## Supporting Information of

## Polytypic phase transition

## in alkyl chain-functionalized valence tautomeric complexes

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**Figure S1.** TG-DTA curves of a) the solvated **CoC0bpy**, b) the solvated **CoC1bpy**, and c) the solvated **CoC5bpy** recrysallized from toluene/acetonitrile. Each weight loss corresponds to the removal of the solvated toluenes, affording the desolvated samples.



**Figure S2.** XRPD patterns of the solvated **CoC***n***bpy** (n = 0, 1, and 5) and the desolvated samples. The observed changes in the XRPD profiles are due to the removal of the toluene.



**Figure S3.** DSC curves of a) **CoC9bpy** and b) **CoC13bpy** under a scan rate of 1, 5, 10, and 20 K min<sup>-1</sup>.