Supplementary Material (ESI) for CryEngComm

A 3D Porous Metal-Organic Framework Constructed of 1D Zigzag and Helical Chains Exhibiting Selective Anion Exchange

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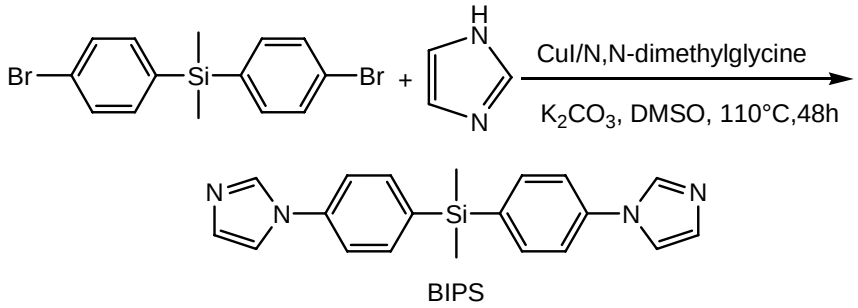
I. General Information.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Dimethyl sulfoxide (DMSO) was first dried over CaH_2 at 80° C for 1 day and distilled under vacuum pressure. Then DMSO was stored with 4Å molecule sieves prior to use. Bis(4-bromophenyl)dimethylsilane was synthesized as previously reported.[1] FTIR were recorded on a Bruker Tensor27 spectrophotometer; test conditions: potassium bromide pellets, scanning 32 times, resolution are $4cm^{-1}$. The data were treated with OPUS spectroscopy software of version 6. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on a Bruker AVANCE-400 NMR Spectrometer using DMSO as solvent and referenced to TMS. Elemental analyses (C, H, N) were obtained on a PerkinElmer 240 elemental analyzer. Molecular weights were determined by Aglient HP1100 LC-Applied Biosystems API4000 TQ Mass Spectrometer. Photoluminescence spectra were performed on a Perkin Elmer LS 50B luminescence spectrometer.

II. Preparation of BIPS and coordination polymer 1

Caution! Although we experienced no problems with the compounds reported in this work, perchlorate silver and compound **1** are potentially explosive and should be handled with great caution.

Preparation of Bis(4-(imidazol-1-yl)phenyl)dimethylsilane (BIPS).[2] The reaction routine for BIPS was shown in scheme 1. A four-bottled flask was charged with bis(4-bromophenyl)dimethylsilane (10mmol), imidazole (25mmol), K_2CO_3 (40 mmol), CuI (2 mmol) and N, N-dimethlyglycine (4 mmol) and backfilled with argon, followed by addition of 25ml DMSO. Then the system was heated at 110 ºC for 48h before it was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layers were washed with ethyl acetate. The combined organic layers were washed with brine, dried with $MgSO_4$, and concentrated in vacuum. A white powder was obtained by column chromatography (CH_2Cl_2/MeOH as eluent). Yield: 41%. ^{1}H NMR (400MHz, DMSO): δ 8.26 (s, 2H), 7.75(s, 2H), 7.65(s, 8H), 7.11(s, 2H)，0.60(s, 6H). ^{13}C NMR (90 MHz, DMSO): δ 138.2, 136.6, 136.0, 135.9, 130.4, 120.3, 118.4, -2.3. EI-MS m/z 345.5(M^{+}).



Scheme 1 Synthesis of BIPS via Ullmann condensation reaction

Synthesis of $[Ag(BIPS)]_{0.5}[Ag(BIPS)]_2 \cdot 2.5ClO_4 \cdot 5H_2O$ (1) A methanol solution (4ml) of $AgClO_4$ (0.02g) was diffused into a dichloromethane solution (4ml) of BIPS (0.005g). Colorless crystals were formed and obtained for a week in 30% yield. Anal. Cal. for **1**: C 42.16, H 3.89, N 9.83. Found: C 40.53, H 3.81, N 9.56. IR: ν (ClO_4^-): 1096, 622cm^{-1}.

III. Crystal structure determination of BIPS and 1

Single-crystal X-ray diffraction was performed using a Bruker Apex II CCD diffractometer equipped with a fine-focus sealed-tube X-ray source (Mo_{Ka} radiation, graphite monochromated). Structures were solved by direct methods using SHELXTL and were refined by full-matrix least-squares on F^2 using SHELX-97. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. For complex 1, the SQUEEZE program was used to remove scattering from the highly disordered solvent molecules (H_2O molecules) and a new .HKL file was generated. The structure was refined using the new generated HKL file.

Table S1 Crystal Data Collection and Structure Refinement for BIPS and **1**

	BIPS	**1**
empirical formula	$C_{20}H_{21.52}N_4O_{1.52}Si$	$C_{50}H_{60}Ag_{2.5}Cl_{2.5}N_{10}O_{15}Si_{2.5}$
formula weight	371.97	1469.60
temp (K)	298(2)	298(2)
crystal system	orthorhombic	orthorhombic
space group	Pnma	Pnna
a (Å)	5.772(2)	24.328(5)
b (Å)	19.128(7)	31.067(6)
c (Å)	17.295(6)	16.658(4)
α(deg)	90.00	90.00
β(deg)	90.00	90.00
γ(deg)	90.00	90.00

V (Å3)	1909.5(12)	12590(4)
Z	4	4
ρcalc (g/cm3)	1.282	1.551
F(000)	776	5960
data/restraints/params	2272/0/ 124	6620/0/ 713
GOF on *F*2	1.018	1.008
final *R* indices [$I > 2\acute{o}(I)$]	R1 = 0.0694, wR2 = 0.1862	R1 = 0.0768, wR2 = 0.2095

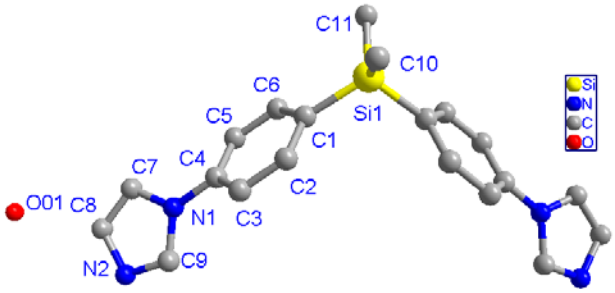


Fig. S1 X-ray structure of BIPS. (C=gray; N=blue; Si=yellow; O=red). Hydrogen atoms are omitted for clarity.

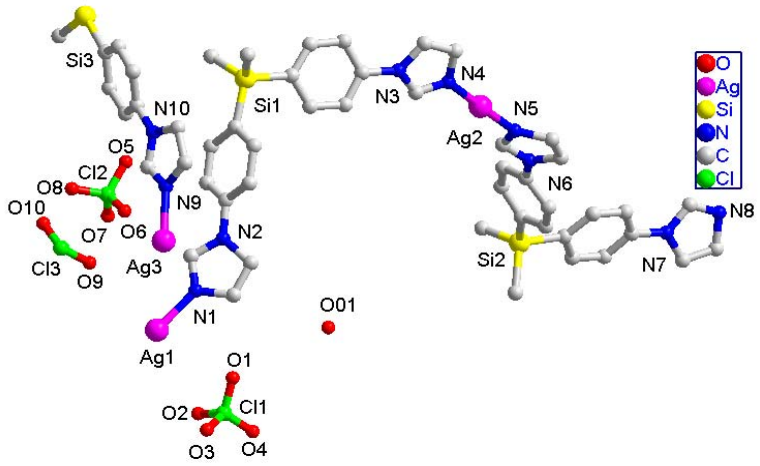


Fig. S2 X-ray structure of **1**. A view of the BIPS ligand and Ag(I) coordination environment. (C=gray; N=blue; Si=yellow; Ag=purple; O=red; Cl=green). Hydrogen atoms are omitted for clarity.

IV. Anion Exchange of 1 with $NaPF_6$ and $NaCF_3SO_3$

Compound 1 (0.005g) was added into a methanol (5ml) solution of NaX (X=PF_6^-, $CF_3SO_3^-$) (0.1g) at room temperature. The reaction mixture was stirred, and the precipitate was monitored by IR and ^{19}F NMR. After one week and two weeks, the reaction mixture was filtered and washed with amounts of methanol.

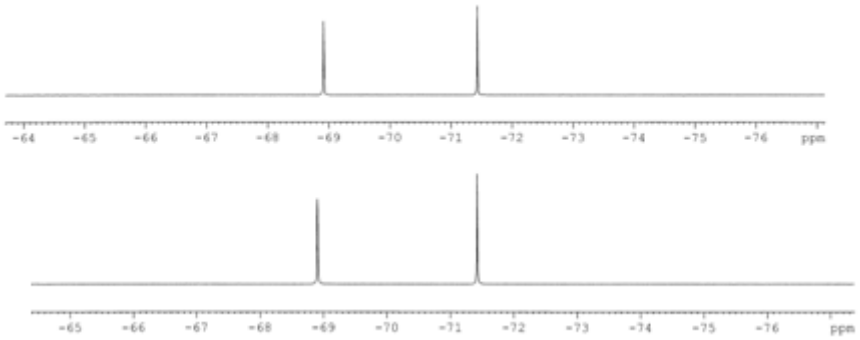


Fig. S3 ^{19}F NMR spectras for the exchange products with PF_6^-. Top: the product after one week; Bottom: the product after two weeks. δ, PF_6^- (d, 70.2).

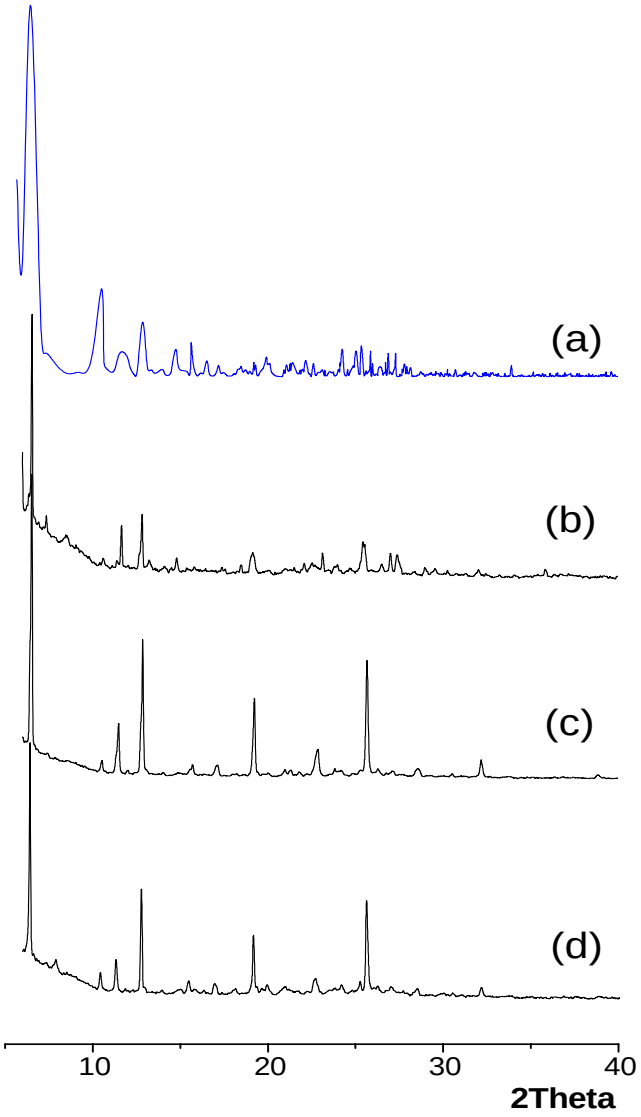


Fig. S4 XRD patterns: (a) simulated from single-crystal data for 1; (b) measured for 1; (c) measured for the exchange product with PF_6^- after one week; (d) measured for the exchange product with PF_6^- after two weeks.

V. TGA and DSC analysis.

The thermogravimetric analysis (TGA) for complex **1** was carried out between room temperature and 900°C in a static N_2 with a heating rate of 10°C/min, while the differential scanning calorimetry (DSC) were carried out between room temperature and 450°C in a static N_2 with a heating rate of 10°C/min.

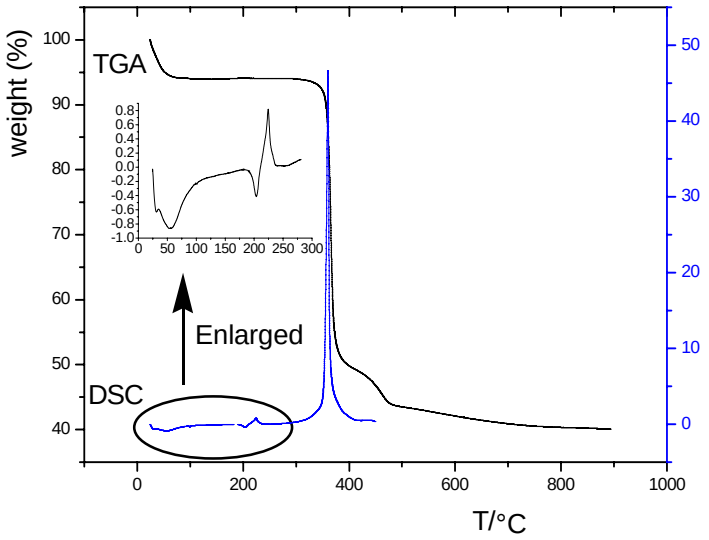


Fig. S5 Overlay of TGA and DSC of compound **1**

VI. Fluorescence properties for BIPS and 1

Both BIPS and **1** were measured in the solid state at room temperature.

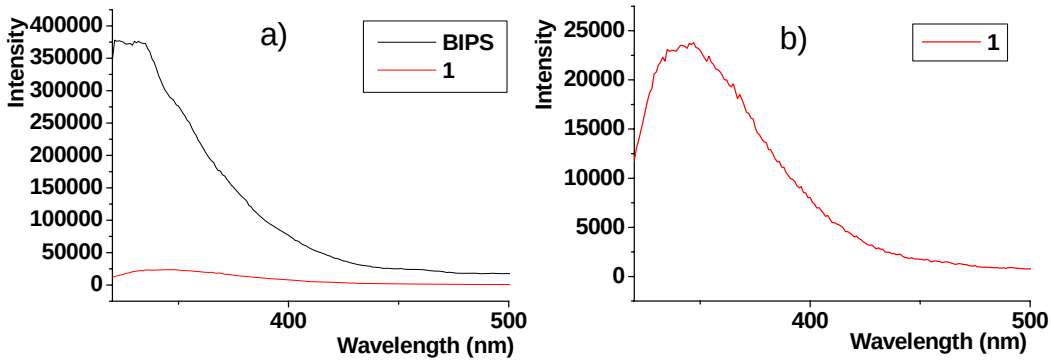


Fig. S6 a) Emission spectra of BIPS and compound 1; b) Emission spectra of compound 1 (Enlarged). (λ_{ex}=290nm)

References:

(1) T. Doi, A. S. Ichimura, N. Koga and H. Iwamura, *J. Am. Chem. Soc.*, 1993, **115**, 8928.
(2) H. Zhang, Q. Cai and D. W. Ma, *J. Org. Chem.*, 2005, **70**, 5164.