M spectrometer. The powder XRD diffractograms were obtained on a Riguku D/Max-2400 X-ray Diffractometer with Cu sealed tube (λ =1.54178 Å). FT-IR spectra were recorded as KBr pellets on JASCO FT/IR-430. UV-Vis spectra were measured on a HP 8453 spectrometer. 4,4',4''-benzene-1,3,5- triyl-tri-benzoic acid (btb) was synthesized according to the published procedure.[S1] FITC was purchased from Sun Chemical Technology (Shanghai) Co,. Ltd. Fluorescence spectra of the solution were obtained using an FS920 spectrometer (Edinburgh Instruments). Both excitation and emission slit widths were 2 nm. Fluorescence measurements were carried out in a 1 cm quartz cuvette with stirring the suspension of **FITC@BTPY**-NH_2. The adsorption abilities of **FITC@BTPY**-NH_2 for Ag^+ in water were measured using an inductively coupled plasma spectrometer (Perkin Elmer). All Fluorescence Microscopy (FM) micrographs were collected by Nikon Eclipse TE2000-5 inverted fluorescence microscope. All Confocal Laser Scanning Microscopy (CLSM) micrographs were collected by Olympus Fluoview FV1000.

2. Syntheses and Reactions

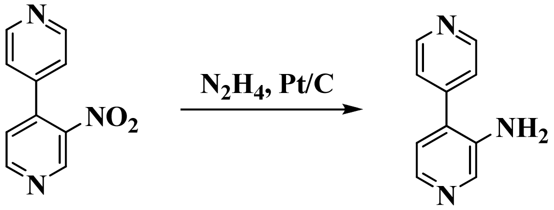
2.1. Ligand Synthesis and characterizations

(a) Synthesis of 3-nitro-4, 4'-bipyridine[S2]



Trifluoroacetic anhydride (10mL, 42mmol) was chilled in an ice bath and 4,4'- bipyridine (2.66g, 17mmol) were slowly added and stirred at chilled conditions for 2h followed by the dropwise addition of concentrated nitric acid (1.9mL, 36mmol). After stirring for 9–10h, the solution was dripped slowly into a chilled aqueous solution of sodium metabisulfite (3.2g, 17mmol in 25mL of water). After 24h, the solution was brought to pH 6–7 from pH 2–3 by addition of 25% NaOH solution, extracted with methylene chloride and the extract was dried over anhydrous sodium sulfate; the solvent was evaporated to give the crude product which was further purified by column chromatography using methylene chloride: ethyl acetate (20: 1). Yield: 0.6g (2.98mmol, 18%). 1H NMR: (400MHz, DMSO-d6): δ 7.49 (d, 2H), 7.70 (d, 1H), 8.72 (d, 2H), 8.98 (d, 1H), 9.3 (s, 1H) ppm.

(b) Synthesis of 3-amino-4,4'-bipyridine (bipy-NH$_2$)



3-nitro-4, 4'-bipyridine (2.01g, 10mmol) was dissolved in ethanol (50mL). 10% Pd/C (250mg) and excess hydrazine hydrate was added, and the reaction mixture was refluxed for 2h. After filtering the reaction mixture, the filtrate was then reduced in volume *in vacuo* to afford the faint yellow solid. Yield: 1.65g (9.6 mmol, 96%). ^{1}H NMR: (400 MHz, DMSO-d6): δ5.30 (s, 2H), 7.03 (d, 1H), 7.50(d, 2H), 7.85 (d, 1H), 8.14 (s, 1H), 8.66(d, 2H) ppm.

2.2. Synthesis of bipy –FITC[S3]

The typical modification procedure of bipy-NH$_2$ by **FITC** is as follows: 32.8 mg (0.11mmol) **FITC** was dissolved into 2mL DMF solvent followed by 17.1mg (0.1mmol) 3-amino-4, 4'-bipy. The reaction mixture was stirred for 3 days at room temperature in dark place and dried under vacuum. The targeted product was confirmed in the residue by ESI-MS. $[M+H^+]^+$, m/z =561.2; $[M+Na^+]^+$, *m/z* = 583.1.（Fig. S4）.

2.3. Preparations of BTPY-NH$_2$ micro crystals

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (30mg, 0.1mmol), btb (29.37mg, 0.067mmol) and bipy-NH$_2$ (8.56mg, 0.05mmol) was dissolved in DMF (6mL) in a Pyrex tube and heated at 85℃ for 3 days.

Then the mixture was cooled to room temperature, yielding yellow transparent hexagonal crystals which were collected and repeatedly washed with DMF three times. Phase purity was confirmed by powder X-ray diffraction (PXRD).

2.4. Post-modification of BTPY-NH_2 with FITC

Fluorescein 5-isothiocyanate (**FITC**) (194.5mg, 0.5 mmol) was dissolved in 5mL DMF. Fresh crystals of **BTPY**-NH_2 (177mg, 0.2mmol) were added after briefly dried on a filter paper. The reaction mixture was shaken at room temperature in dark place for 3 days. The resulting orange-red crystals were washed with DMF thoroughly until the washings become colorless.

2.5. Quantitative analysis in UV-vis

The washed **FITC@BTPY**-NH_2 (8mg) was digested by 1M HCl (0.5 mL). Na_2CO_3 was added to adjust pH to 10.0. The digested crystals were dissolved. The resultant clear solution with orange-yellow color was diluted to 10 mL with water. Absorption experiments were performed on a HP 8453 UV-Vis spectrophotometer. The concentration of **FITC** was determined by comparing the UV-Vis absorption with a standard curve on pH =10.0.

2.6. General procedure of luminescence sensing and absorption

Luminescence sensing of **FITC@BTPY**-NH_2 for Ag^+: **FITC@BTPY**-NH_2 (2mg) was added to 2mL water. The fluorescence spectrum was recorded at 515nm within 2min from the addition of metal ions to the suspension of **FITC@BTPY**-NH_2. Adsorption Ability of **FITC@BTPY**-NH_2 for Ag^+: **FITC@BTPY**-NH_2 (20 mg) was added to 50mL Ag^+ solution (about 20 or 10 *ppm*) and stirred overnight. After filtration, the concentrations of original and residual Ag^+ in the filtrate were both analyzed by ICP mass spectrometer.

3. Characterizations

3.1. X-ray Crystallography (Single-crystal diffraction)

Intensity data of **BTPY**-NH_2 was collected on Bruker Smart APEX II–CCD single crystal X-ray diffractometer equipped with a graphite-monochromated MoKa radiation (λ=0.71073 Å) using the SMART and SAINT programs.[S4] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL-97.[S5] The amino groups and the carbon atoms on the pyridine rings were disordered into two parts with the site occupied factor (s. o. f) of each part being refined using free variable. Except N atom on the disordered NH_2 group, other non-hydrogen atoms on the backbone were anisotropically refined. Except the solvent molecules, hydrogen atoms were geometrically fixed and refined by the use of a riding model. The distances between the neighbour atoms within the pyridine rings were fixed at 1.39 Å. The two disordered N atoms on the NH_2 groups were fixed within the Pyridine they attached, and the C-N distances between them and the attached C atoms on the pyridine rings were fixed at 1.45 Å. And SQUEEZE was used.

Table S1. Crystal Data and Structure Refinement for **BTPY**-NH_2

formula	$C_{46}H_{42}N_3O_{16}Zn_2$
Fw	1023.57
crystal system	Cubic
Space group	*P*-43n
$a=b=c$, Å	27.6571(16)
$\alpha=\beta=\gamma$, °	90
V, Å^3	21155(2)
Z	6
D_c, g/cm^3	0.482
μ (Mo K_α), mm^{-1}	0.365
θ_{min}, θ_{max} , °	2.08, 24.99
no. total reflns.	98676
no. uniq. reflns (R_{int})	6210 (0.1405)
no. obs. [I≥2σ(I)]	1689
no. params	185
$R1$,$wR2$ [I≥2σ(I)]	0.0825, 0.1605
$R1$,$wR2$ (all data)	0.2066, 0.1743
GOF	1.029

$R_1 = \Sigma (|F_0|-|F_C|) / \Sigma |F_0|$, $wR_2 = [\Sigma w (|F_0|-|F_C|)^2 / \Sigma w F_0^2]^{1/2}$.

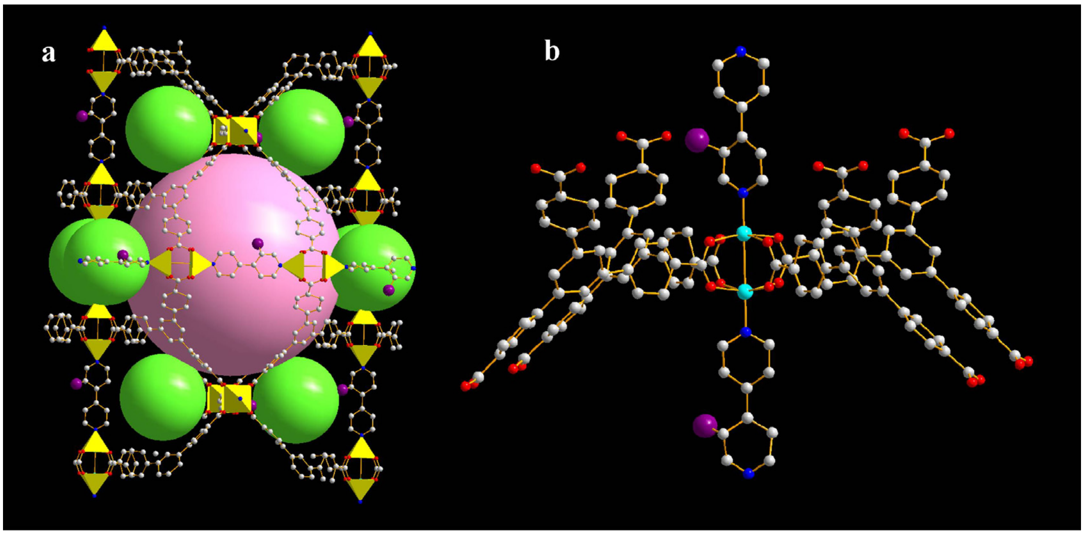


Figure. S1 Crystal structure of **BTPY**-NH_2. (a) Two different types of pores are represented by the pink sphere and the green sphere. (b) Zn(II) paddle-wheels SBU. white = C; red = O; blue = N; turquoise = Zn, purple = amino group. Solvent molecules and hydrogen atoms have been omitted for clarity.

Table S2 Selected bond lengths (Å) and angles (º) for **BTPY-**$\mathbf{NH_2}$

Zn(1)-O(2)#1	1.939(7)	O(2)-Zn(1)-O(1)#3	87.99(18)
Zn(1)-O(2)	1.939(7)	N(1)-Zn(1)-O(1)#3	98.66(14)
Zn(1)-N(1)	1.942(5)	O(1)#2-Zn(1)-O(1)#3	162.7(3)
Zn(1)-O(1)#2	2.070(4)	O(2)#1-Zn(1)-Zn(1)#3	81.84(13)
Zn(1)-O(1)#3	2.070(4)	O(2)-Zn(1)-Zn(1)#3	81.84(13)
Zn(1)-Zn(1)#3	2.8677(14)	N(1)-Zn(1)-Zn(1)#3	180.000(1)
O(1)-Zn(1)#3	2.070(4)	O(1)#2-Zn(1)-Zn(1)#3	81.34(14)
O(2)#1-Zn(1)-O(2)	163.7(3)	O(1)#3-Zn(1)-Zn(1)#3	81.34(14)
O(2)#1-Zn(1)-N(1)	98.16(13)	C(11)#1-N(1)-Zn(1)	121.7(4)
O(2)-Zn(1)-N(1)	98.16(13)	C(11)-N(1)-Zn(1)	121.7(4)
O(2)#1-Zn(1)-O(1)#2	87.99(18)	C(11')#1-N(1)-Zn(1)	118.1(4)
O(2)-Zn(1)-O(1)#2	89.56(18)	C(11')-N(1)-Zn(1)	118.1(4)
N(1)-Zn(1)-O(1)#2	98.66(14)	C(1)-O(1)-Zn(1)#3	117.9(4)
O(2)#1-Zn(1)-O(1)#3	89.56(18)	C(1)-O(2)-Zn(1)	129.5(5)

Symmetry transformations used to generate equivalent atoms:
#1: -x, y, -z+1; #2: -z+1/2, -y+3/2, x+1/2; #3: z-1/2, -y+3/2, -x+1/2.

3.2 Powder-XRD

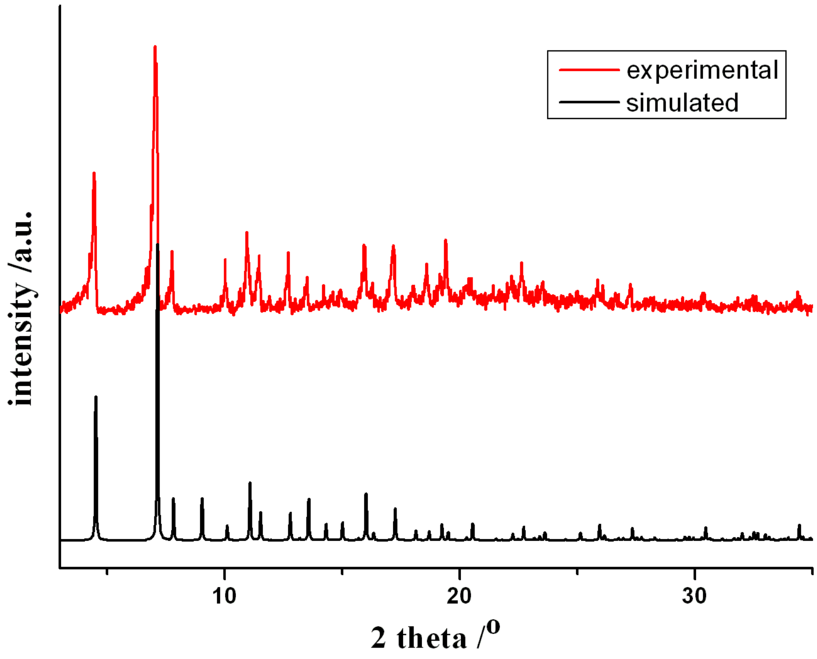


Figure. S2 PXRD patterns of experimental empty BTPY-NH2 micro crystals; and simulated BTPY-NH2.

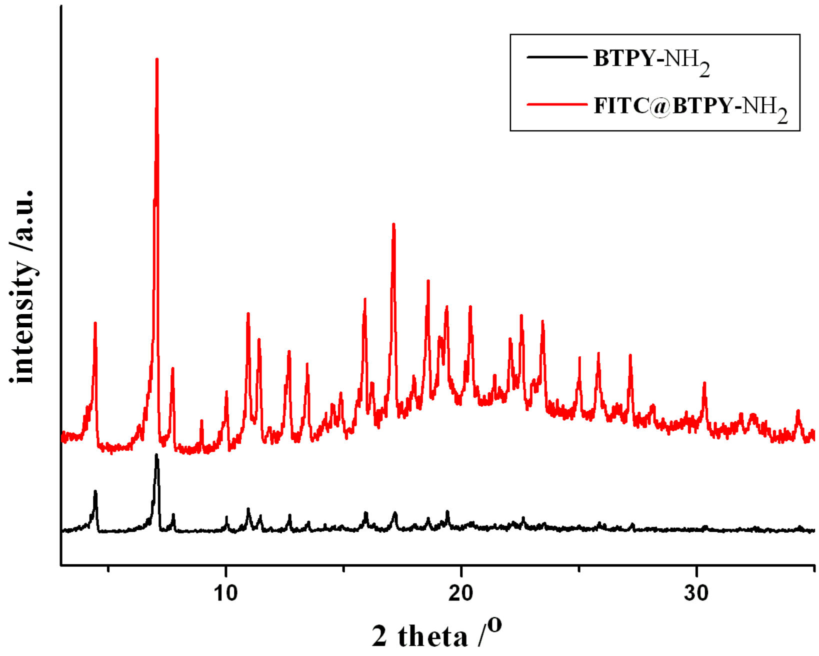


Figure. S3 PXRD patterns of **FITC@BTPY**-NH2; and experimental empty **BTPY**-NH2 micro crystals

3.3 ESI-MS

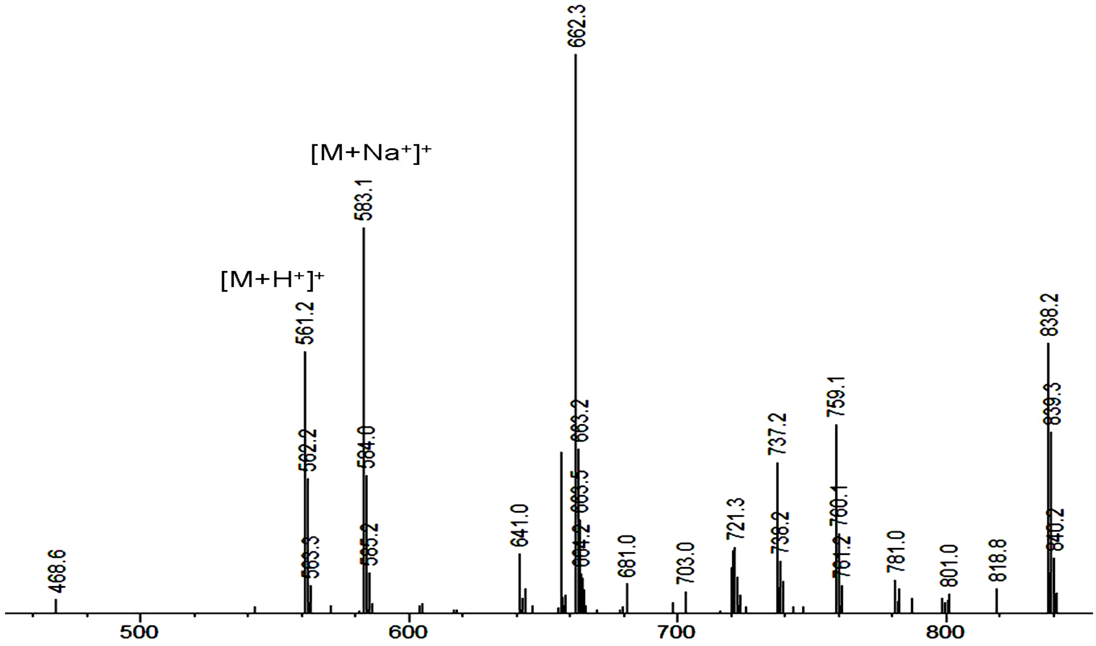


Figure. S4 ESI-MS spectra of bipy-FITC compound.

3.4 ^{1}H-NMR

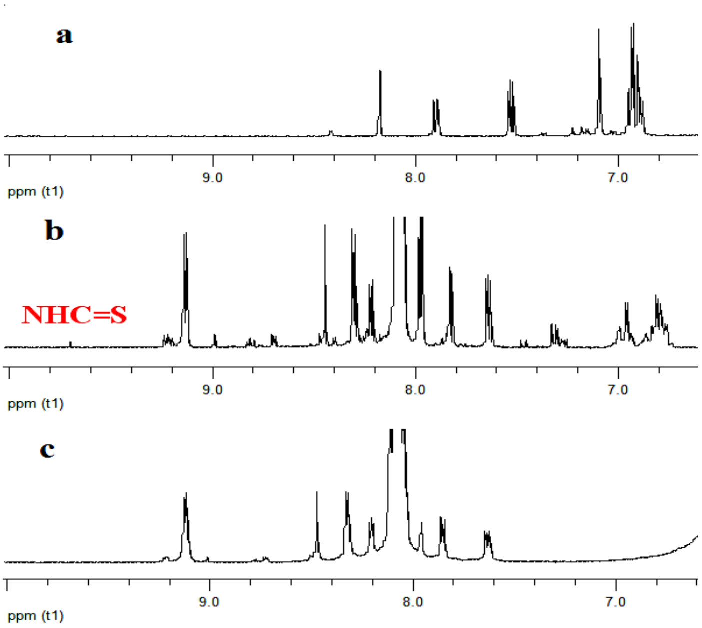


Fig. S5 ^{1}H NMR spectra of MOFs digested in DMSO-d_6/DCl and FITC in DMSO-d_6/DCl (a) **FITC**, (b) **FITC@BTPY**-NH_2, (c) **BTPY-**NH_2.

3.5 FT-IR

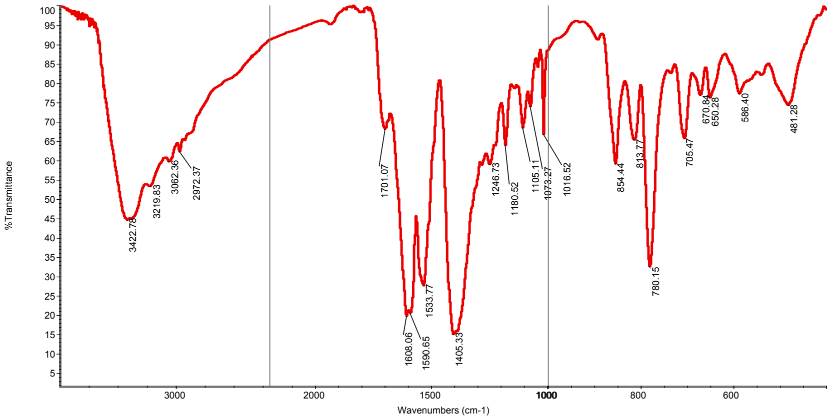


Fig. S6 FT-IR spectra of **BTPY**-NH_2.

3.6 Fluorescence microscopy

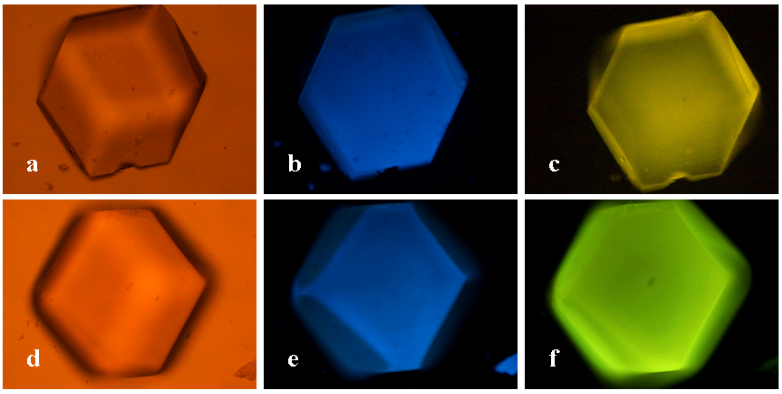


Fig. S7 Fluorescence micrographs of empty (a, b, c) and modified (d, e, f) **BTPY**-NH2. (a,d) Brightfield images; (b, e) excited at 405nm; (c, f) excited at 488nm.

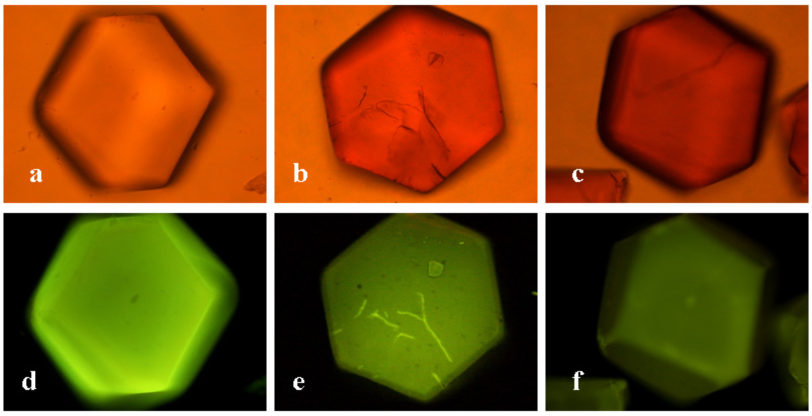


Fig. S8 Brightfield images (a, b, c), Fluorescence micrographs at λ_{ex}=488nm (d, e, f). (a, d) **FITC@BTPY**-NH_2 in DMF. (b, c) **FITC@BTPY**-NH_2 immersed in 1 mM Ag^+ solution for 5min. (c, f) **FITC@BTPY**-NH2 immersed in 1mM Ag^+ solution for 10min.

3.7 UV-Vis absorption

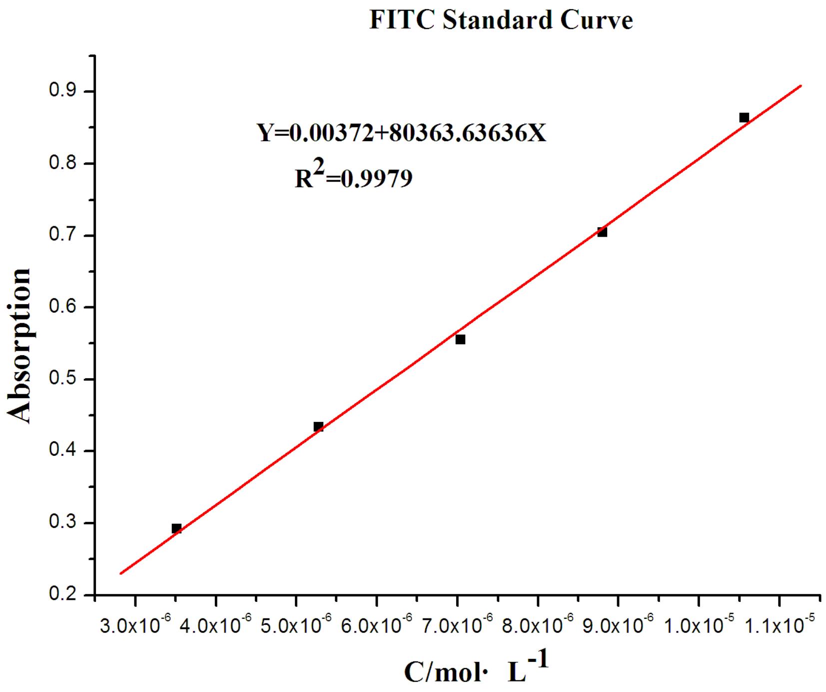


Fig S9 The standard curve of FITC

3.8 ICP

Table S3. The variation of C_{Ag+} after absorption by **FITC@BIPY**-NH_2 (detected by ICP).

	C_{Ag+}/*ppm*	C_{Ag+}/*ppm*
Control	0.1806	0.0609
+ **FITC@BTPY**-NH_2	0.0463	0.0206
adsorption capacity	74.36%	66.17%

4. References

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