Supplementary Information for

A Cationic Thorium-Organic Framework with Triple Single-Crystal-to-Single-Crystal Transformation Peculiarities for Ultrasensitive Anion Recognition

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Section 1. Iodate concentration-dependent PL study.

In a typical measurement, 2 mg finely ground **Th-SINAP-200** powder was mixed with 2 mL $NaIO_3$ solutions with increasing concentrations. The mixture was treated by ultrasonication for 1 min to obtain a homogeneous suspension and stand for 30 another minutes. Then the PL spectrum was collected from 400 nm to 700 nm under 365 nm UV light irradiation. All spectra were collected for three times to obtain the average value and minimize instrumental fluctuations. The emission spectra of **Th-SINAP-200** in deionized water was also recorded using the same procedure for comparison.

Section 2. Detection Limit Study. In a typical measurement, 1 mg finely ground **Th-SINAP-200** powder was mixed with 2 mL $NaIO_3$ solution with a concentration of 0.5 ~ 10 mg/kg. PL spectra of **Th-SINAP-200** in different $NaIO_3$ solution were recorded using similar procedure. The detection limit was calculated using the following equations.

$$D = 3\sigma/slope$$

$$\sigma = 100 \times (I_{SE}/I_0)$$

where D is the detection limit, I_{SE} is the standard error of the luminescence intensity measurement, which is determined by the baseline measurement of blank samples monitored at 510 nm, and I_0 is the measured luminescence intensity of **Th-SINAP-200** in deionized water. The slope was obtained from the linear fit of the iodate concentration-dependent luminescence intensity (monitored at 510 nm) curve in the low concentration region.

Section 3. Selectivity Study. For the study of selectivity toward cation, 2 mg finely ground **Th-SINAP-200** powder was mixed with 2 mL 500 mg/kg $MCl_X \cdot nH_2O$ solution (X= Na^+, K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Zn^{2+}, Ni^{2+}, Mg^{2+}, or Al^{3+}). For the selectivity toward the anion, 2 mg of finely ground **Th-SINAP-200** powder was mixed with 2 mL 500 mg/kg $NaX \cdot nH_2O$ (X= F^-, Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}, CO_3^{2-}, or BO_3^{3-}) solutions. The emission spectra of **Th-SINAP-200** in deionized water was also recorded using the same procedure for comparison. All spectra were recorded for three times to minimize instrumental fluctuations and the data used for the plots was in an average value.

Section 4. Competing Cation/Anion Exchange Study. 20 mg of **Th-SINAP-200** powder was dispersed into 20 mL mixed solution containing 5 mg/kg $Cr_2O_7^{2-}$ and 5 mg/kg Sr^{2+}. The mixture was stirred for different contact times (0, 1, 3, 10, 30, 40, 50, 60, 90, and 120 min). The resulting solutions were filtered with 0.22 μm nylon membrane filters, and the Cr and Sr concentrations were determined by ICP-MS (Agilent 7800).

Section 5. Iodate Adsorption Kinetic Study. The iodate adsorption kinetic study was carried out at room temperature and the solid/liquid ratio was 1 g/kg. 50 mg of **Th-SINAP-200** powder was dispersed into 50 mL $NaIO_3$ solution with an initial concentration of 10 ppm. The mixture was then stirred for certain time (0, 1, 3, 10, 30, 90, 180, and 300 min). The solution was filtered with a 0.22 μm nylon membrane filter, and the iodate concentration was determined by ICP-MS. The removal ratios (R) of iodine were calculated using the equation of $R = (C_0 − C_t)/C_0 × 100\%$ (where C_0 and C_t represent the initial concentration and concentration at time t, respectively). Sorption kinetics was fitted to a pseudo-second-order kinetics model, $t/q_t = 1/h + t/q_e$ (where q_t, q_e represent the amounts of adsorbate at certain time t or at equilibrium time, h is the initial adsorption rate, $h = kq_e^2$, and k is the rate constant).

Section 6. Iodate Adsorption Isotherm Study. Isotherm study was carried out at room temperature, and the solid/liquid ratio was 1g/L. 10 mg of **Th-SINAP-200** crystal was dispersed into 10 mL $NaIO_3$ solution with the concentration range from 0 to 600 ppm. Then the mixture was stirred for 24 h and was filtered with a 0.22 μm nylon membrane filter. The iodate concentration was determined by ICP-MS. The Langmuir isotherm model was fitted to interpret the experimental data and is expressed as followed:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m}$$

Where q_m is the maximum sorption capacity corresponding to complete monolayer coverage (mg/g) and k_L is a constant indirectly related to sorption capacity and energy of sorption (L/mg), which characterizes the affinity of the adsorbate with the adsorbent.
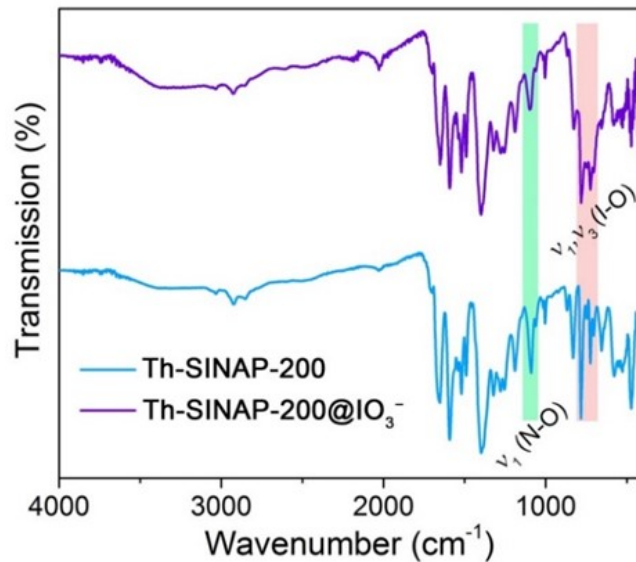
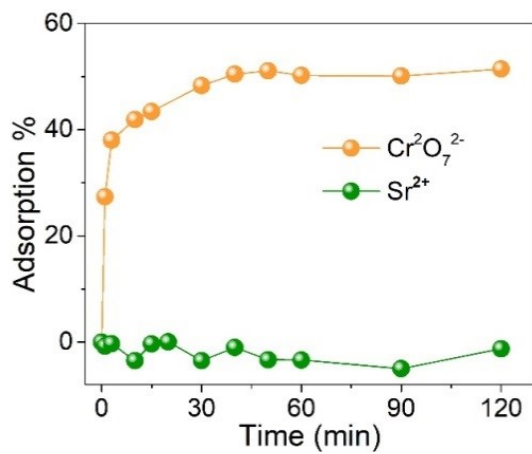**Fig. S1** FTIR spectra of **Th-SINAP-200** (a) before and (b) after soaking in $NaIO_3$ solution.

Fig. S2 Competing cation/anion exchange study (Sr^{2+} vs. $Cr_2O_7^{2-}$), showing rapid $Cr_2O_7^{2-}$ uptake and approximately unchanged concentration of Sr^{2+} upon addition of **Th-SINAP-200**.

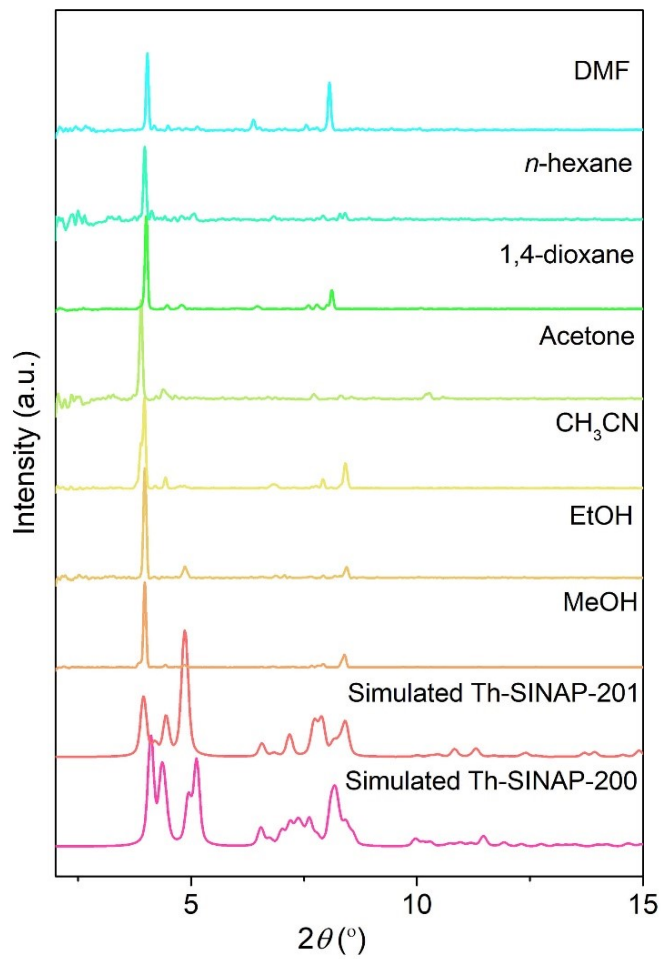**Fig. S3** PXRD patterns of **Th-SINAP-200** after soaking in different organic solvents.

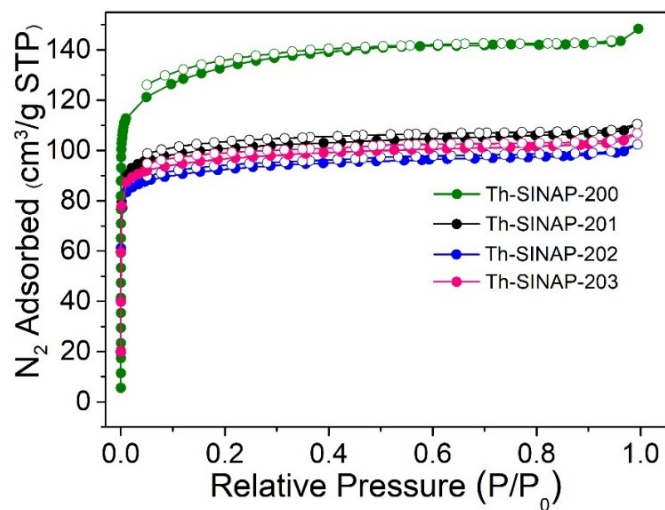**Fig. S4** N_2 sorption (filled symbols) and desorption (open symbols) isotherms of **Th-SINAP-200**, **201**, **202**, and **203**.
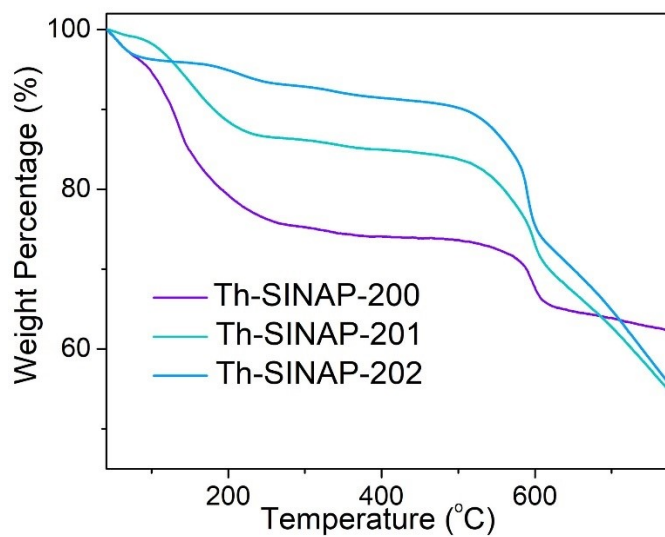

Fig. S5 TGA curves of **Th-SINAP-200**, **Th-SINAP-201**, and **Th-SINAP-202**.
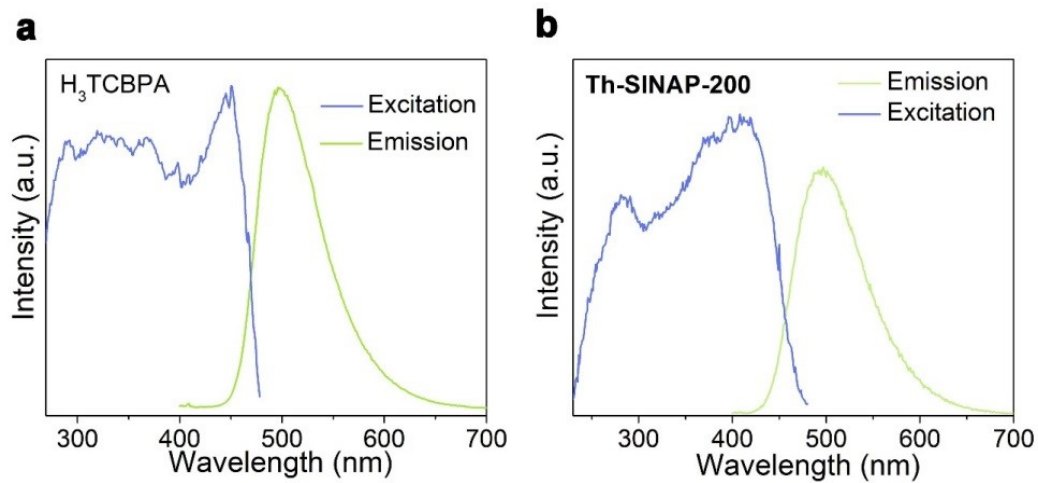
Fig. S6 Excitation and emission (λ_{exc}= 365 nm) spectra of (a) **Th-SINAP-200** and (b) H$_3$TCBPA.
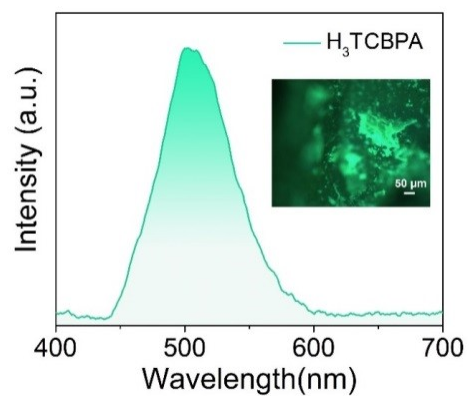

Fig. S7 Solid-state PL spectrum and optical micrographs of H$_3$TCBPA under 365 nm UV excitation.
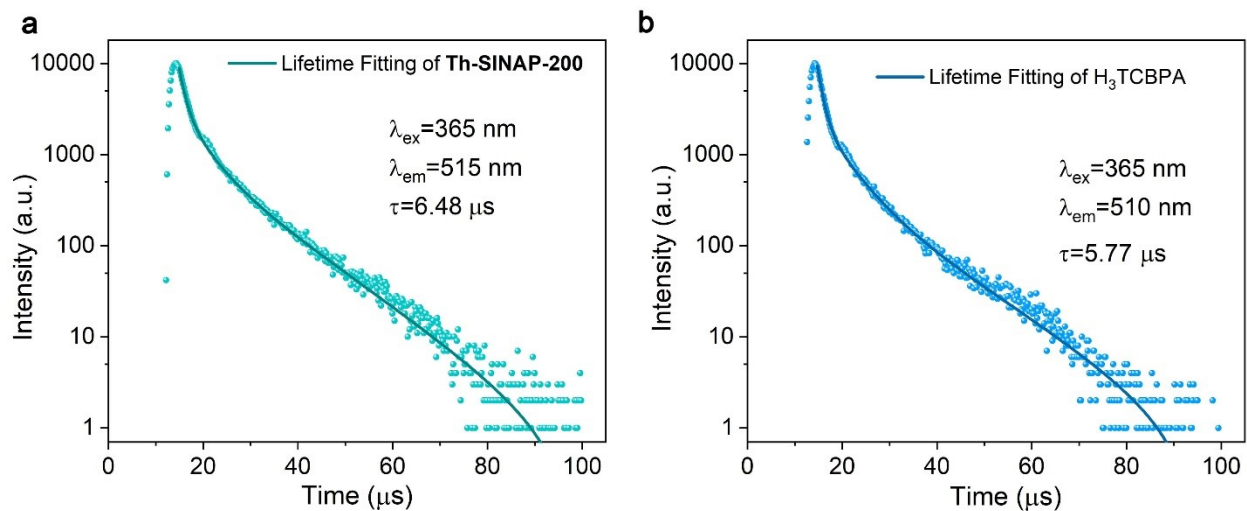
Fig. S8 PL lifetimes of (a) **Th-SINAP-200** and (b) H$_3$TCBPA.

Fig. S9 Excitation line of reference sample (BaSO$_4$), excitation line and emission spectra of **Th-SINAP-200**, and excitation line and emission spectra of H$_3$TCBPA. Quantum yields of **Th-SINAP-200** and H$_3$TCBPA were calculated to be 26.64% and 2.51%, respectively.
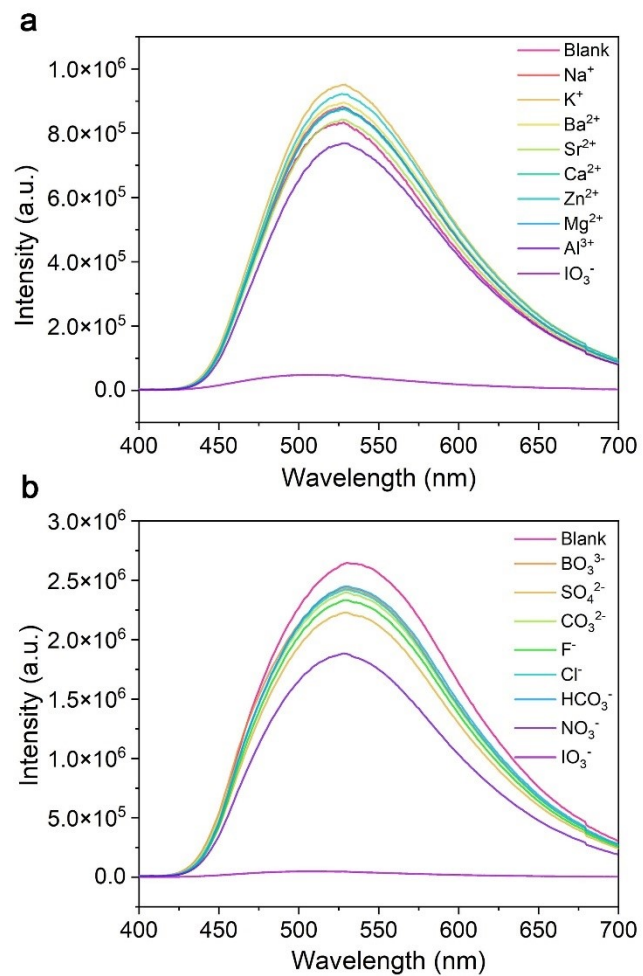
Fig. S10 PL spectra of **Th-SINAP-200** immersed in different (a) cation and (b) anion containing solutions.
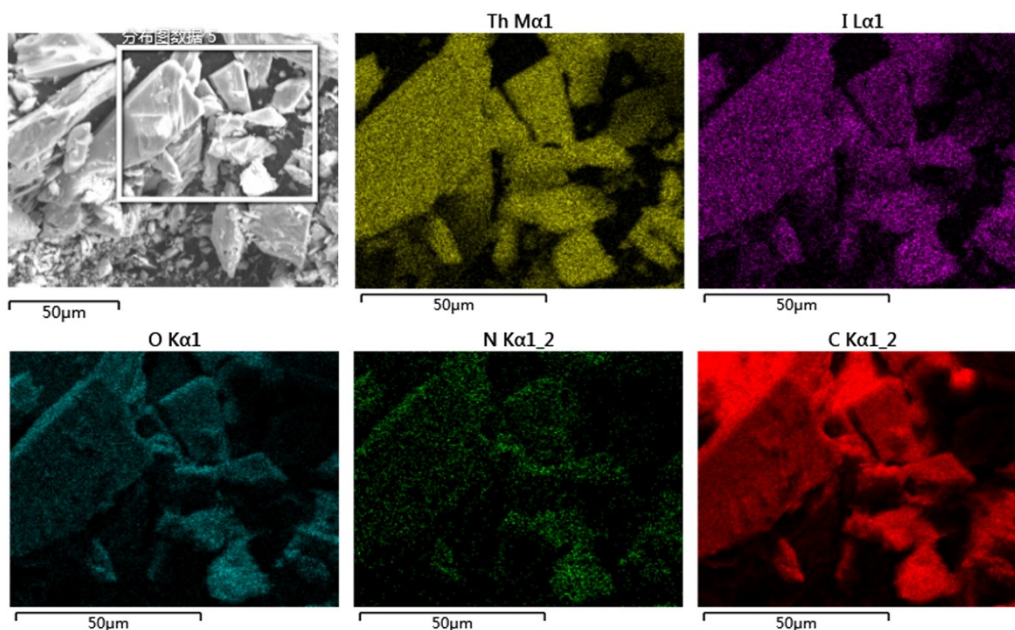
Fig. S11 SEM-EDS mapping of **Th-SINAP-200** after immersion in NaIO$_3$ solution for half an hour.
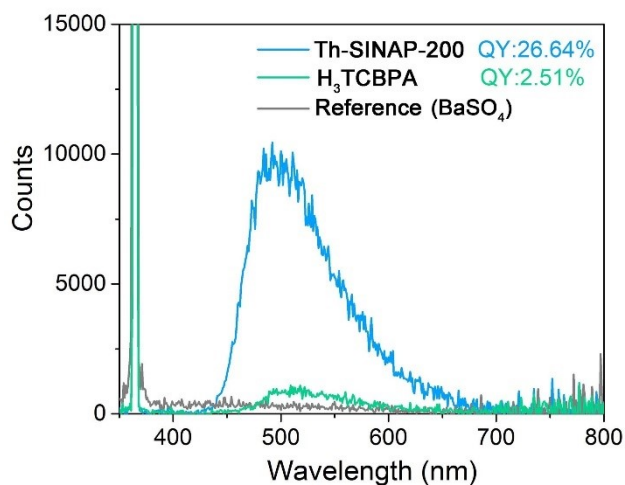

Fig. S12 The electronic transition levels of TCPBA^{3-} and the proposed quenching mechanism. S$_0$= ground state, S$_2$= ground state, S$_1$= ground state, ISC= intersystem crossing, T$_1$= triplet excited state, k$_{[Q]}$= IO$_3^-$ or other quencher induced quenching constant, and k$_{[nr]}$= non-radiative decay constant.

Table S1 Crystallographic data for **Th-SINAP-200**, **201**, **202**, and **203**.

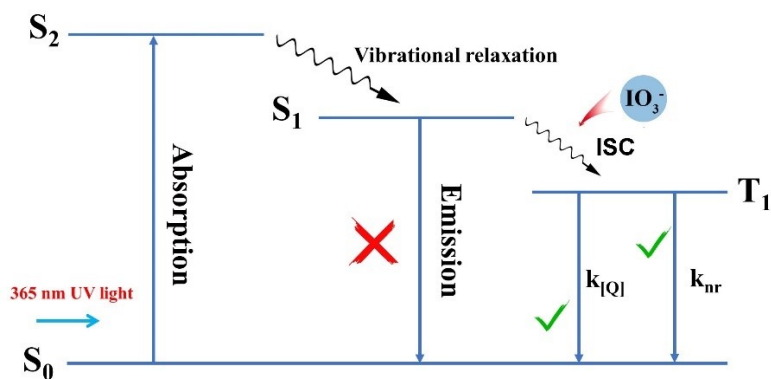| Code	Th-SINAP-200	Th-SINAP-201	Th-SINAP-202	Th-SINAP-203
CCDC No.	2065485	2065486	2065487	2065488
formula	$C_{161}H_{105}N_5O_{40}Th_6$	$C_{79}H_{49}N_2O_{19}Th_3$	$C_{156}H_{96}N_4O_{37}Th_6$	$C_{312}H_{192}N_8O_{72}Th_{12}$
formula weight	4140.73	2026.32	4010.60	7989.20
habit	block	block	block	block
space Group	P-1	$C2/m$	$C2/c$	P-1
a (Å)	24.6432(12)	42.013(2)	48.68(3)	24.163(9)
b (Å)	25.1083(12)	25.8483(14)	20.234(11)	26.423(9)
c (Å)	25.5393(13)	26.0312(14)	43.14(2)	36.034(13)
α	117.118(2)	90	90	93.359(10)
β	114.422(2)	120.728(2)	109.987(16)	92.771(11)
γ	91.982(2)	90	90	90.421(9)
V (Å3)	12312.2(11)	24300(2)	39938(38)	22939(14)
Z	2	8	8	2
T (K)	120	120	120	120
λ (Å)	0.71073	0.71073	0.71073	0.71073
Max. 2θ (°)	58.864	55.22	33.032	37.696
ρ_{calcd} (g cm^{-3})	1.117	1.108	1.334	1.157
μ (mm^{-1})	3.660	3.707	4.510	3.925
GoF on F^2	1.027	1.054	1.467	1.169
R_1, wR_2 [I > 2σ(I)]	0.0572, 0.1298	0.0476, 0.1235	0.2099, 0.5158	0.1935, 0.4924
R_1, wR_2 (all data)	0.1080, 0.1563	0.0791, 0.1368	0.2508, 0.5659	0.3032, 0.5742
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/e (Å^{-3})	2.49, -4.76	1.52, -2.55	7.36, -2.10	4.35, -2.77

Table S2 Limit of detection (LOD) based on different spectrometric methods and chemosensor toward iodate.

Method Type	Method or Material	LOD (µg/kg)	Reference
Spectrometric methods	ion chromatography	0.1	1
	ion chromatography	14.83	2
	GC-MS	0.05	3
	LPME-GC-MS	0.015	4
	HPLC	0.2	5
	LC-MS/MS	0.07	6
	ESI-MS	0.0139 ng	7
	reverse flow injection analysis	8	8
Chemosensor	electrochemical sensor	6354	9
	electrochemical sensor	0.597	10
	AuNPs sensor	8.7	11
	AuNPs sensor	0.355	12
	amperometric sensor	1903.5	13
	amperometric sensor	105.5	14
	MWCTs amperometric sensor	317.3	15
	MWCTs amperometric sensor	126.9	16
	Th-SINAP-200	0.107	This work

Table S3 Quenching constants (K_{SV}) of various cation and anion species.

Anion	IO_3^-	BO_3^{3-}	SO_4^{2-}	CO_3^{2-}	F^-	Cl^-	HCO_3^-	NO_3^-
K_{sv}	41321.9	100.6	358.5	124.3	50.8	65.4	98.1	500.5
Cation	Na^+	K^+	Ba^{2+}	Sr^{2+}	Ca^{2+}	Zn^{2+}	Mg^{2+}	Al^{3+}
K_{sv}	-24.9	-96.5	-187.5	-18.3	-37.2	-124.9	-24.8	45.6

Table S4 Kinetic parameters of the pseudo-second-order model for iodate adsorption toward **Th-SINAP-200**.

q_0 ($mg \cdot g^{-1}$)	Removal (%)	Second-order kinetic model			
		q_e ($mg \cdot g^{-1}$)	h ($mg \cdot g^{-1} \cdot min^{-1}$)	k ($g \cdot mg^{-1} \cdot min^{-1}$)	R^2
10	45.18	3.126	3.3518	0.343	0.9912

Table S5 Fitting results of the iodate sorption isotherms of **Th-SINAP-200** according to the Langmuir and Freundlich models.

Langmuir			Freundlich		
Q_m (mg/g)	K_L (L/mg)	R^2	k_F ($L^n/mol^{n-1}g$)	n	R^2
145.86593	0.01034	0.9802	6.36855	2.02926	0.9399

Table S6 Torsion angles of biphenyl groups in TCBPA^{3-} ligands of **Th-SINAP-200** and **Th-SINAP-203**.

Th-SINAP-200		Th-SINAP-203			
TCBPA^{3-} (N1)	26.63° 37.26° 11.60°/11.47°	TCBPA^{3-} (N1)	21.42° 41.74° 15.61°	TCBPA^{3-} (N5)	19.43° 24.42° 18.32°
TCBPA^{3-} (N2)	32.67° 39.52° 17.18°/24.91°	TCBPA^{3-} (N2)	47.09° 33.59° 24.58°	TCBPA^{3-} (N6)	5.96° 33.33° 36.94°
TCBPA^{3-} (N3)	32.69°/20.90° 29.49° 33.90°	TCBPA^{3-} (N3)	30.54° 17.87° 44.66°	TCBPA^{3-} (N7)	27.76° 38.81° 28.68°
TCBPA^{3-} (N4)	7.93°/22.11° 33.69°/27.04° 36.71°/11.26°	TCBPA^{3-} (N4)	28.28° 15.43° 16.56°	TCBPA^{3-} (N8)	42.16° 13.48° 19.42°

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