

Fig. s1 The view of the 1-D supramolecular column formed by [Cu(1)(2,2-bpy)₂]²⁺ complexes in compound **1** along the c axis.

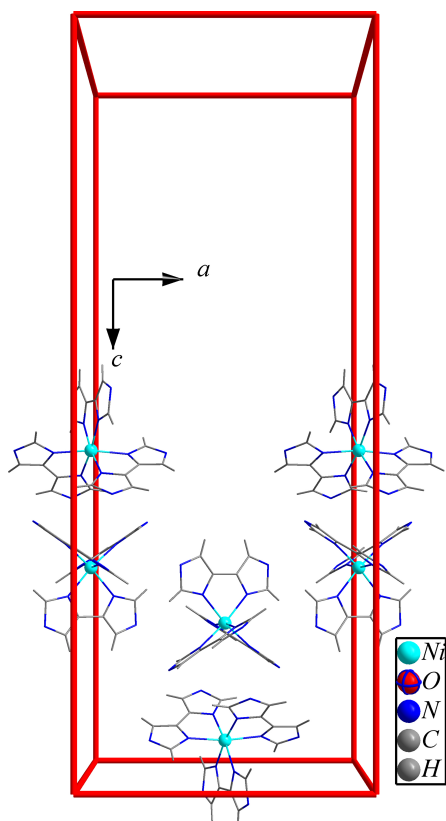
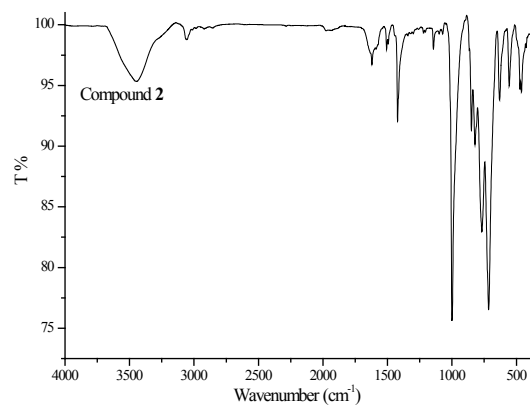
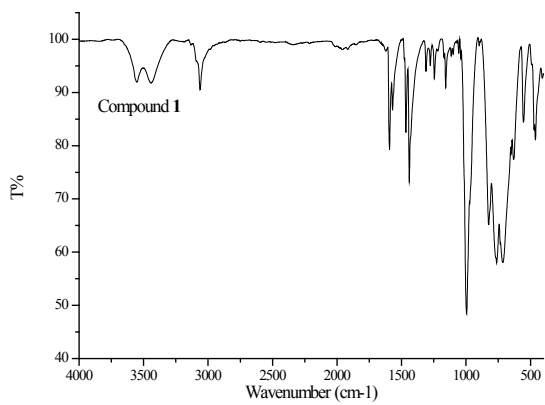


Fig. s2 the packing structure of the TMCs in compound **3**.



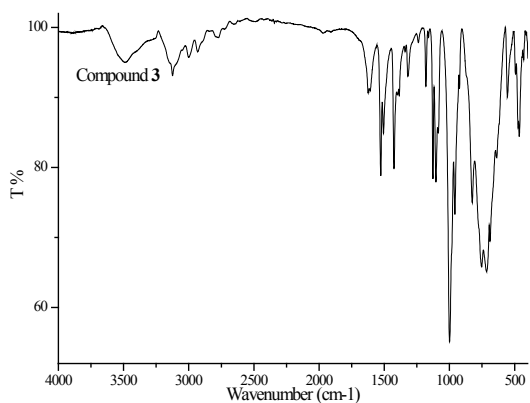
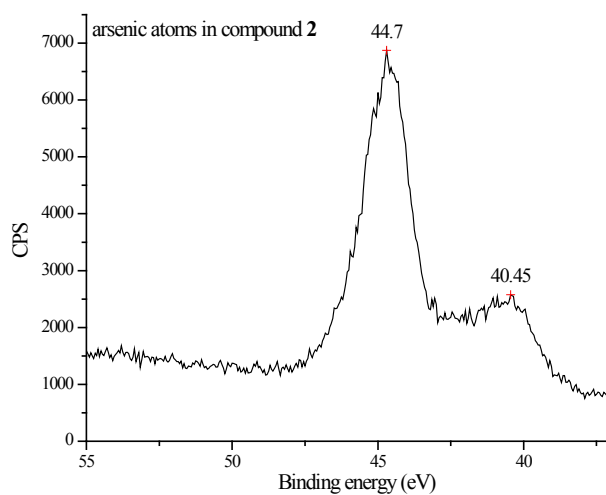
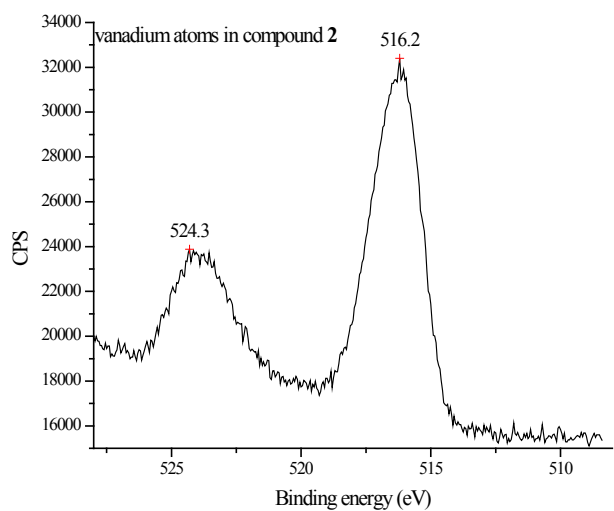
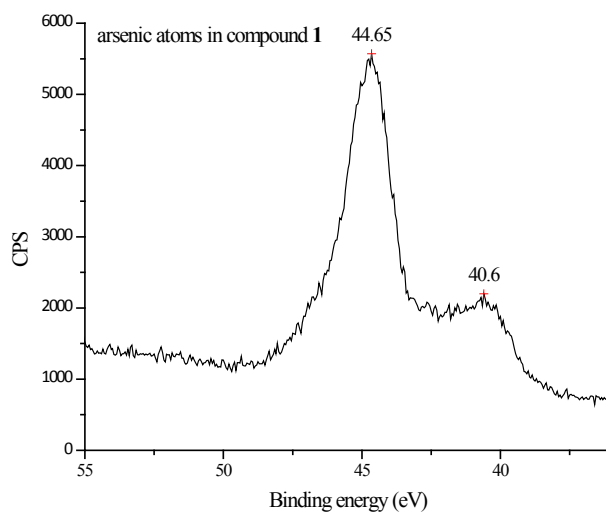
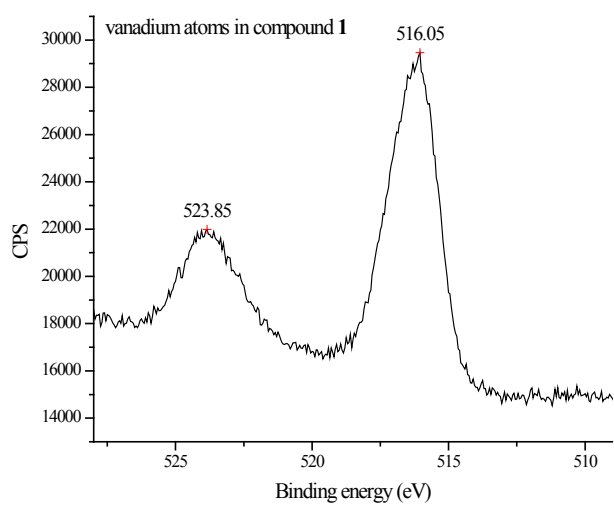


Fig. s3 the IR spectra for compounds 1-3.



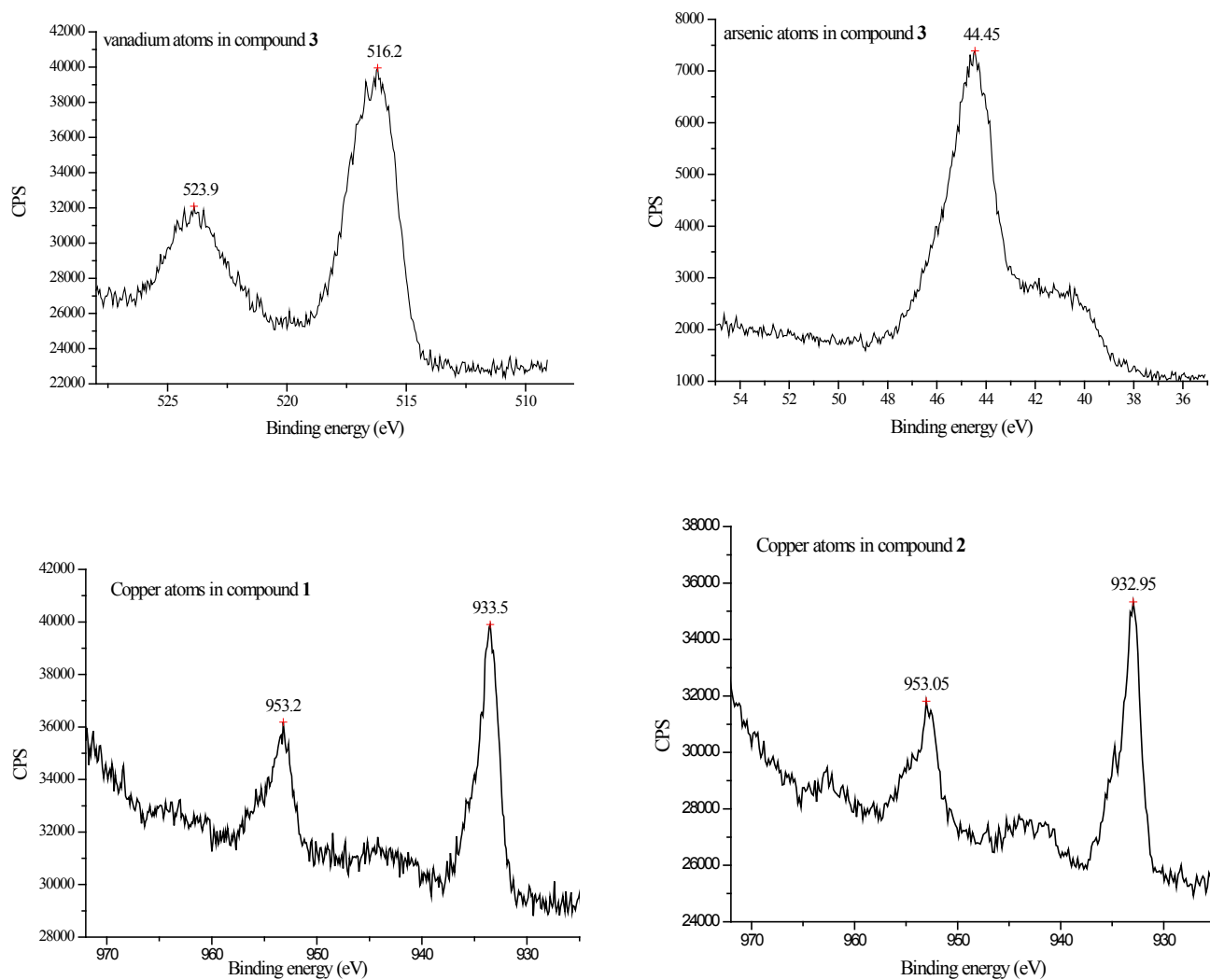
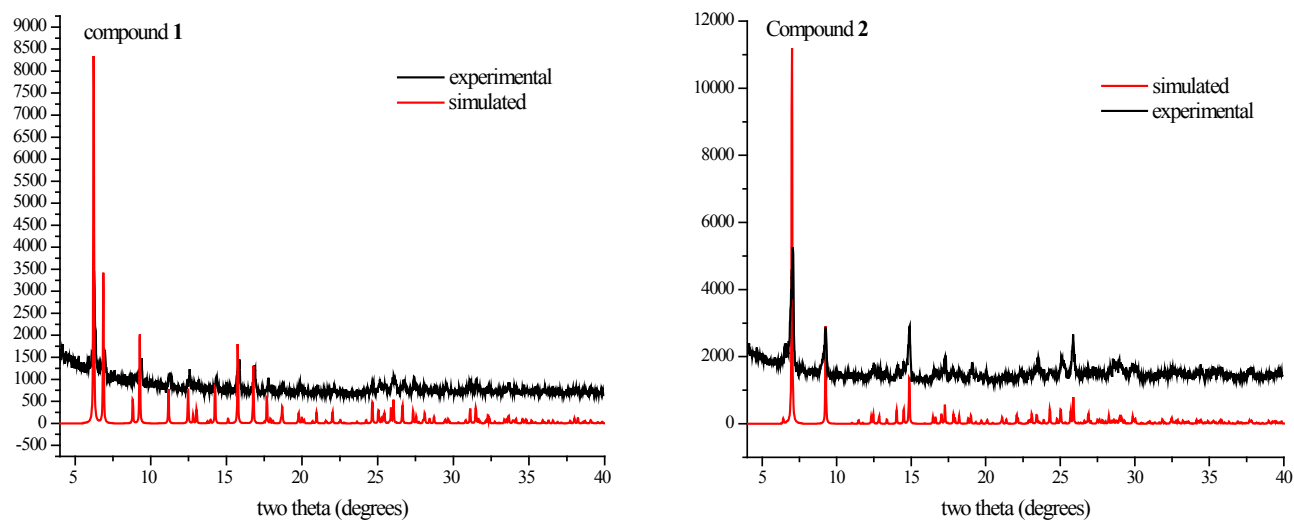


Fig. s4 the XPS spectra of vanadium, arsenic in compounds 1-3 and XPS spectra of copper in compounds 1-2.



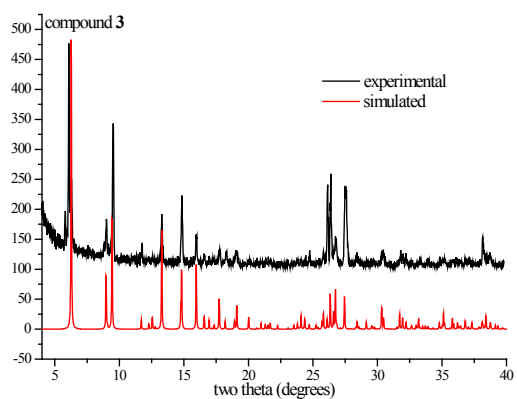


Fig. s5 the experimental and simulated XRD patterns for compounds 1-3.

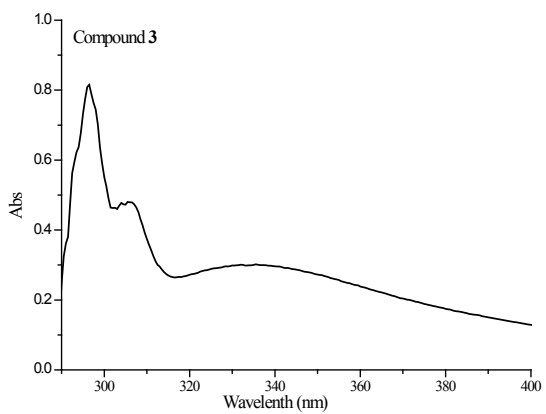
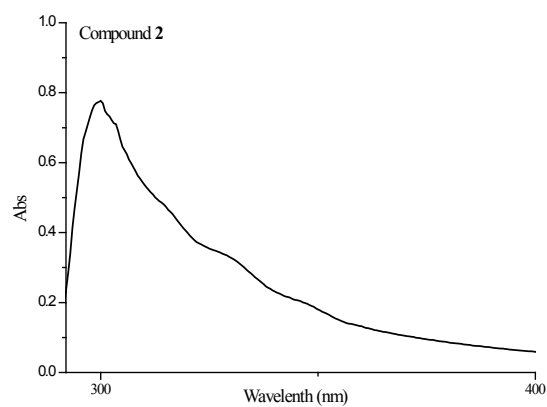
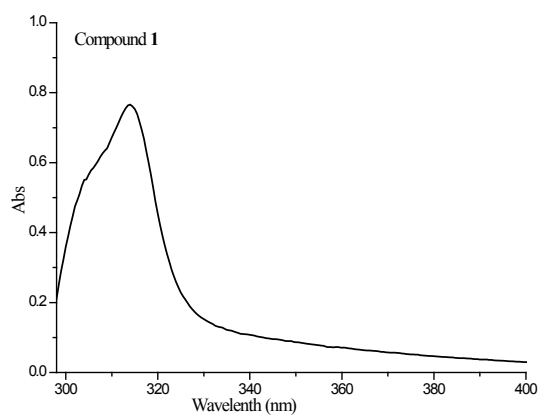


Fig. s6 the UV-Vis spectra of DMSO solutions of compounds 1-3.

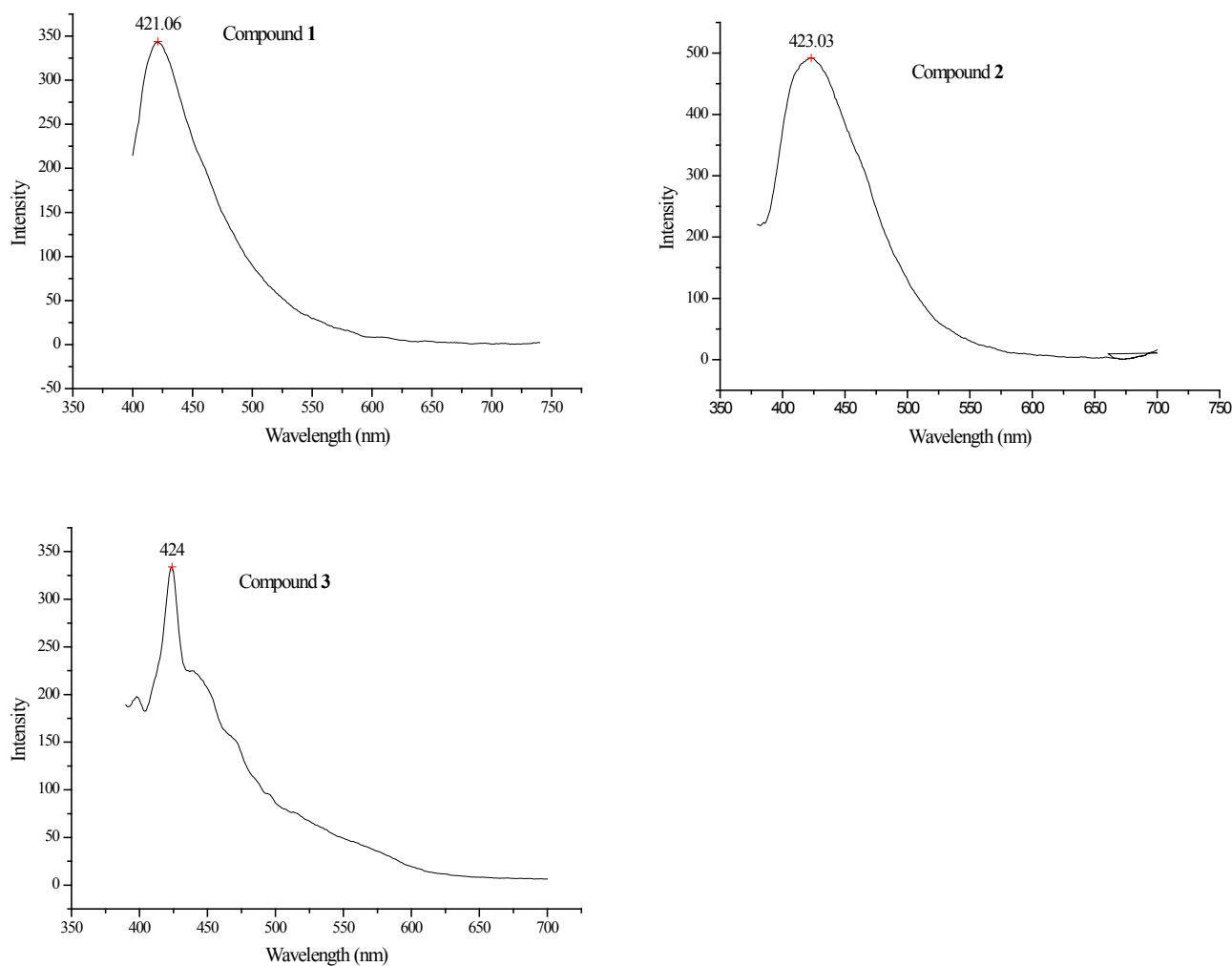


Fig. s7 the photoluminescence properties of DMSO solutions of compounds **1-3**. The photoluminescence properties of DMSO solutions of compounds **1-3** were studied. The emission spectrum of compound **1** at room temperature is depicted in Fig. s6. It can be observed that an intense emission occurs at 421 nm ($\lambda_{\text{ex}} = 380$ nm), which can be assigned to the emission of intra-ligand charge transfer. The emission peak in compound **1** is red shifted relative to that of the free 2,2-bpy ligand ($\lambda_{\text{max}} = 415$ nm). The red shift has been regarded as due to the complexation of the organic ligand with the copper atom. The emission spectra of compounds **2-3** at room temperature are depicted in Fig. s6. Compound **2** exhibits an emission peak at 423 nm ($\lambda_{\text{ex}} = 360$ nm), compound **3** exhibits an emission peak at 424 nm ($\lambda_{\text{ex}} = 371$ nm), respectively. The photoluminescence mechanism of compounds **2-3** can also be attributed to the intra-ligand transition because that similar emission is also observed for pure organic ligands.