Materials with solid-solid phase transition characters have attracted intensive attentions due to their potential applications in data storage, sensing, and signal processing. In this work, the solid to solid phase transitions of 4’-(2-Furyl)-2,2’:6’,2”-terpyridine (ftpy) was characterized by variable temperature of powder x-ray diffractions (PXRD) and differential scanning calorimetry (DSC). Two different polymorphs of α-ftpy and β-ftpy were obtained by different synthetic strategies. The colorless single crystal of α-ftpy is crystallized in P 21/c space group with cell constants $a = 10.395(1)$ Å, $b = 13.195(1)$ Å, $c = 11.376(1)$ Å, and $\beta = 105.457(3)^\circ$, but the celadon powder of b-ftpy is crystalized in P 21/n space group with cell constants $a = 10.6142(1)$ Å, $b = 35.4639(2)$ Å, $c = 3.8687(4)$ Å, and $\beta = 91.671(2)^\circ$. The structure of β-ftpy is determined by simulated annealing algorithm in real space. In comparison with packing structures of both polymorphs, the shortest π-π interaction distances are ~3.9 Å and ~3.3 Å for α-ftpy and β-ftpy, respectively. A DSC study of powder b-ftpy shows that an endothermic event occurs at ~148.6 °C. The variable-temperature PXRD studies of b-ftpy indicate that α-ftpy appears at ~398 K, and the phase transform is complete at ~408 K. However, the α-ftpy cannot transforms back to β-ftpy by further cooling experiments. In the study of luminescence characters of both polymorphs at solid state, both display the maximum intensity of emission peak at 403nm with absolute quantum yield 4.9% and 3.8% for α-ftpy and β-ftpy, respectively.