

## Supporting Information

### Synthesis

In our synthesis, NaHCO<sub>3</sub> (4.17 mmol, 0.350 g) was added to a mixture of V<sub>2</sub>O<sub>5</sub> (0.56 mmol, 0.101 g), I<sub>2</sub>O<sub>5</sub> (1.39 mmol, 0.464 g), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.56 mmol, 0.134 g), 2,2'-bipy (0.56 mmol, 0.088 g), HCl (38%, 0.170 mL) and distilled water (5.0 mL) with molar ratio of 7.5: 1: 2.5: 1: 1: 10: 500. The mixture was stirred with glass muddler and crystallized in sealed 15mL Teflon-lined stainless steel autoclave at 120 °C for 7 days under autogenous pressure. Pillared crystalline product was obtained, filtered off, washed with distilled water, and dried at ambient temperature.

### Determination of crystal structure

The data collection and the structural analysis were performed on a Bruker Smart CCD diffractometer equipped with a normal-focus, 2.4 kW sealed tube X-ray source (graphite-monochromated Mo K $\alpha$  radiation,  $\lambda$  = 0.71073 Å). Direct methods were used to solve the structure using the SHELXL crystallographic software package. All non-hydrogen atoms in the framework of the structure were easily found from the difference Fourier map, but the non-hydrogen atoms in the channels of the structure could not be confirmed easily only by the difference Fourier map. For this purpose, we used other methods; first we confirmed the presence of chlorine and iodine guest molecules by XPS. Then we confirmed the numbers of the guest molecules by the thermogravimetric analysis and element analysis. Finally we adjusted the occupancy rate of the guest molecules to make them have suitable temperature factors. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. Hydrogen atoms on the water molecules of crystallization in the compounds were not located. All non-hydrogen atoms were refined anisotropically.

### Elemental analysis and ICP analysis

Anal. Calcd for the compound: C, 20.95; H, 2.24; N, 4.89; Cu, 11.09. Found: C, 21.20; H, 3.04; N, 5.50; Cu, 10.37.

**FT-IR analysis** (KBr phase, cm<sup>-1</sup>): 3424.8 (m), 3106.9 (w), 3081.9 (m), 3032.6 (w),

2364.6 (w), 2340 (w), 1600.7 (s), 1563.9(m), 1473.6 (m), 1444.5 (s), 1313.4 (s), 1155.6 (m), 1112.7 (w), 1029.3 (s), 802.2 (m), 773.3 (s), 661.6 (w), 494.7 (w).

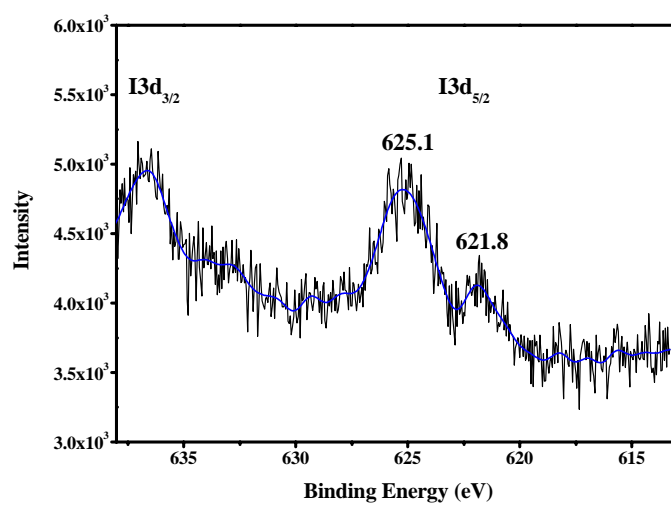
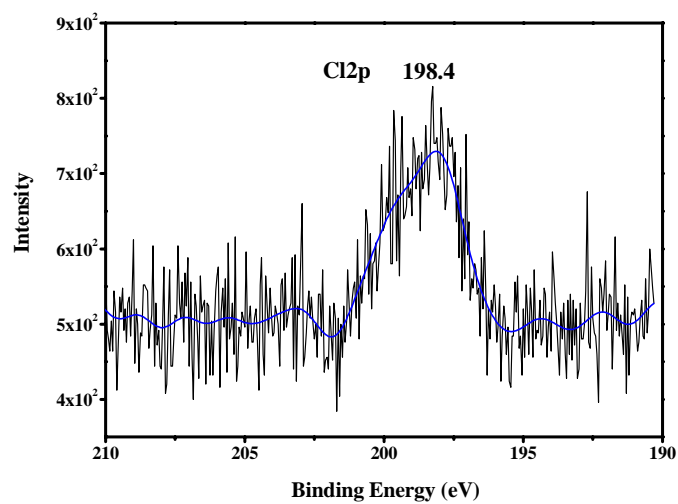
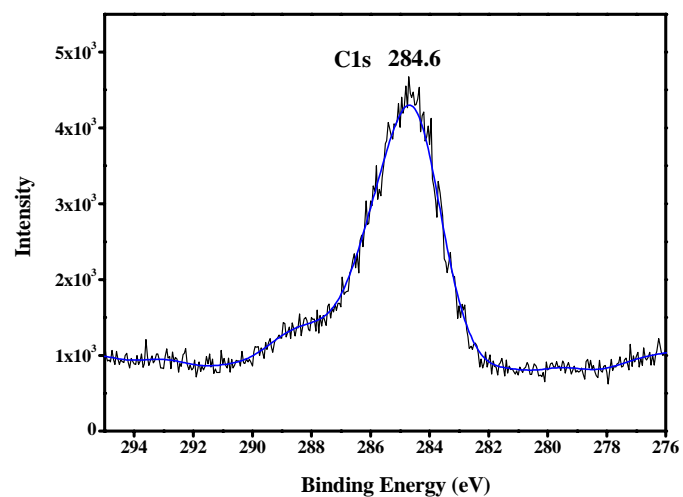
**Fig. 1.** ORTEP drawing of the asymmetric units of **1**. (thermal ellipsoids are shown at 50% probability)

**Fig. 2.** XPS valence bands spectra of **1**.

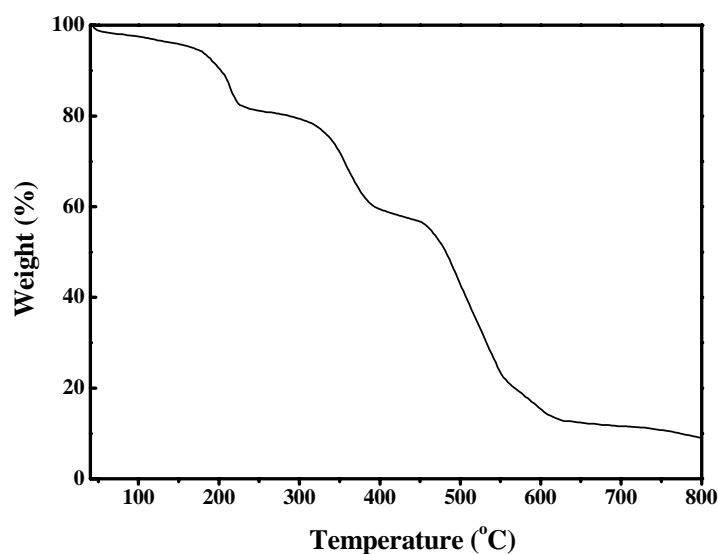
**Fig. 3.** Thermogravimetric pattern for **1**.

**Fig. 4.** Infrared spectrum of **1**.

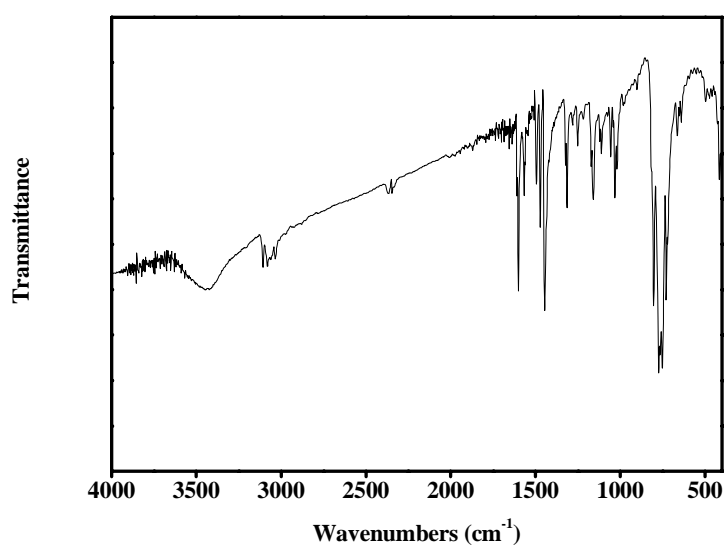




**Fig. 2.** XPS valence bands spectra of **1**.



**Fig. 3.** Thermogravimetric pattern for **1**. Thermal analyses for **1** was performed in air from 40 to 800 °C. The TG curve for **1** showed that the initial weight loss in the temperature range 170-222 °C was due to the removal of chlorine, water and iodine guest molecules (weight loss exptl 15.00%, calcd 15.99%). Over the range 303-400 °C, the weight loss should correspond to the decomposition of 2,2'-bipy (weight loss exptl 26.06%, calcd 27.21%). Further, loss in weight is observed from 454 to 608 °C which is attributed to the condensation of  $\text{IO}_3$  group into  $\text{I}_2\text{O}_5$  and the volatilization of iodine groups (weight loss exptl 41.72%, calcd 40.44%). Beyond 610 °C, the weight becomes constant owing to the formation of metal oxide.



**Fig. 4.** Infrared spectrum of **1**.