Electronic Supplementary Information

A nanoporous Ag(I) coordination polymer for selective adsorption of carcinogenic dye Acid Red 26

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Experimental details

Materials and general methods. All the starting reagents were obtained commercially and used as received. The ligand L^{234} was synthesized according to a literature procedure.[1] Fourier transform (FT) IR spectra (KBr pellets) were carried out on an AVATAR-370 (Nicolet) spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/max-2500 diffractometer with Cu Kα radiation (λ = 1.5406 Å), with a step size of 0.02° in 2θ and a scan speed of 2 ° min^{-1}. The simulated PXRD patterns were calculated from single-crystal X-ray diffraction data using the diffraction-crystal module of Mercury.[2] Thermogravimetric analysis (TGA) experiments were carried out under N_2 atmosphere on a TGA Q500 thermal analyzer with a heating rate of 10 °C min^{-1}. The gas adsorption isotherms were collected on a Micromeritics 3Flex surface area and pore size analyzer under ultrahigh vacuum in a clean system, with a diaphragm and turbo pumping system. The experimental temperatures were maintained by dry ice-acetone baths (195 K) and temperature-programmed water bath (273 and 293 K). Ultrahigh-purity-grade (> 99.999%) gases were used in all measurements. UV-Vis spectra were recorded on a PerkinElmer Lambda 35 spectrophotometer.

Single-crystal X-ray diffraction. Single crystal X-ray diffraction data were collected on an Agilent SuperNova Dual diffractometer with an AtlasS2 detector and Cu Kα radiation (λ = 1.54184 Å) at 293 K for **1·ClO$_4$** and **1·BF$_4$**, and a Bruker Apex II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 173 K for **1·ClO$_4$·BF$_4$**. All three structures were solved by direct methods using the SHELXS program of SHELXTL and refined with SHELXL by full-matrix least-squares methods on F^2.[3] Generally, C-bound H atoms were located geometrically and refined as ridings, and isotropic displacement parameters of H atoms were derived from their parent atoms. For the highly disordered nature of the solvents, they could not be finely determined in most cases and thus, the SQUEEZE routine of PLATON was applied to remove their diffraction contribution.[4]

Syntheses

$[Ag_7(L^{234})_6](ClO_4)_7(solvent)_x$ ($1·ClO_4$). A methanol solution (4 mL) of L^{234} (15.0 mg, 0.05 mmol) was carefully layered onto acetic ether buffer solution (2 mL), below which a DMF solution (4 mL) of $AgClO_4$ (20.7 mg, 0.1 mmol) was placed in a straight glass tube. Colorless block-shaped crystals of **$1·ClO_4$** (24.8 mg) were obtained upon slow evaporation of the solvents. IR (cm^{-1}): 1663s, 1591m, 1483m, 1457m, 1391w, 1144m, 1112m, 1086vs, 996w, 827m, 791w,711m, 629m, 534w.

$[Ag_7(L^{234})_6](BF_4)_{0.75}(ClO_4)_{6.25}(solvent)_x$ ($1·ClO_4·BF_4$). Single-crystal samples of **$1·ClO_4$** (10 mg) were immersed into an aqueous solution (5 mL) of excess $NaBF_4$ (1 M), which was left to stand at the room temperature. Colorless similar-shaped single crystals of **$1·ClO_4·BF_4$** were obtained after ca. three days. IR (cm^{-1}): 1663s, 1591m, 1483m, 1457m, 1391w, 1144m, 1112s, 1086vs, 1029w, 996w, 827m, 791w,711m, 629m, 534w.

$[Ag_7(L^{234})_6](BF_4)_7(solvent)_x$ ($1·BF_4$). Single-crystal samples of **$1·ClO_4$** (10 mg) were immersed into an aqueous solution (5 mL) of excess $NaBF_4$ (1 M), which was left to stand at the room temperature. Colorless similar-shaped single crystals of **$1·BF_4$** were obtained after ca. ten days. IR (cm^{-1}): 1659s, 1593m, 1484m, 1457m, 1390w, 1086s, 1029vs, 996m, 791w, 827m, 711m, 613w, 532w.

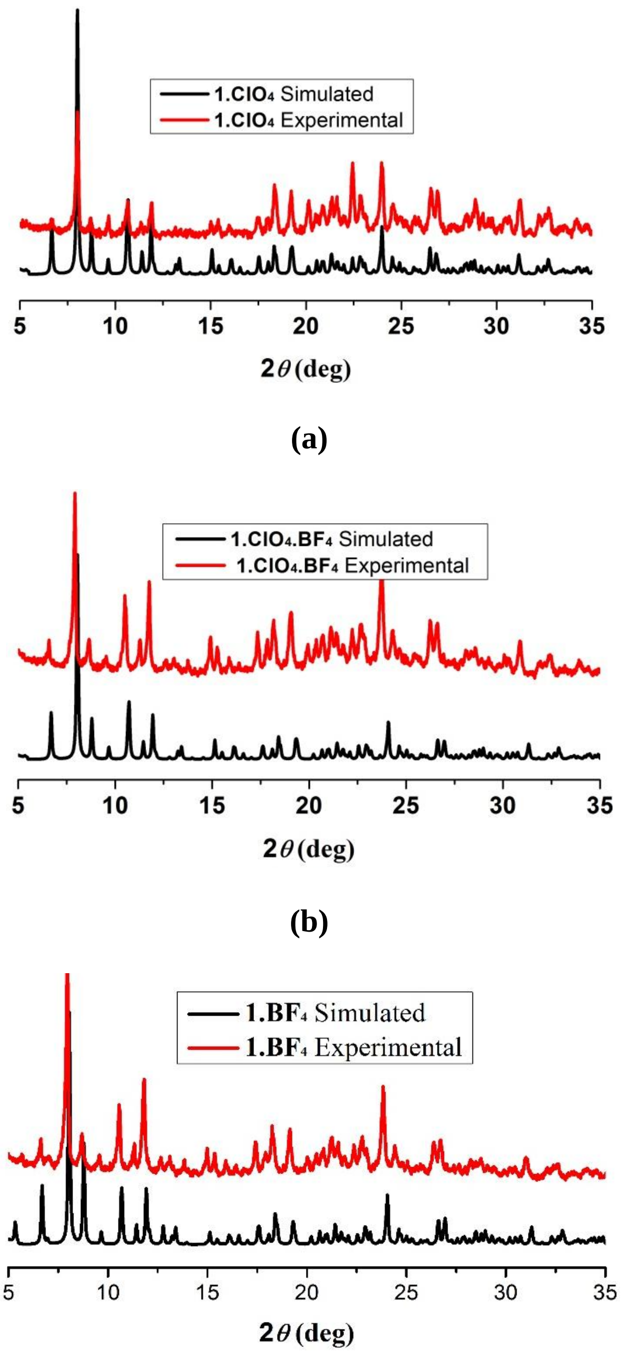
Activation of $1·ClO_4$ and $1·BF_4$

The as-synthesized sample (ca. 100 mg) was soaked into CH_2Cl_2 (50 mL) for 24 h and the extract was discarded. Fresh CH_2Cl_2 (50 mL) was subsequently added and the sample was allowed to soak for another 24 h. After the removal of CH_2Cl_2 by decanting, the sample was placed in a pre-weighed 12 mm sample tube, evacuated ($< 10^{-3}$ torr) at the room temperature overnight, then dried with the outgas function of the adsorption instrument for 3 h at 300 °C before gas sorption measurements.

Adsorption of organic dyes

For a typical adsorption procedure of dye, the as-synthesized sample (ca. 15 mg) was soaked into a DMF solution (10 mL) of dye molecule with a certain concentration (e.g. $C_0 = 5.0 \times 10^{-5}$ mol L^{-1}, diluted if exceeding detection limit). The setup was kept still during the entire adsorption process. UV-Vis absorbance measurements were performed at regular intervals on the supernatant liquid to determine the concentration decrease as a function of time until equilibrium was reached (at least after 24 h), by taking advantage of the working curve for each dye that was prepared beforehand. The adsorption capability of **1·ClO$_4$** can be calculated from equation **1**, where R_e represents the relative uptake amount (wt%) by **1·ClO$_4$**, C_0 is the initial concentration (mg L^{-1}) of dye and C_e is the equilibrium concentration (mg L^{-1}) of dye after 24 h of adsorption.

$$\boldsymbol{R_e = \frac{(C_0 - C_e)}{C_0} \times 100\%} \qquad (\mathbf{1})$$



(a)

(b)

(c)

Fig. S1 Simulated and experimental PXRD patterns for **$1{\cdot}ClO_4$** (a), **$1{\cdot}ClO_4{\cdot}BF_4$** (b) and **$1{\cdot}BF_4$** (c).

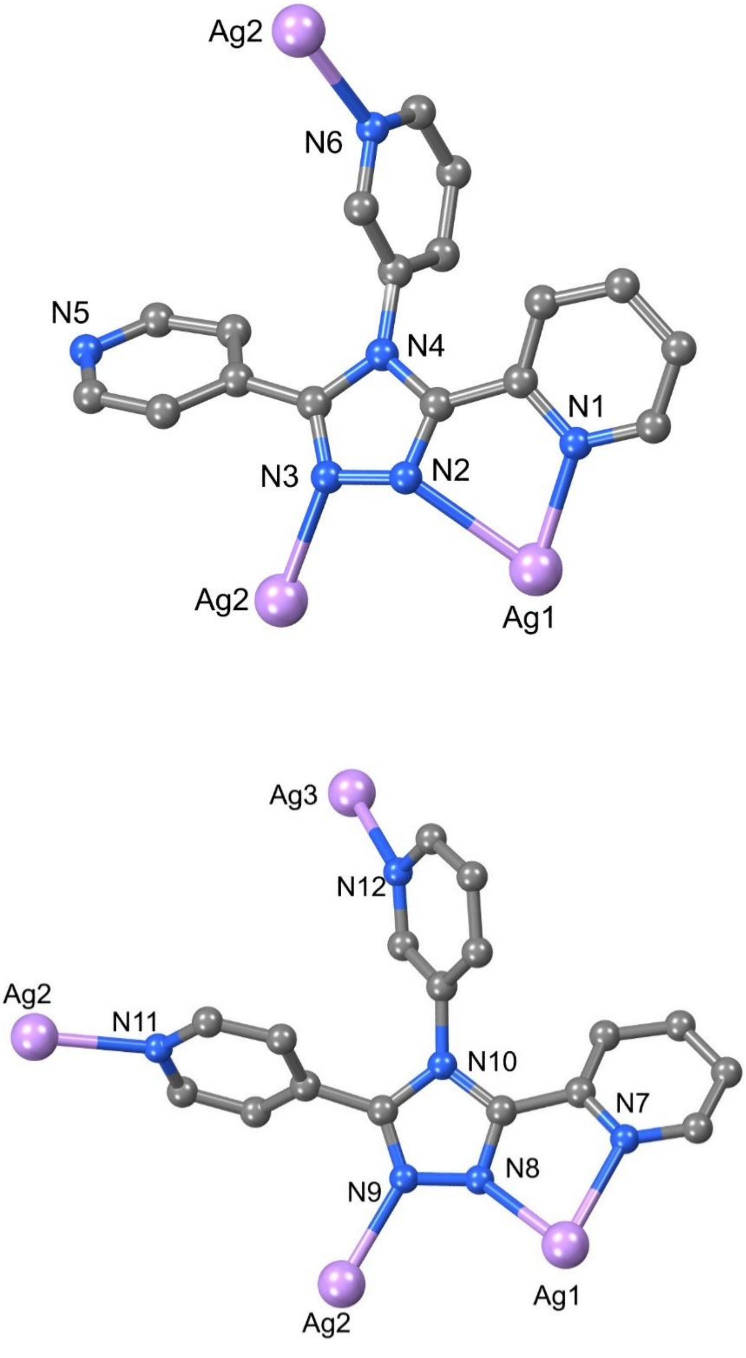


Fig. S2 Coordination modes of the two independent L^{234} ligands in **1·ClO$_4$**.

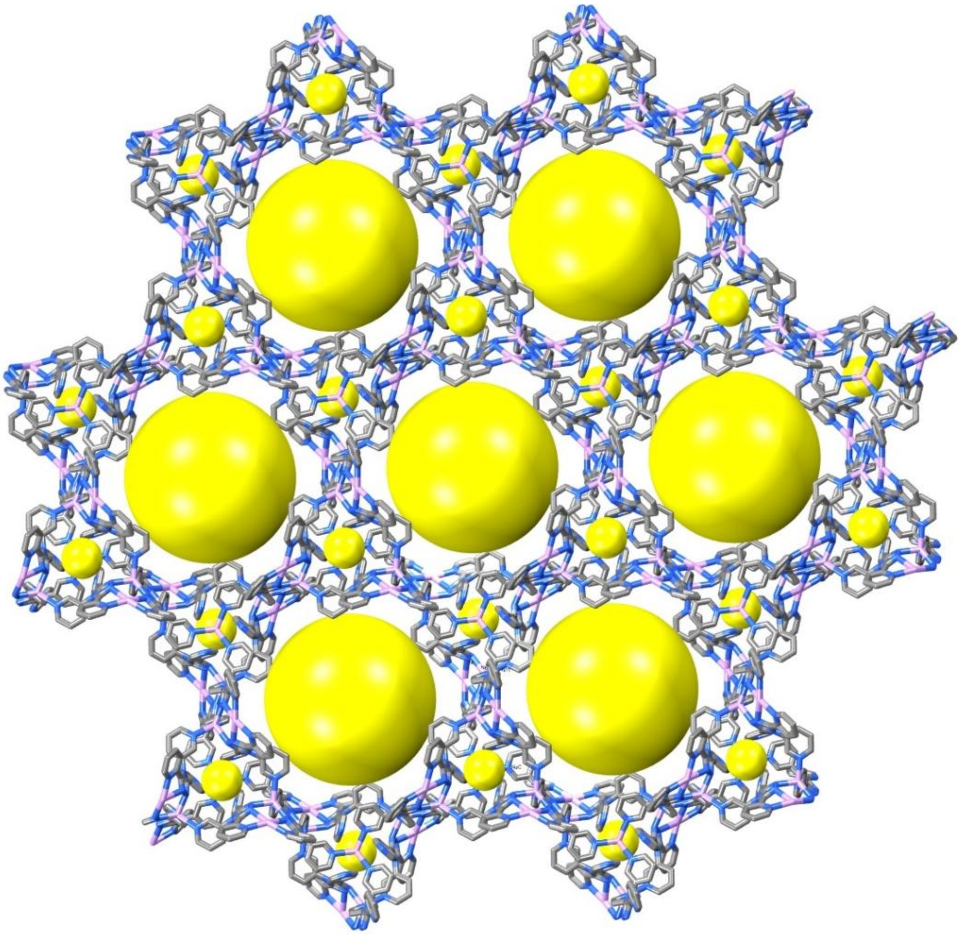


Fig. S3 Packing diagram of the cationic framework for **1·ClO_4** with the channels and interspaces for ClO_4^- anion accommodation shown in space filling model.

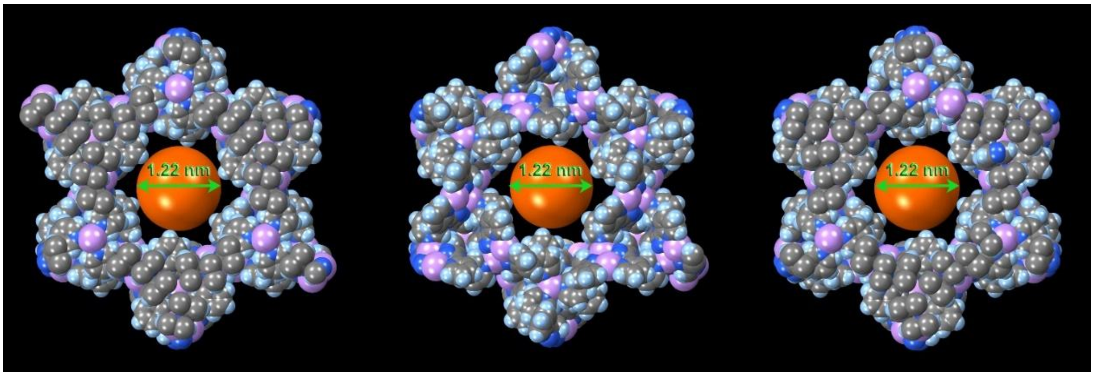


Fig. S4 A portion view of the 1D channel in **1·ClO$_4$** (left), **1·ClO$_4$·BF$_4$** (middle) and **1·BF$_4$** (right).

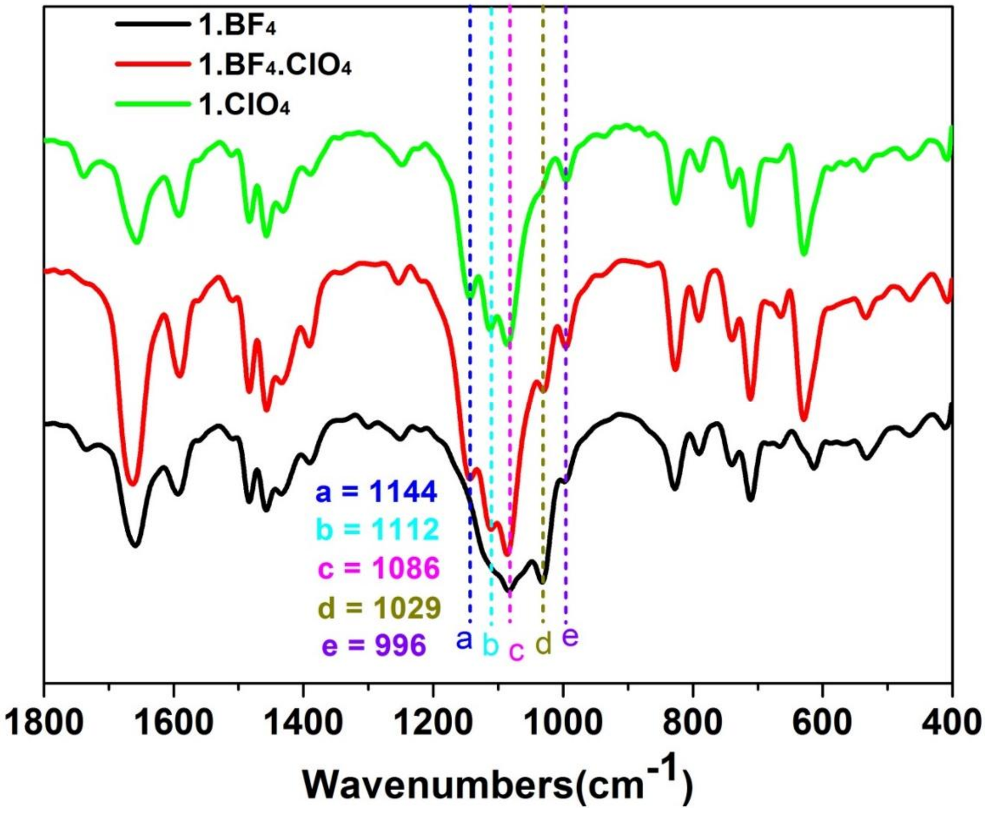
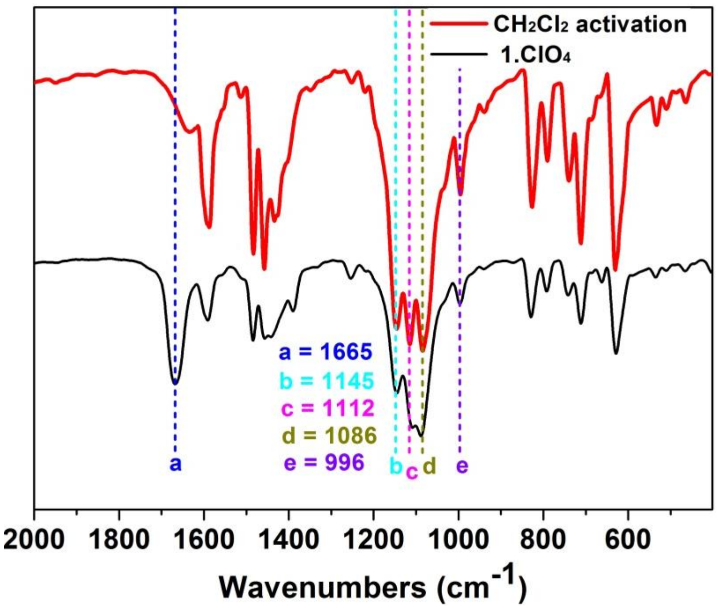
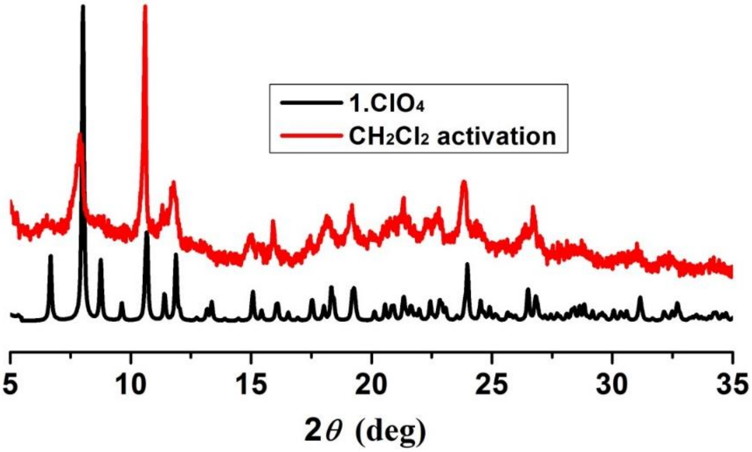


Fig. S5 IR spectra for **1·ClO$_4$**, **1·ClO$_4$·BF$_4$** and **1·BF$_4$**, in which the characteristic peaks of ClO$_4^-$and BF$_4^-$ anions are highlighted with colored dash-lines.

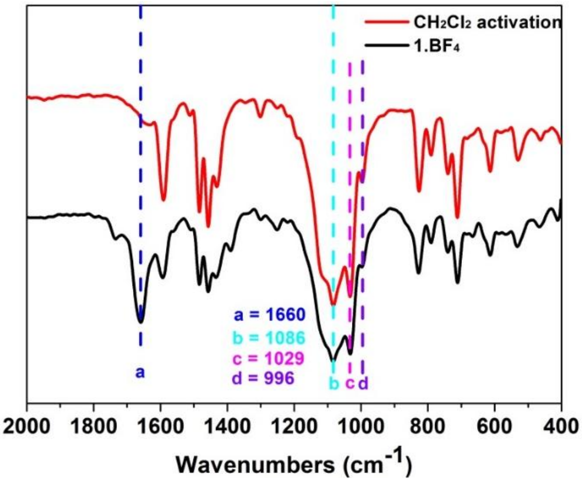


(a)

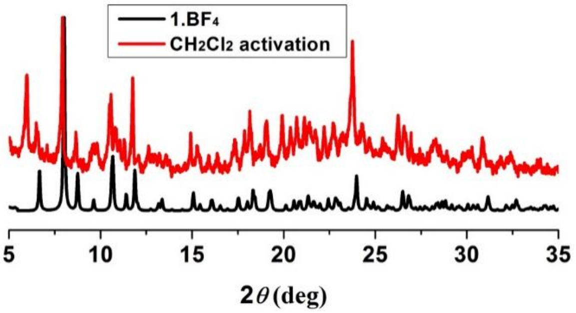


(b)

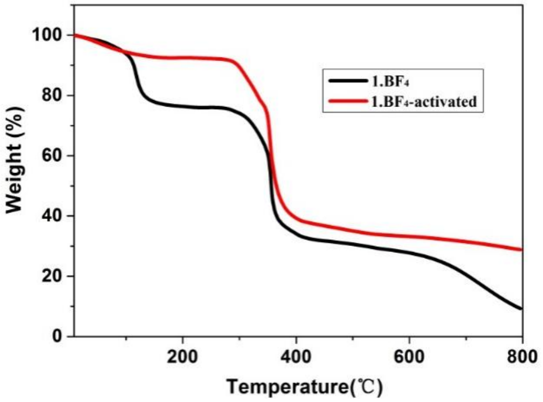
Fig. S6 Comparison of the IR (a) and PXRD (b) plots for **$1\cdot ClO_4$** before and after activation.



(a)



(b)



(c)

Fig. S7 Comparison of the IR (a), PXRD (b) and TGA plots for **1·BF_4** before and after activation.

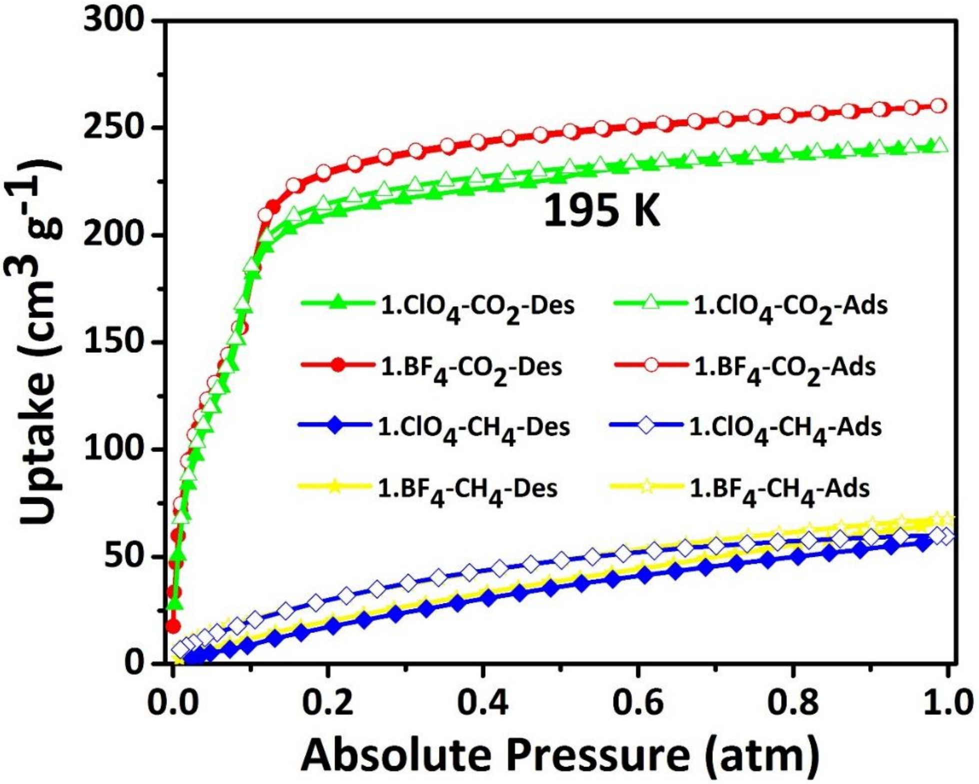


Fig. S8 CO_2 and CH_4 sorption isotherms for **1·ClO$_4$** and **1·BF$_4$** at 195 K.

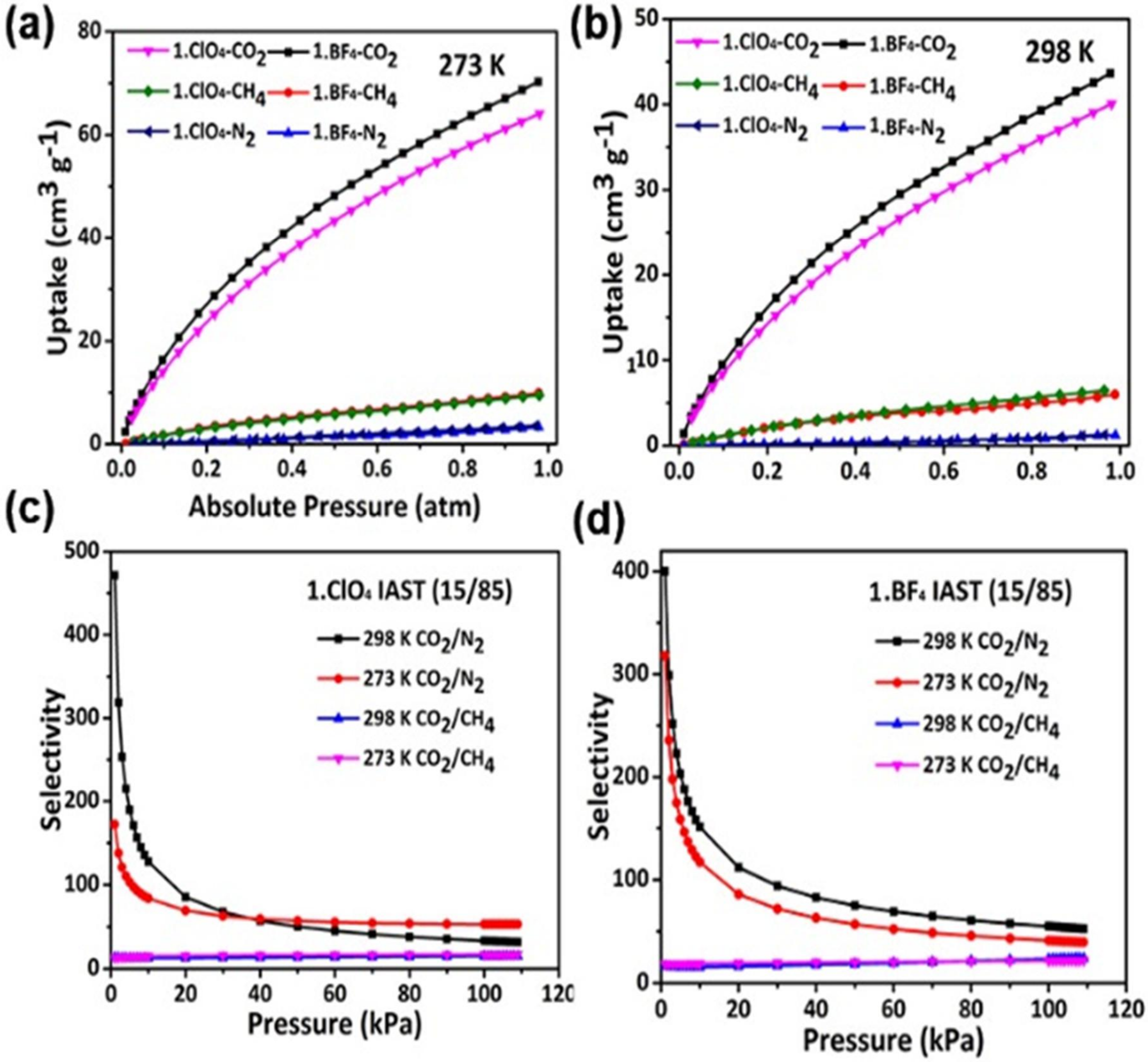
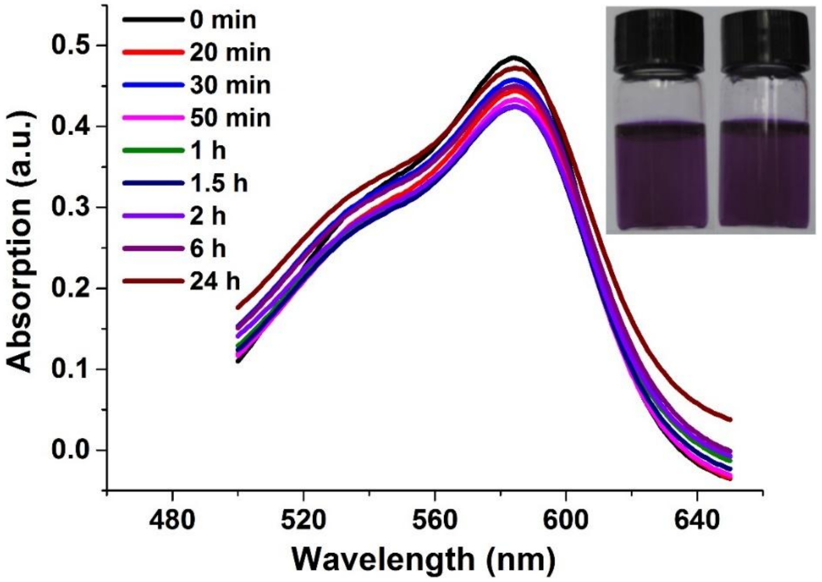
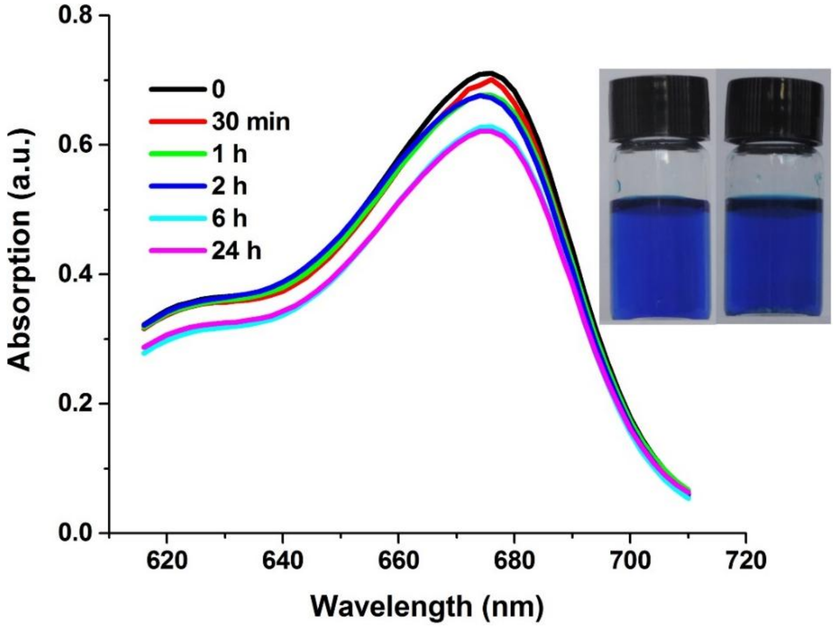


Fig. S9 CO_2, CH_4, and N_2 adsorption isotherms of **1·ClO₄** and **1·BF₄** at 273 K (a) and 298 K (b). IAST selectivity of **1·ClO₄** (c) and **1·BF₄** (d) for a binary gas mixture (15% for CO_2 and 85% for N_2 or CH_4) at 273 and 298 K.


0 min
20 min
30 min
50 min
1 h
1.5 h
2 h
6 h
24 h
Absorption (a.u.)
0.5
0.4
0.3
0.2
0.1
0.0
480
520
560
600
640
Wavelength (nm)

(a)


0
30 min
1 h
2 h
6 h
24 h
Absorption (a.u.)
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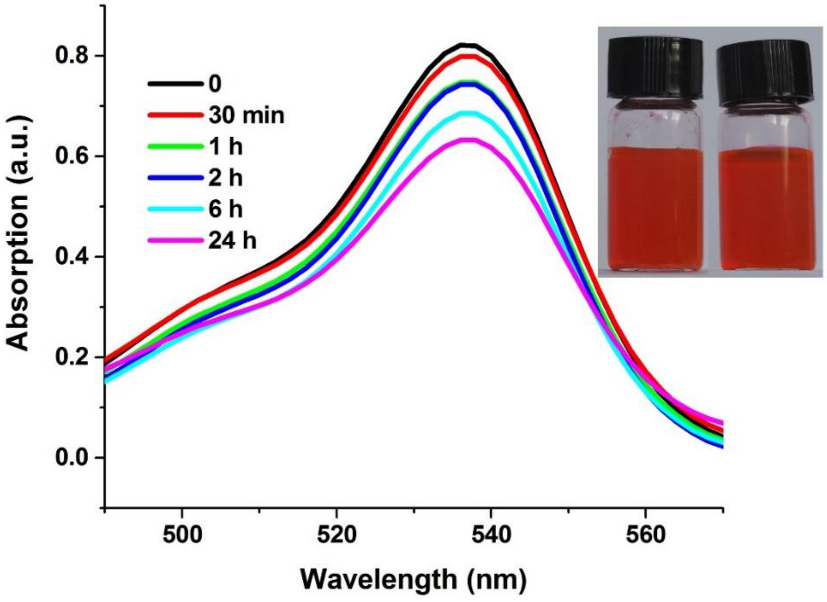
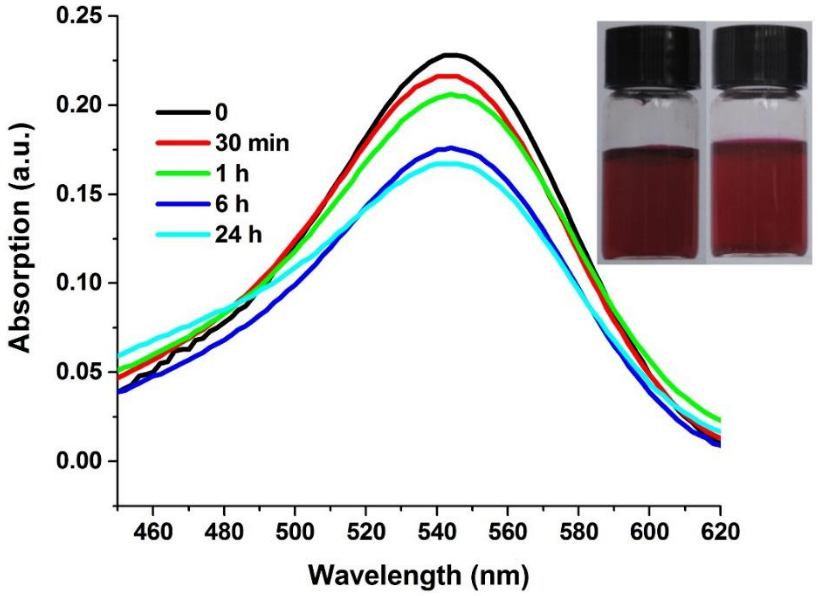
0.6
0.4
0.2
0.0
620
640
660
680
700
720
Wavelength (nm)

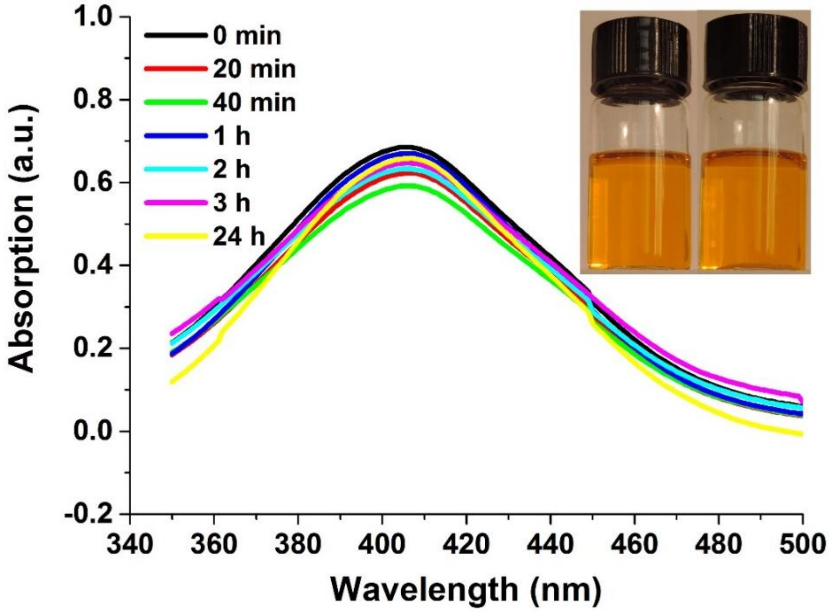
(b)


0
30 min
1 h
2 h
6 h
24 h
Absorption (a.u.)
0.0
0.2
0.4
0.6
0.8
500
520
540
560
Wavelength (nm)

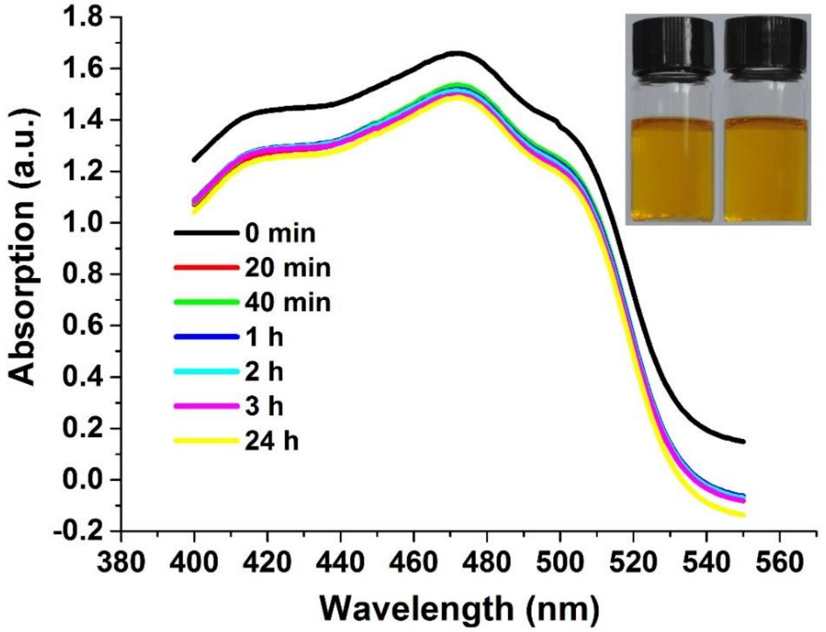
(c)


0
30 min
1 h
6 h
24 h
Absorption (a.u.)
0.00
0.05
0.10
0.15
0.20
0.25
460
480
500
520
540
560
580
600
620
Wavelength (nm)

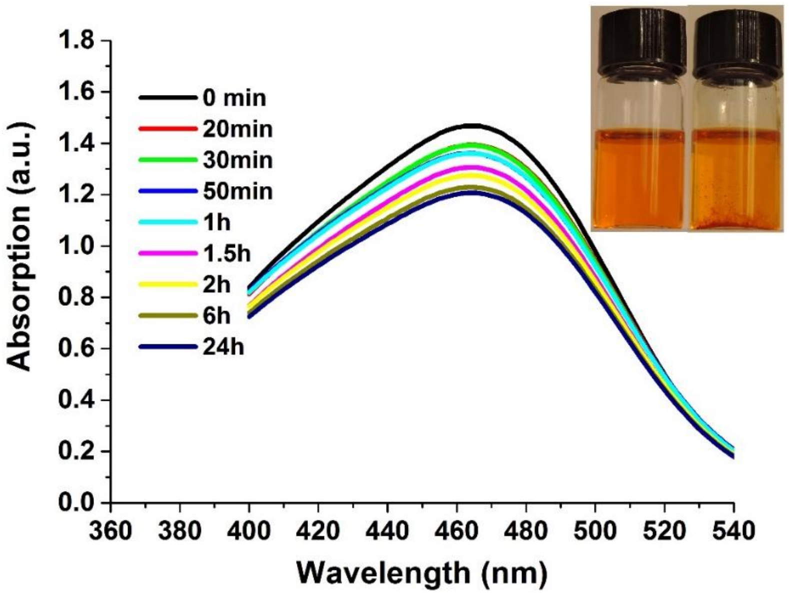
(d)


0 min
20 min
40 min
1 h
2 h
3 h
24 h
Absorption (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
340
360
380
400
420
440
460
480
500
Wavelength (nm)

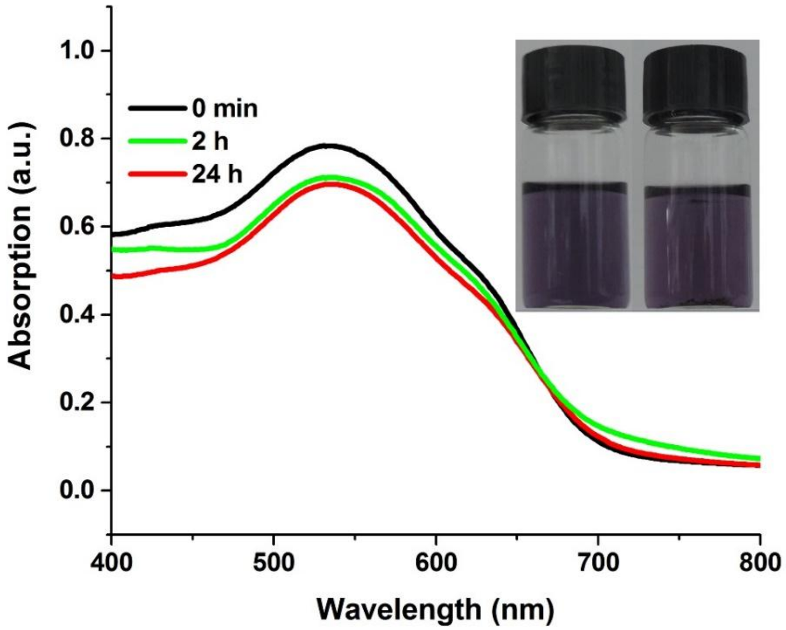
(e)


0 min
20 min
40 min
1 h
2 h
3 h
24 h
Absorption (a.u.)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
380
400
420
440
460
480
500
520
540
560
Wavelength (nm)

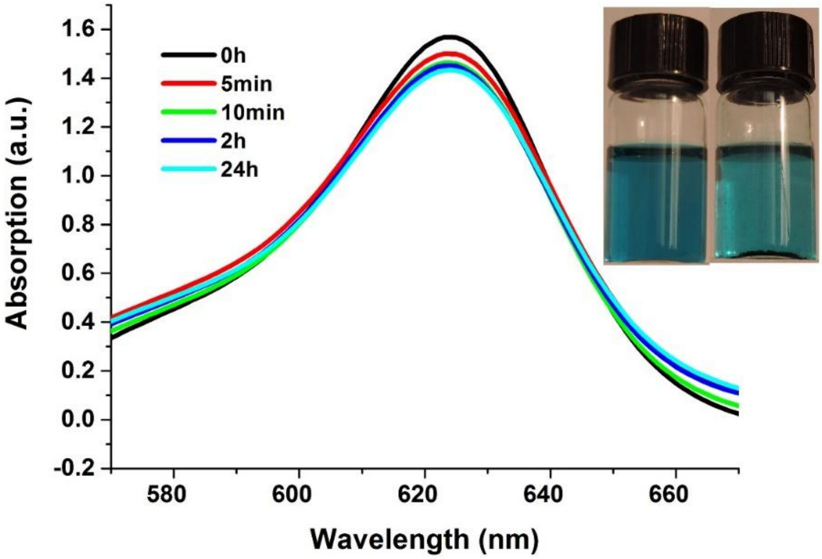
(f)


Absorption (a.u.)
Wavelength (nm)
0 min
20min
30min
50min
1h
1.5h
2h
6h
24h
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
360
380
400
420
440
460
480
500
520
540

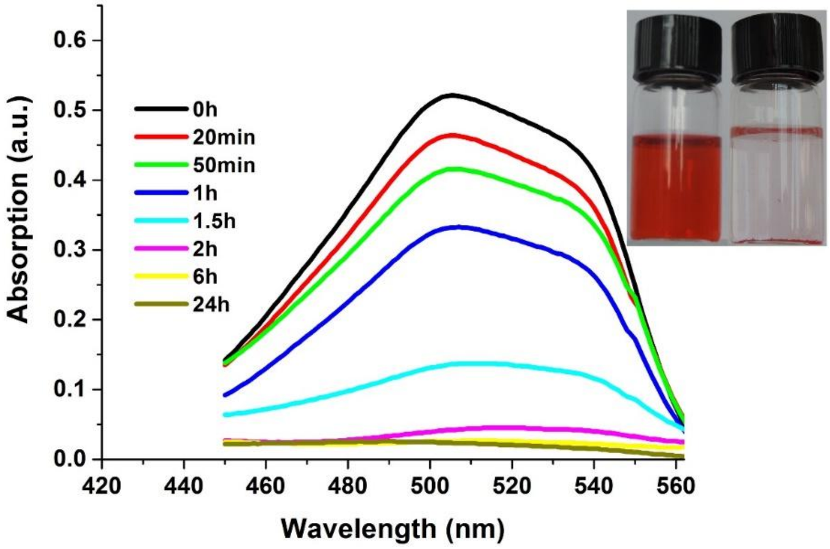
(g)


Absorption (a.u.)
Wavelength (nm)
0 min
2 h
24 h
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
800

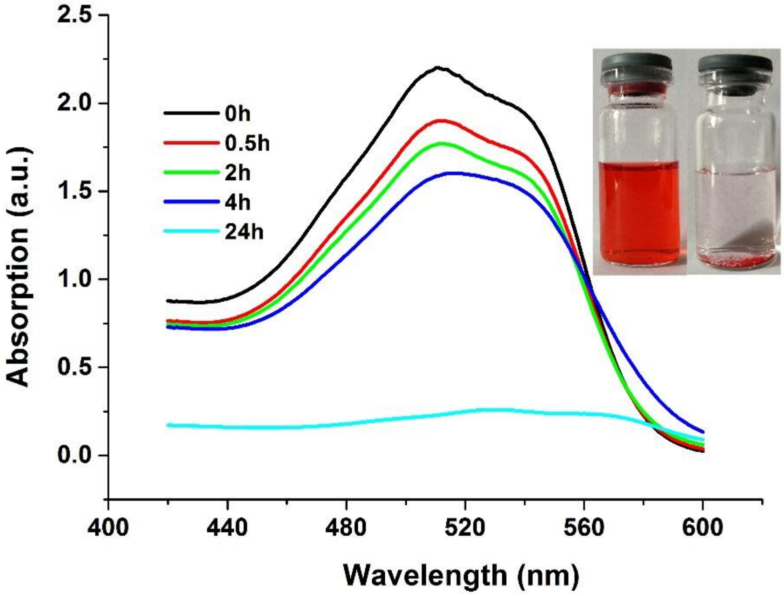
(h)


Absorption (a.u.)
Wavelength (nm)
0h
5min
10min
2h
24h
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
580
600
620
640
660

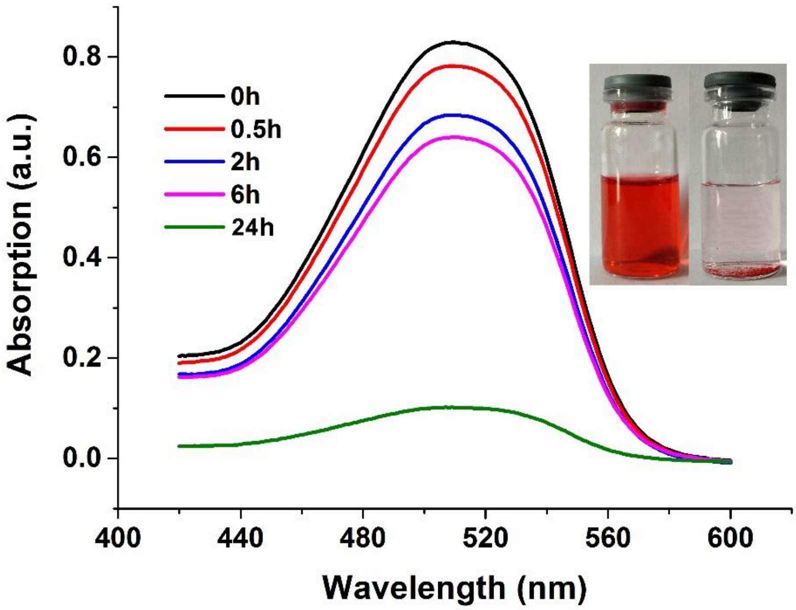
(i)


Absorption (a.u.)
Wavelength (nm)
0h
20min
50min
1h
1.5h
2h
6h
24h
0.0
0.1
0.2
0.3
0.4
0.5
0.6
420
440
460
480
500
520
540
560

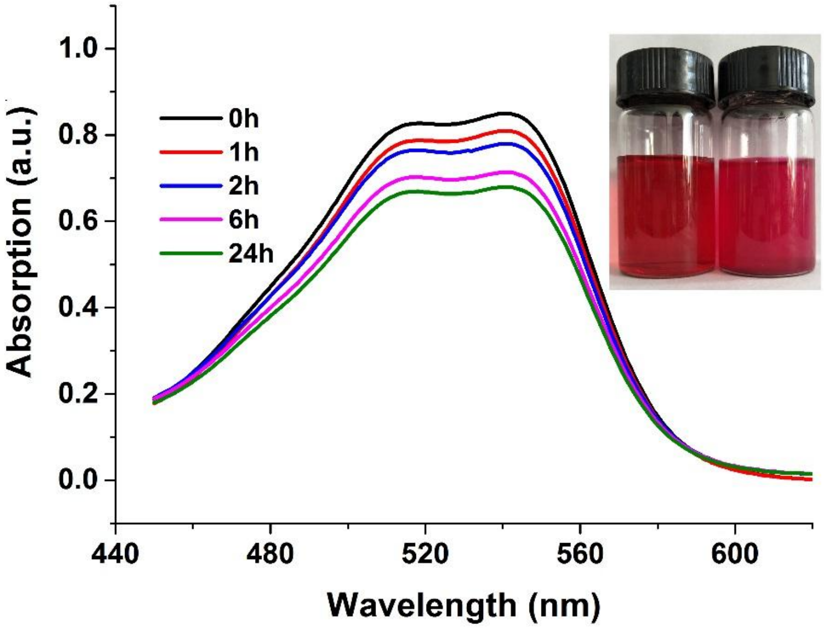
(j)


Absorption (a.u.)
Wavelength (nm)
0h
0.5h
2h
4h
24h
2.5
2.0
1.5
1.0
0.5
0.0
400
440
480
520
560
600

(k)


Absorption (a.u.)
Wavelength (nm)
0h
0.5h
2h
6h
24h
0.8
0.6
0.4
0.2
0.0
400
440
480
520
560
600

(l)



(m)

Fig. S10 UV-Vis absorbance of dyes adsorbed into **1·ClO$_4$** upon different time intervals: **CV**$^+$ (a), **MB**$^+$ (b), **R6G**$^+$ (c), **NR**^{0} (d), **MY**^{0} (e), **TR**^{0} (f), **MO**$^-$ (g), **EBT**$^-$ (h), **FG**$^{2-}$ (i), **AR26**$^{2-}$ (j), **MR5**$^-$ (k), **AR4**$^-$ (l), and **RR177**$^{2-}$ (m).

Table S1 Crystallographic data and structural refinement details for **1·ClO$_4$**, **1·ClO$_4$·BF$_4$** and **1·BF$_4$**.

Compound reference	**1·ClO$_4$**	**1·ClO$_4$·BF$_4$**	**1·BF$_4$**
Chemical formula	$C_{102}H_{72}Ag_7N_{36}Cl_7O_{28}$	$C_{102}H_{72}Ag_7B_{0.75}F_{3.01}Cl_{6.25}N_{36}O_{24.99}$	$C_{108.75}H_{87.75}Ag_7B_7F_{28}N_{38.25}O_{2.25}$
Formula mass	3253.19	3243.74	3329.18
Crystal system	Trigonal	Trigonal	Trigonal
a / Å	25.4554(3)	25.3258(4)	25.3416(4)
b / Å	25.4554(3)	25.3258(4)	25.3416(4)
c / Å	16.5591(2)	16.4902(5)	16.5233(3)
α / °	90	90	90
β / °	90	90	90
γ / °	120	120	120
Unit cell volume / Å^3	9292.4(3)	9159.7(4)	9189.6(3)
Temperature / K	293(2)	173(2)	293(2)
Space group	*P*-3	*P*-3	*P*-3
No. of formula units per unit cell, *Z*	2	2	2
Absorption coefficient, μ / mm^{-1}	7.211	0.883	6.502
No. of reflections measured	23276	68982	23539
No. of independent reflections	12247	15187	12160
R_{int}	0.0299	0.0545	0.0638
Final R_1 values ($I > 2\sigma(I)$)	0.0359	0.0349	0.0555
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0918	0.0667	0.1315
Final R_1 values (all data)	0.0437	0.0526	0.0770
Final $wR(F^2)$ values (all data)	0.0948	0.0728	0.1389
Goodness of fit on F^2	1.003	0.969	1.017

Table S2 Selective bond lengths (Å) and angles (°) for **1·ClO$_4$**, **1·ClO$_4$·BF$_4$** and **1·BF$_4$**.

1·ClO$_4$

Ag1–N1	2.242(3)	Ag1–N2	2.615(3)
Ag1–N7A	2.367(2)	Ag1–N8A	2.371(2)
Ag2–N3B	2.382(2)	Ag2–N6	2.329(2)
Ag2–N9	2.233(2)	Ag2–N11C	2.297(2)
Ag3–N12A	2.338(2)	Ag3–N12	2.338(2)
Ag3–N12D	2.338(2)		
N1–Ag1–N2	70.72(9)	N1–Ag1–N7A	122.93(9)
N1–Ag1–N8A	157.22(9)	N7A–Ag1–N2	166.07(8)
N7A–Ag1–N8A	72.23(8)	N8A–Ag1–N2	93.94(8)
N6–Ag2–N3B	95.27(9)	N9–Ag2–N3B	107.18(9)
N9–Ag2–N6	125.69(9)	N9–Ag2–N11C	115.43(8)
N11C–Ag2–N3B	111.23(8)	N11C–Ag2–N6	100.13(9)
N12–Ag3–N12D	111.00(6)	N12A–Ag3–N12D	111.00(6)
N12A–Ag3–N12	111.00(6)		

1·ClO$_4$·BF$_4$

Ag1–N1	2.224(2)	Ag1–N5A	2.294(2)
Ag1–N8	2.378(2)	Ag1–N12B	2.329(2)
Ag2–N2	2.366(2)	Ag2–N4	2.356(2)
Ag2–N7	2.621(2)	Ag2–N10	2.235(2)
Ag3–N6	2.320(2)	Ag3–N6C	2.320(2)
Ag3–N6D	2.320(2)		
N1–Ag1–N5A	115.51(7)	N1–Ag1–N8	106.10(8)

N1–Ag1–N12B	126.24(8)	N5A–Ag1–N8	111.58(7)
N5A–Ag1–N12B	99.73(8)	N12B–Ag1–N8	95.97(8)
N2–Ag2–N7	93.04(7)	N4–Ag2–N2	72.25(7)
N4–Ag2–N7	165.11(7)	N10–Ag2–N2	156.05(8)
N10–Ag2–N4	123.92(8)	N10–Ag2–N7	70.75(8)
N6–Ag3–N6C	112.82(5)	N6C–Ag3–N6D	112.82(5)
N6–Ag3–N6D	112.82(5)		

1·BF$_4$

Ag1–N6A	2.300(4)	Ag1–N11	2.327(4)
Ag1–N9B	2.374(4)	Ag1–N3	2.205(4)
Ag2–N5C	2.323(4)	Ag2–N5D	2.323(4)
Ag2–N5	2.323(4)	Ag3–N2E	2.357(4)
Ag3–N8	2.577(4)	Ag3–N1E	2.390(4)
Ag3–N7	2.244(4)		

N6A–Ag1–N11	100.26(16)	N6A–Ag1–N9B	112.01(15)
N11–Ag1–N9B	95.69(15)	N6A–Ag1–N3	115.76(15)
N11–Ag1–N3	125.60(15)	N3–Ag1–N9B	105.81(15)
N5–Ag2–N5C	112.42(10)	N5–Ag1–N5D	112.42(10)
N5C–Ag2–N5D	112.42(10)	N2E–Ag3–N8	94.81(14)
N2E–Ag3–N1E	71.94(14)	N2E–Ag3–N7	154.78(16)
N8–Ag3–N1E	166.65(14)	N8–Ag3–N7	71.02(16)
N1E–Ag3–N7	120.56(16)		

Symmetry codes for **1·ClO$_4$**: A = 1 – *y*, *x* – *y*, *z*; B = 1 – *x* + *y*, 1 – *x*, *z*; C = 1 – *x*, 1 – *y*, 2 – *z*; D = 1 – *y*, *x* – *y* + 1, *z*; E = –*x* + *y*, 1 – *x*, *z*. Symmetry codes for **1·ClO$_4$·BF$_4$**: A = –*x*, 1 – *y*, –*z*; B = –*x* + *y*, 1 – *x*, *z*; C = –*x* + *y* – 1, –*x*, *z*; D = –*y*, *x* – *y* + 1, *z*. Symmetry codes for **1·BF$_4$**: A = 1 – *x*, 2 – *y*, –*z*; B = 1 – *y*, 1 + *x* – *y*, *z*; C = –*x* + *y*, 2 – *x*, *z*; D = 2 – *y*, *x* – *y* + 2, *z*; E = –*x* + *y*, –*x* + 1, *z*.

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