

Figure S1. The plots of thermogravimetric (TG) and derivative thermogravimetry (DTG) analyses of **1**.

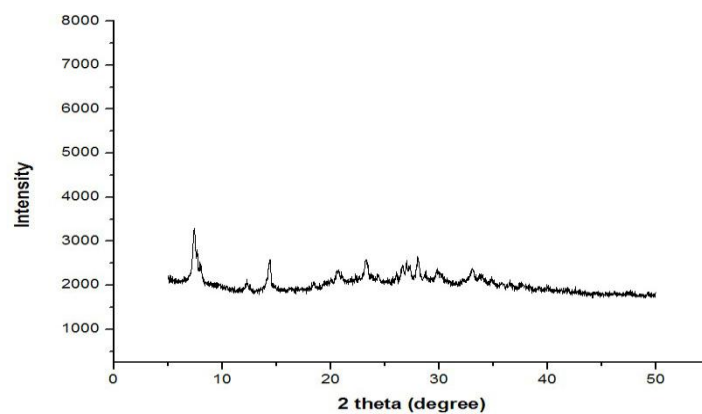


Figure S2. PXRD patterns of **1** after heated at 160 °C.

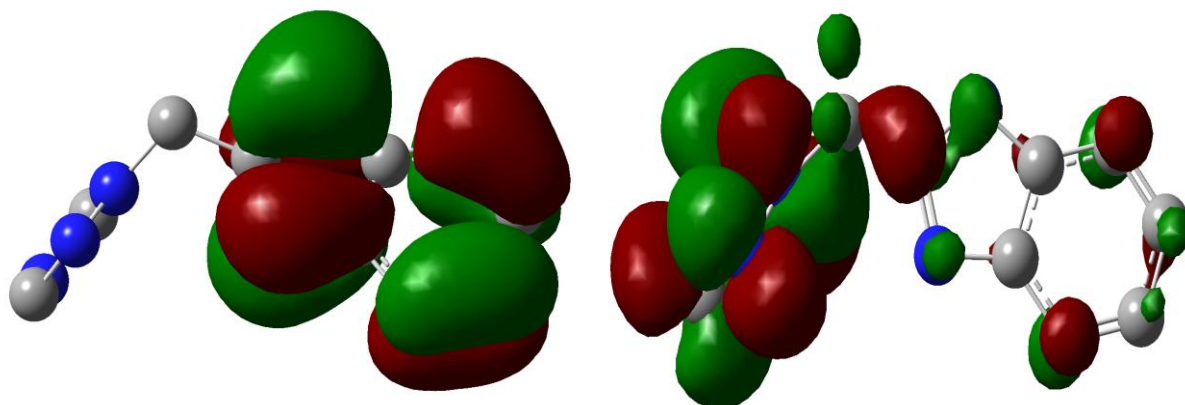


Figure S3. Htmb: (left) HOMO (-0.88 eV); (right) LUMO (3.81 eV)

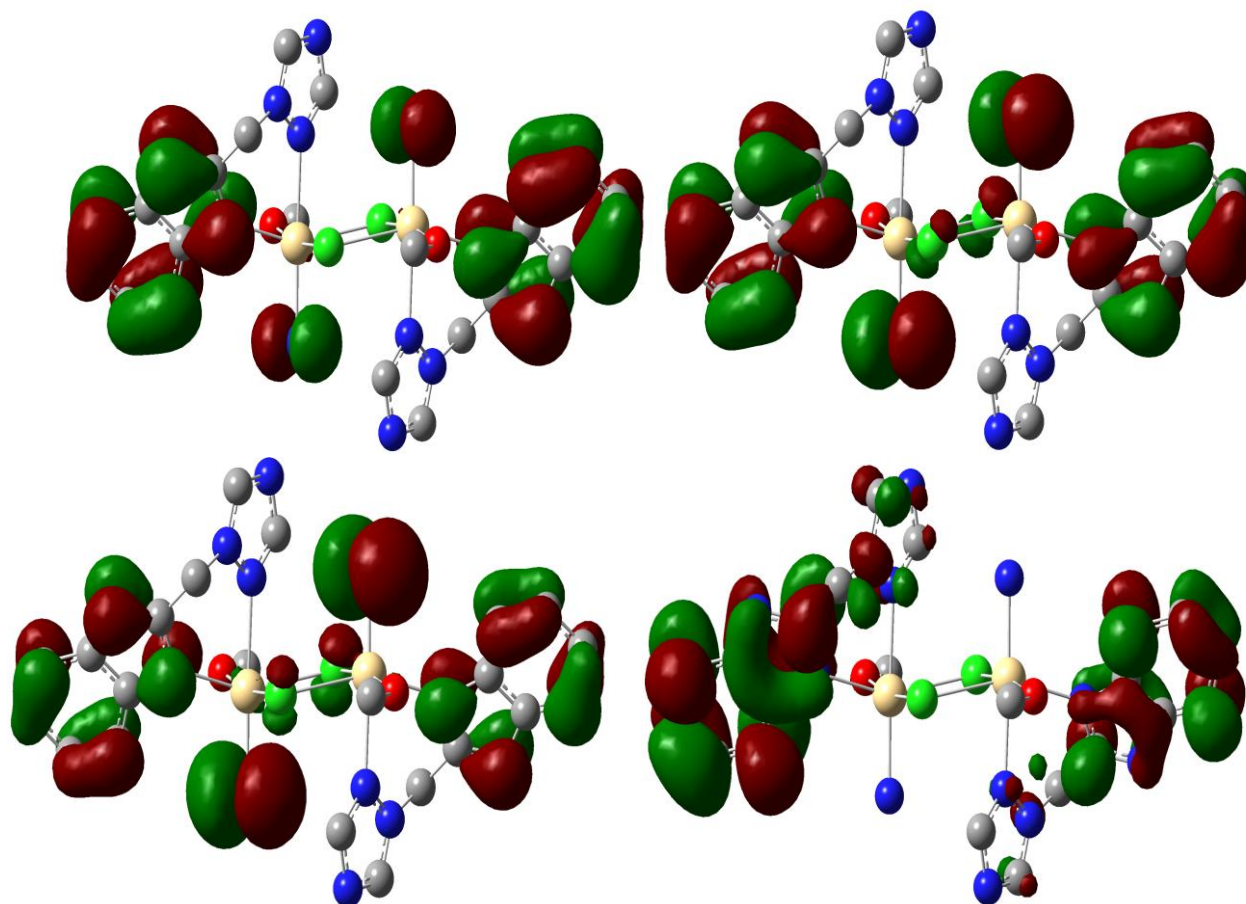


Figure S4. The binuclear unit $[\text{Cd}_2(\text{tmb})_2(\text{Cl})_2(\text{CH}_3\text{OH})_2]$: (left upper) HOMO (-5.67 eV); (right upper) HOMO-1(-5.81 eV); (lower left) LUMO (-0.53 eV); (lower right) LUMO+1(-0.37 eV).

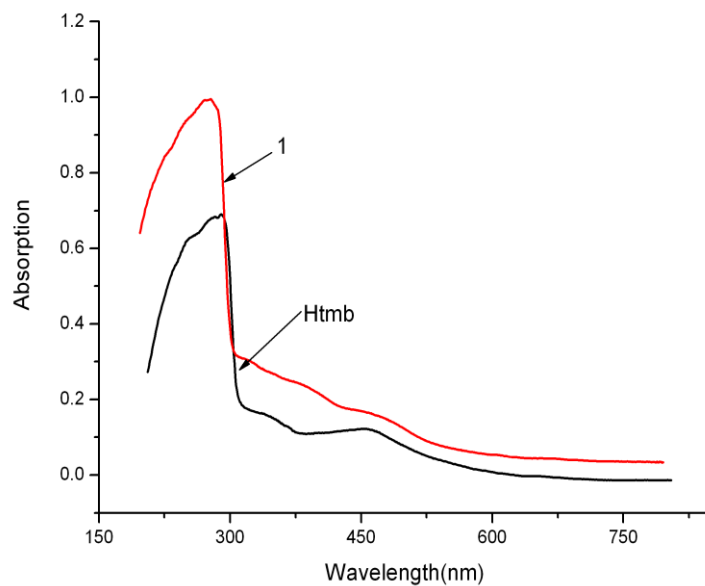


Figure S5. The solid state UV-Vis spectra of the ligand Htmb and **1**

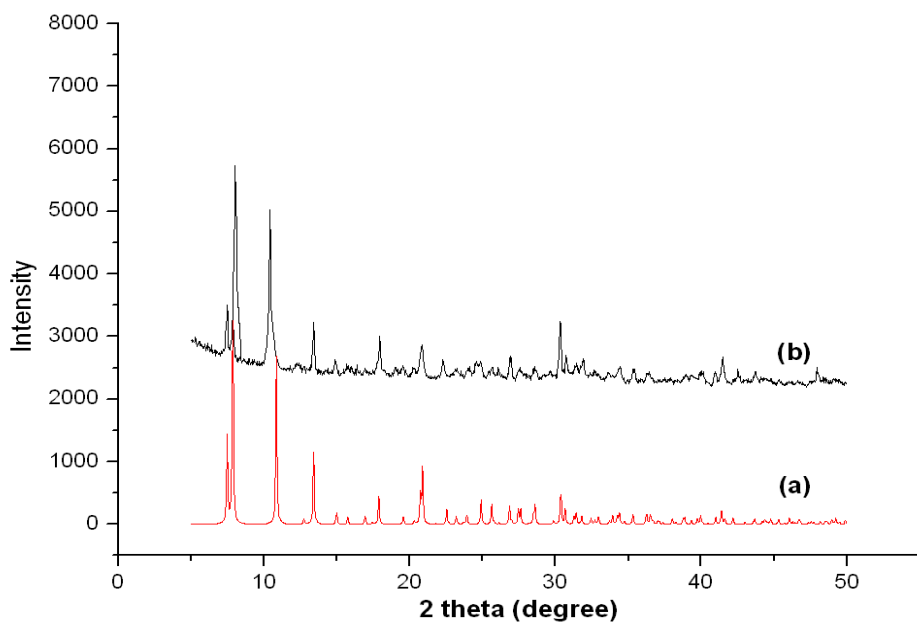


Figure S6. PXRD patterns of **1** simulated from X-ray single-crystal data (a), and experiment data (b).