

Electronic Supplementary Information (ESI)

**Design and Synthesis of Luminescent Porous Coordination
Polymers for Chromaticity Modulation, Sensing Nitrobenzene
and Iodine Encapsulation**

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Materials and methods

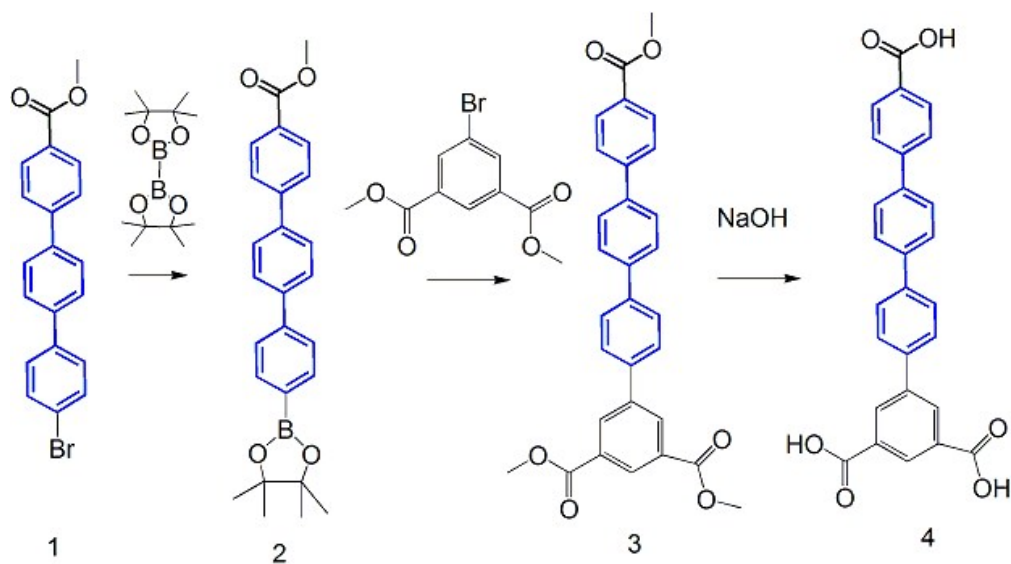
All the reagents and solvents were commercially available and used as received. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. The FTIR spectra were recorded from KBr pellets in the range of 4000-500 cm^{-1} on a VECTOR 22 spectrometer. Thermal analyses were performed on a TGA, STA 209 F1, NETZSCH Instruments from room temperature to 650°C with a heating rate of 10°C/min under flowing nitrogen. The powder X-ray diffraction patterns (PXRD) measurements were carried on a Bruker axS D8 Advance 40kV, 40mA for $\text{CuK}\alpha$ ($\theta = 1.5418 \text{ \AA}$) with a scan rate of 0.2 s/deg at room temperature. Luminescent spectra of the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer. The fluorescence lifetime was measured using an Edinburgh Instruments FLS920 Fluorescence Spectrometer.

Synthesis of ligands

The ligand of Biphenyl-3,4',5-tricarboxylic acid (Bi- H_3L) was commercially available and used as received.

The ligand of [1,1':4',1''-terphenyl]-3,4'',5-tricarboxylic acid (Te- H_3L) was synthesized according to our previous work¹.

The ligand of [1,1':4',1'';4'',1''']-quaterphenyl-3,4''',5-tricarboxylic acid (Qu- H_3L) was synthesized by the Suzuki reactions between 4-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-[1,1':4',1'']terphenyl-4''-carboxylic acid methyl ester (2) and dimethyl 5-bromoisophthalate followed by the base-catalyzed hydrolysis (Scheme 1).



Scheme S1 Synthesis route of Qu-H₃L

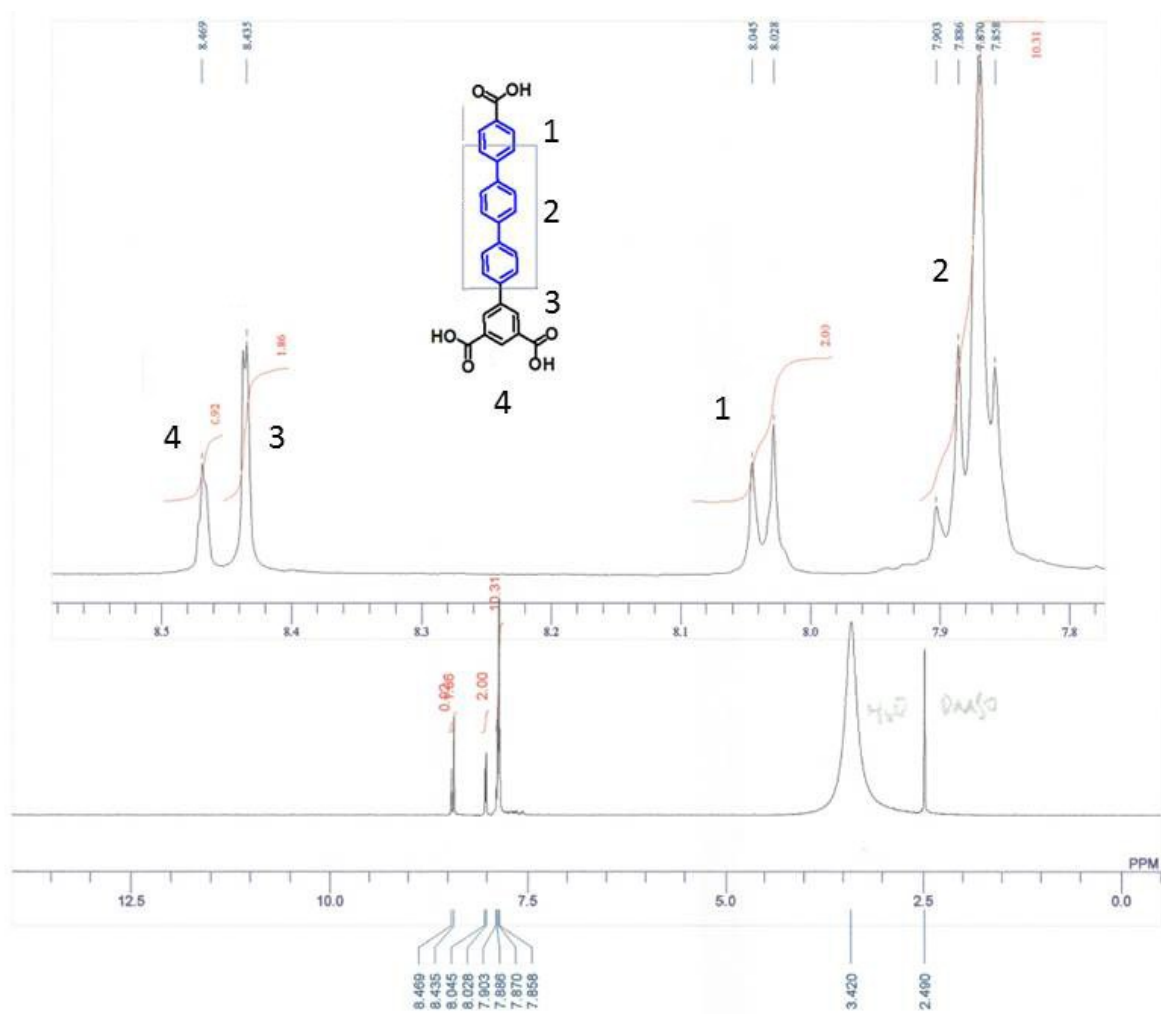


Figure S1 The ¹H NMR of Qu-H₃L

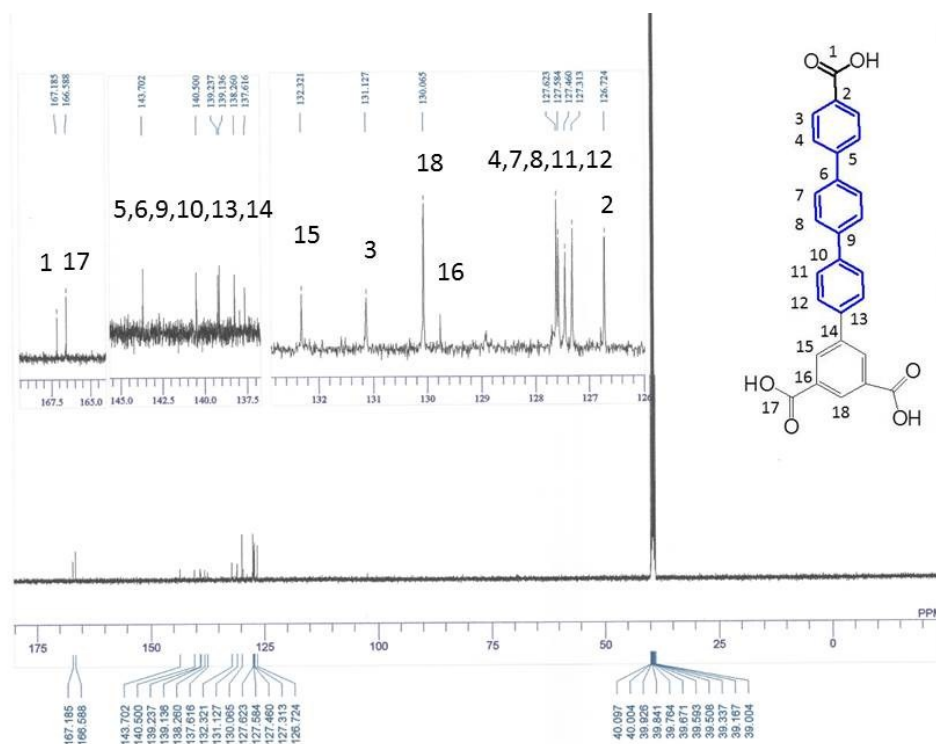


Figure S2 The ^{13}C NMR of Qu-H₃L

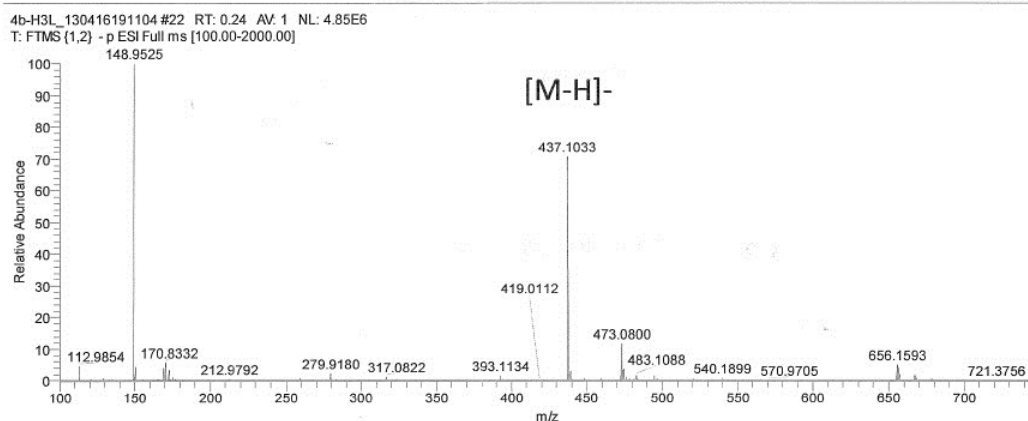
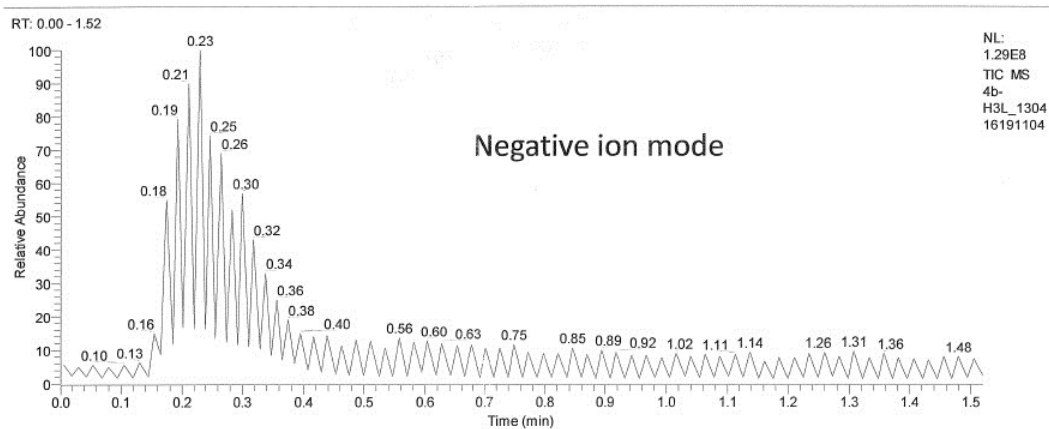


Figure S3 The Mass spectra of Qu-H₃L (The molecular weight of Qu-H₃L is 438)

Crystallographic Analyses

Single-crystal X-ray diffraction data were measured on a Bruker Smart Apex CCD diffractometer at 293 K using graphite monochromated Mo/K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction was made with the Bruker Saint program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package.² Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. The hydrogen atoms of the ligand and water molecules could not be located, but are included in the formula. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE^{3,4} to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; structures were then refined again using the data generated. CCDC 1400342-1400344 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Sample activation

For BET experiments, solvent-exchanged sample was prepared by immersing as-synthesized samples in fresh DMF (one day) for removing residual ligand and metal ions. Then, DMF was exchanged by dry EtOH for 3 days. The completely activated sample was obtained by heating EtOH-exchanged sample at 120 °C under a dynamic high vacuum for 48 hours.

For sensing experiments: EtOH exchanged samples were then soaked in Hexane for 3 day. The extraction was decanted every 10 hours and fresh Hexane was replaced. The hexane exchanged samples were used for sensing benzene derivatives.

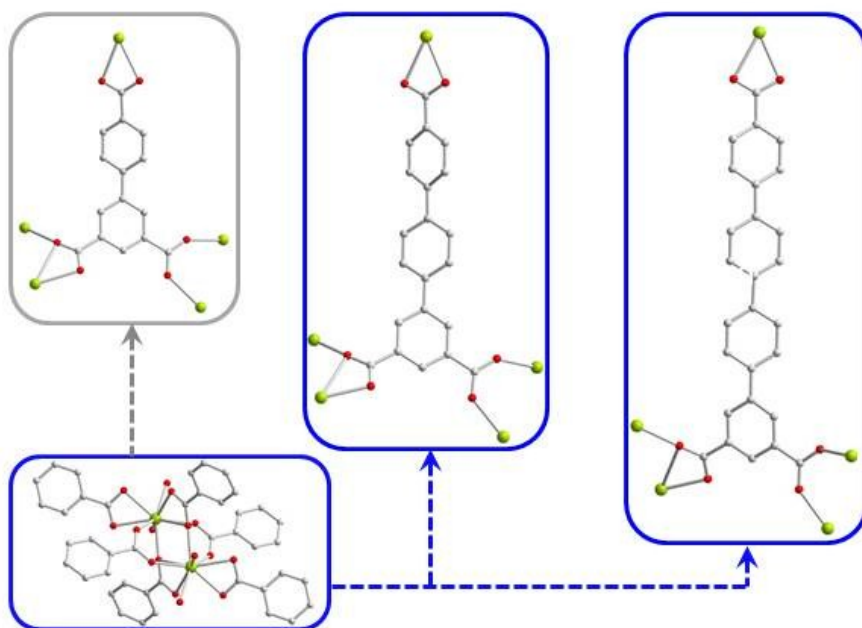


Figure S4 The connections of involved ligands and Ln-Ln clusters in La(Bi-L) and NTU-5 to NTU-10.

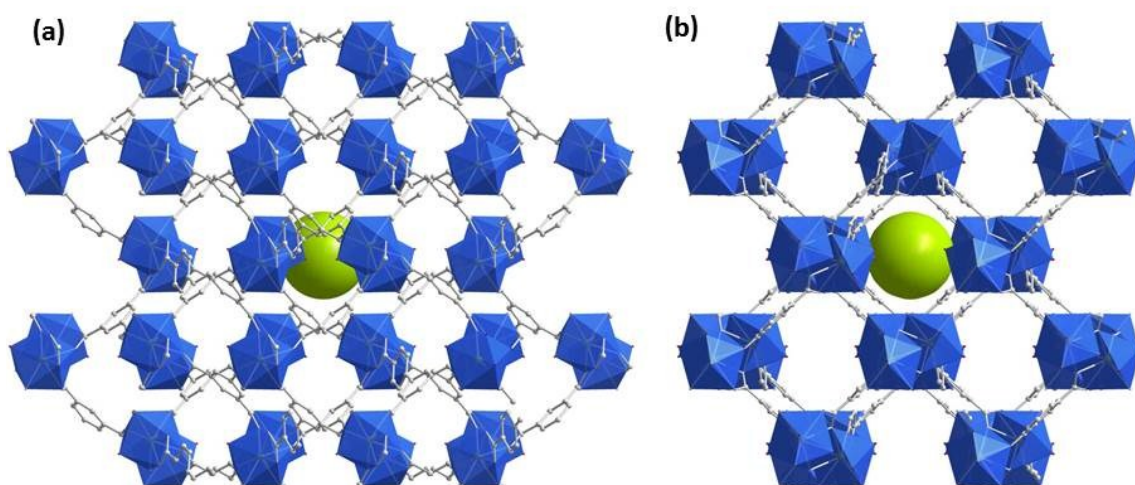


Figure S5 Packing view of La(Bi-L) along a axis (a) and its 1D quadrilateral nanotube (b).

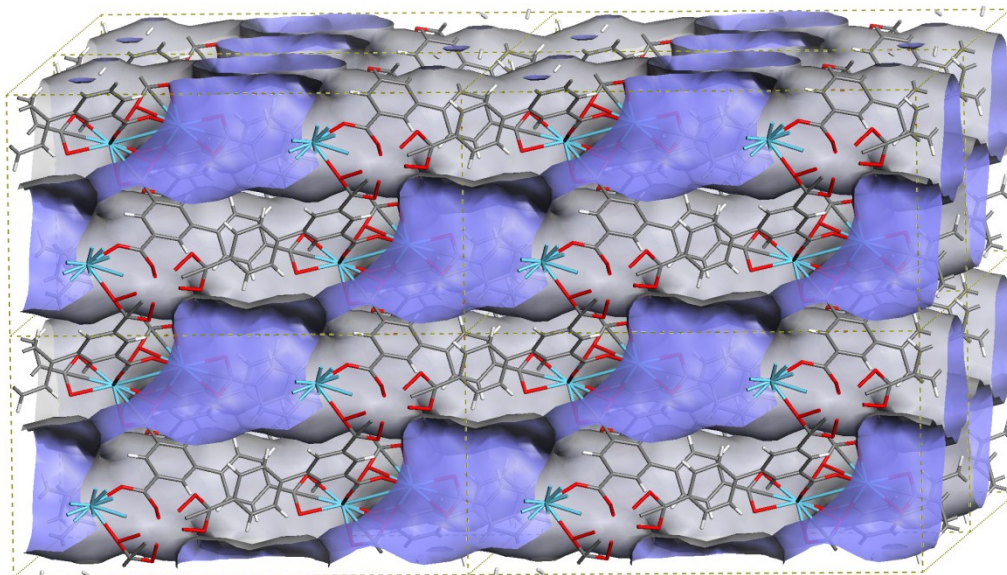


Figure S6 The Connolly surface diagram showing uniform channels in La(Bi-L) (Inner surfaces: purple, outer surfaces: grey).

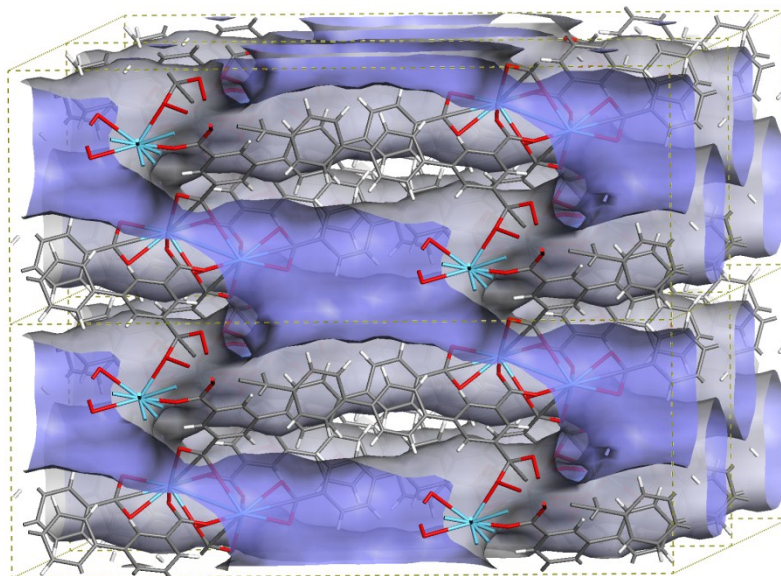


Figure S7 The Connolly surface diagram showing uniform channels in NTU-6 (Inner surfaces: purple, outer surfaces: grey).

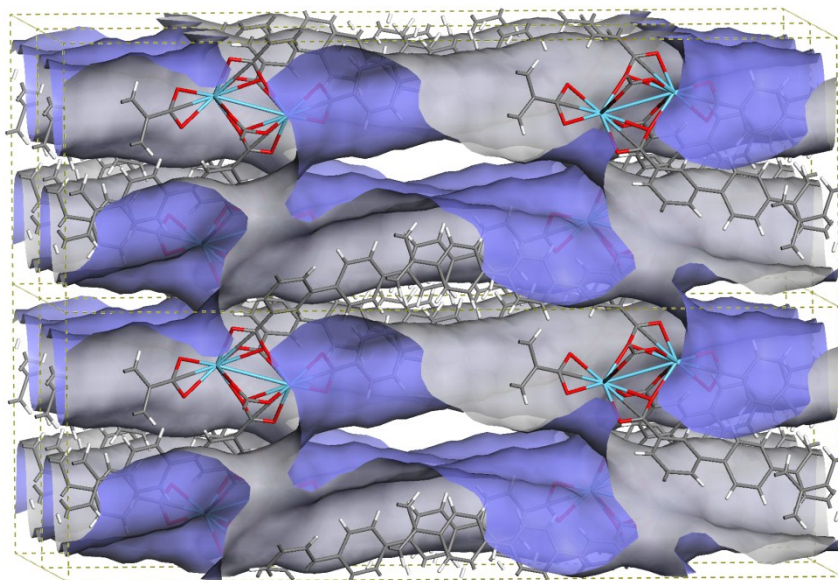


Figure S8 The Connolly surface diagram showing uniform channels in NTU-9. (Inner surfaces: purple, outer surfaces: grey).

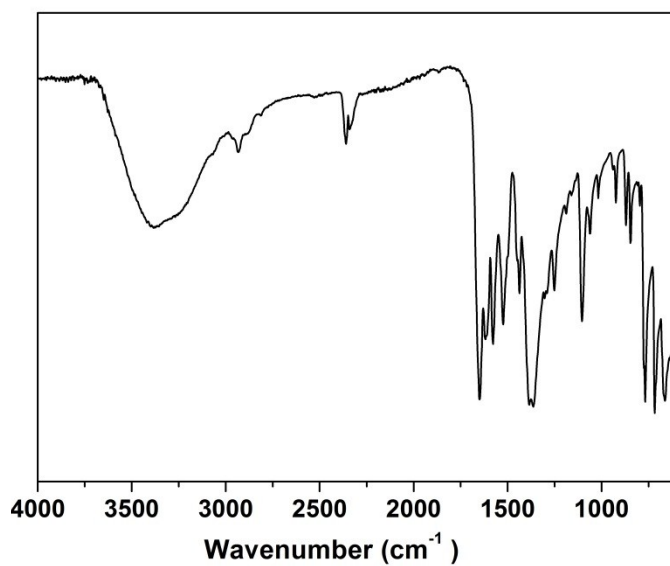


Figure S9 IR of La(Bi-L).

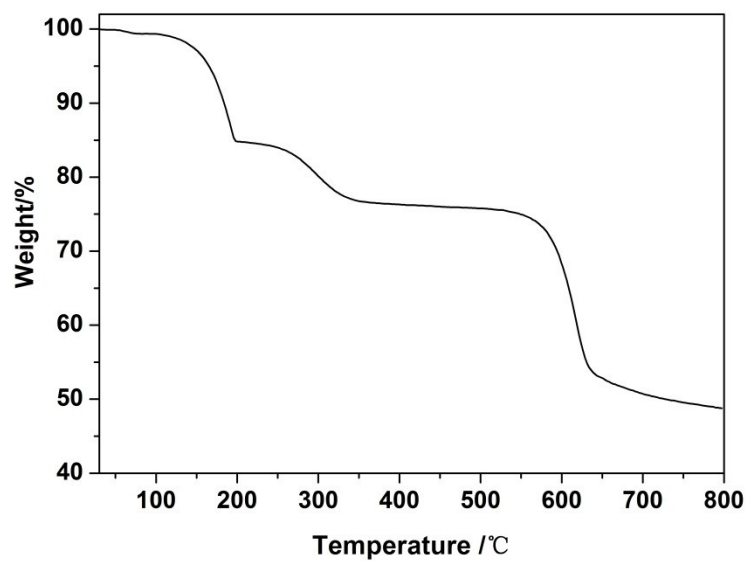


Figure S10 TG of La(Bi-L).

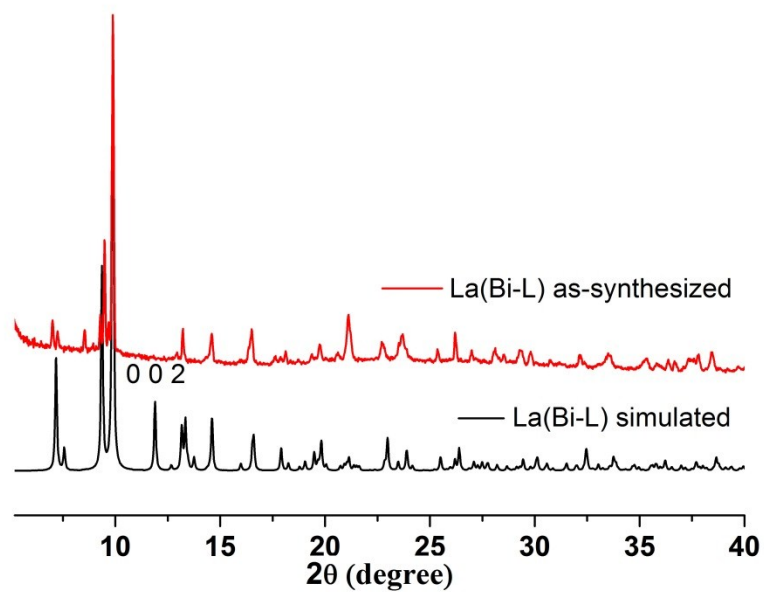


Figure S11 PXRD of La(Bi-L). Not preferred orientation of crystal growth result in peak absence at (0 0 2) crystal surface.

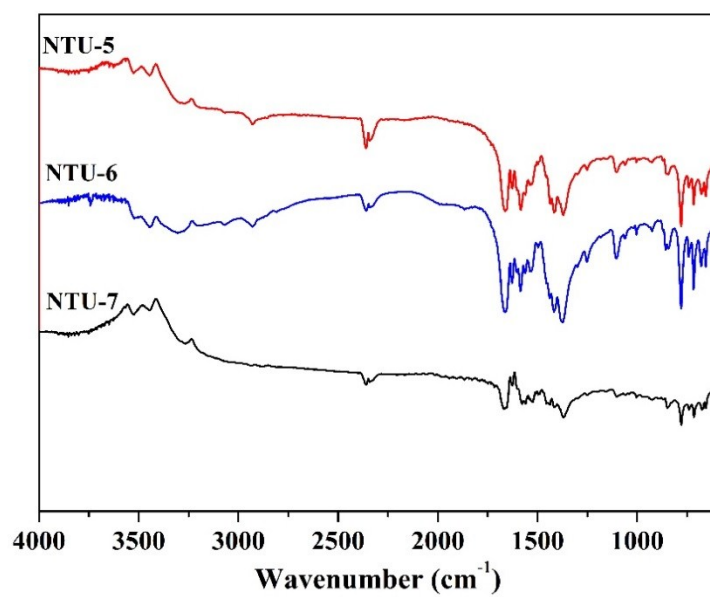


Figure S12 IR of NTU-5, NTU-6 and NTU-7.

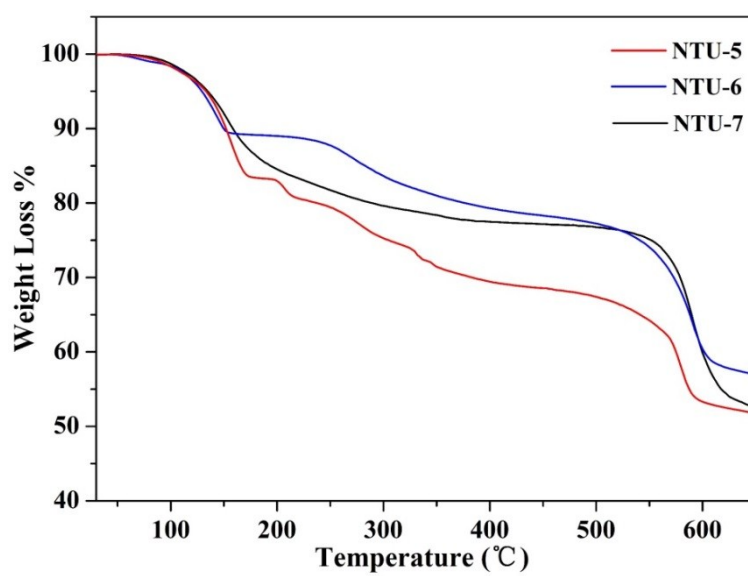


Figure S13 TG of NTU-5, NTU-6 and NTU-7

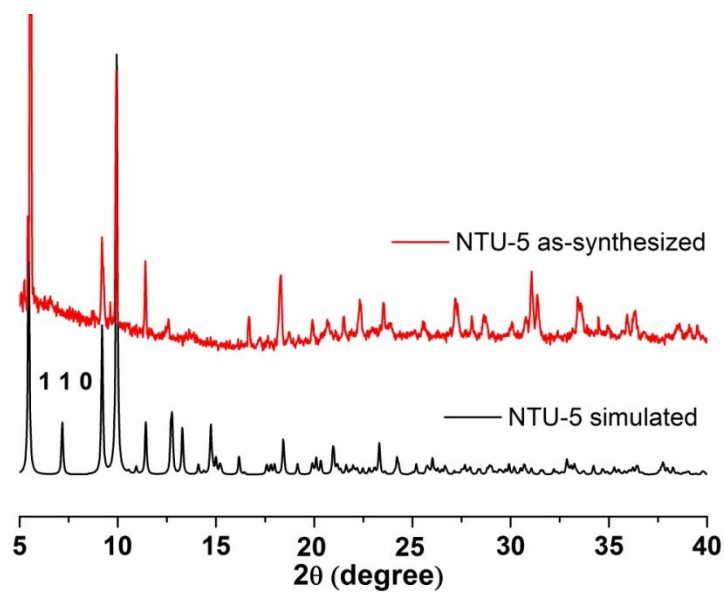


Figure S14 PXRD of NTU-5. Not preferred orientation of crystal growth result in peak absence at (1 1 0) crystal surface.

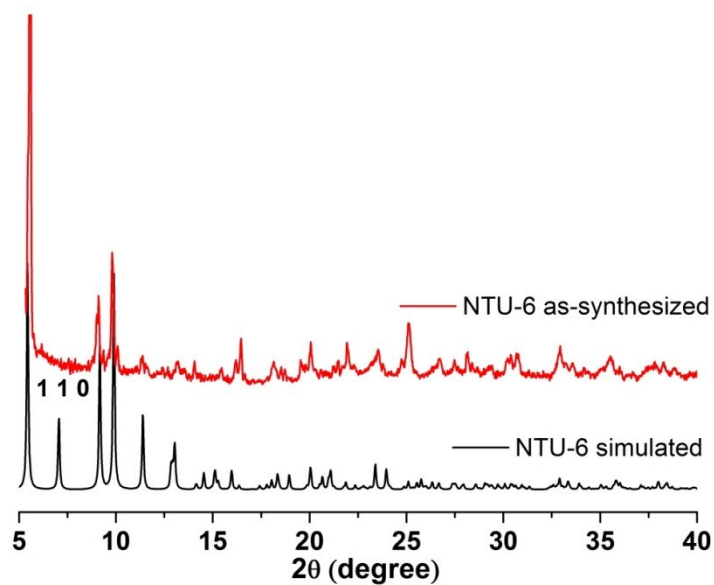


Figure S15 PXRD of NTU-6. Not preferred orientation of crystal growth result in peak absence at (1 1 0) crystal surface.

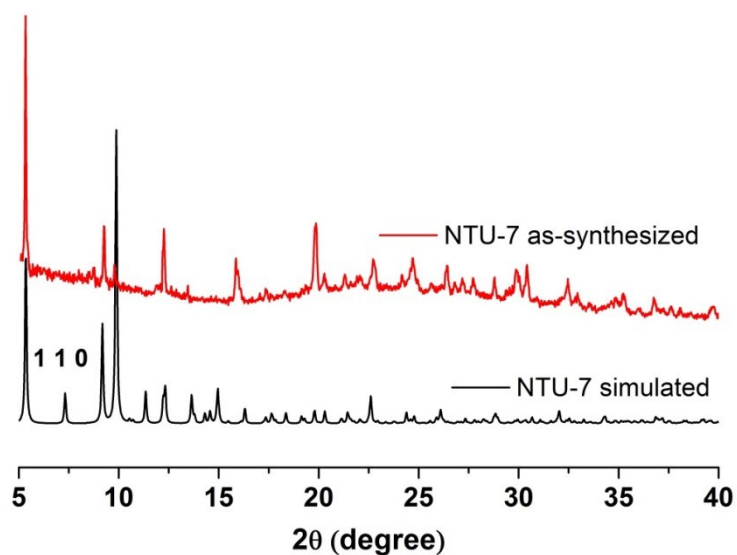


Figure S16 PXR D of NTU-7. Not preferred orientation of crystal growth result in peak absence at (1 1 0) crystal surface.

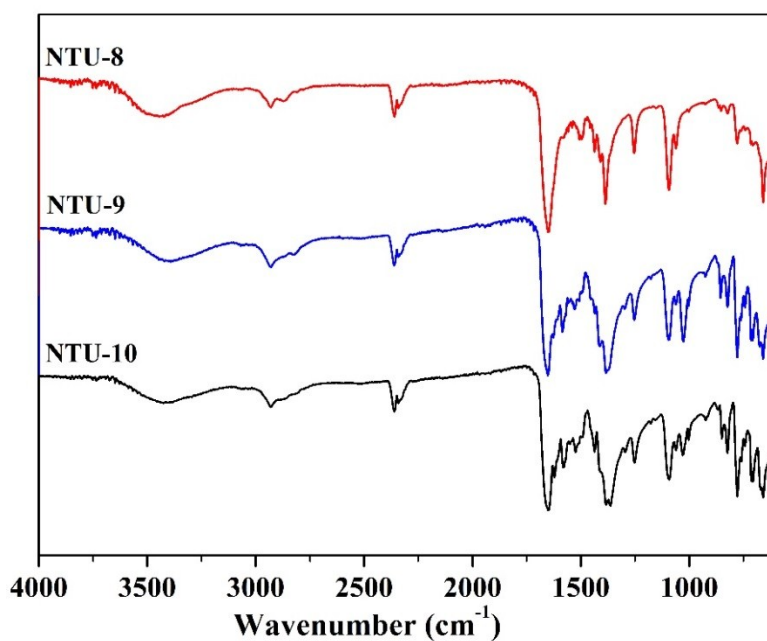


Figure S17 IR of NTU-8, NTU-9 and NTU-10.

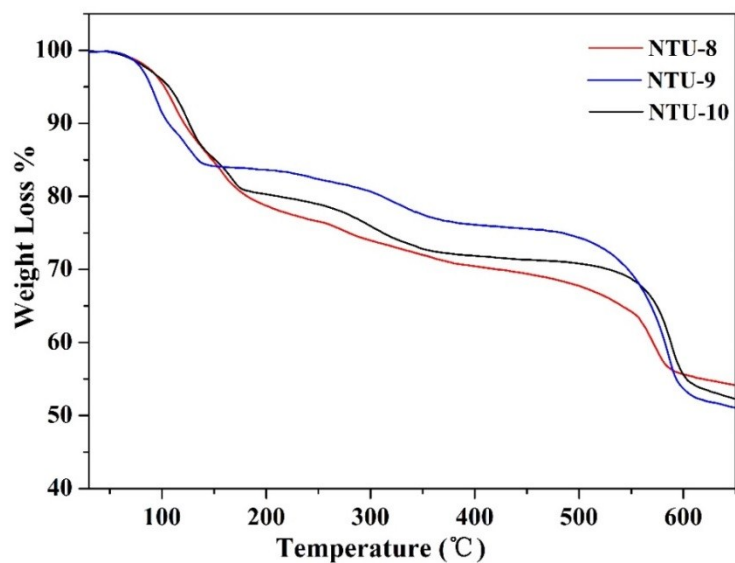


Figure S18 TG of NTU-5, NTU-6 and NTU-7

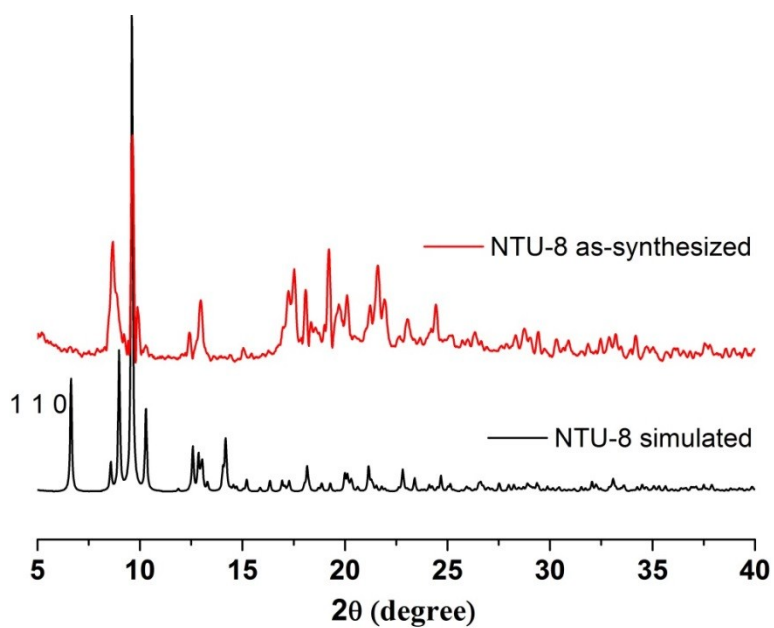


Figure S19 PXRD of NTU-8. Not preferred orientation of crystal growth result in peak absence at (1 1 0) crystal surface.

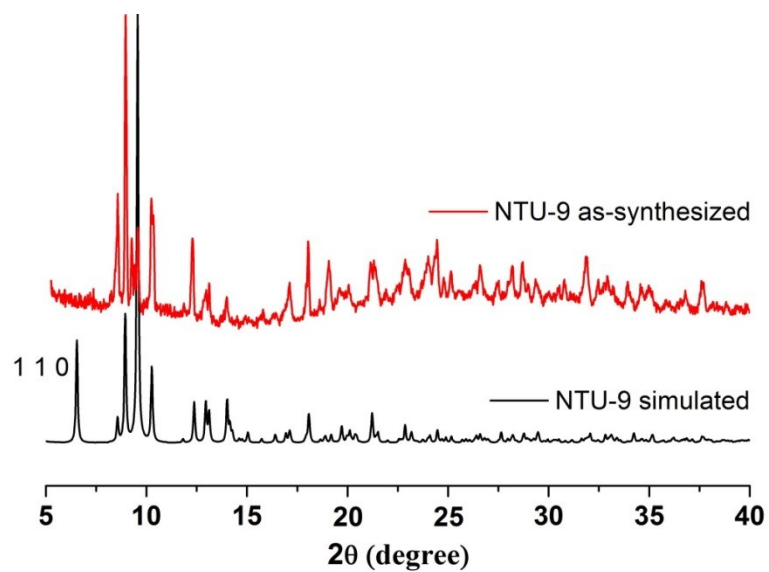


Figure S20 PXRD of NTU-9. Not preferred orientation of crystal growth result in peak absence at (1 1 0) crystal surface.

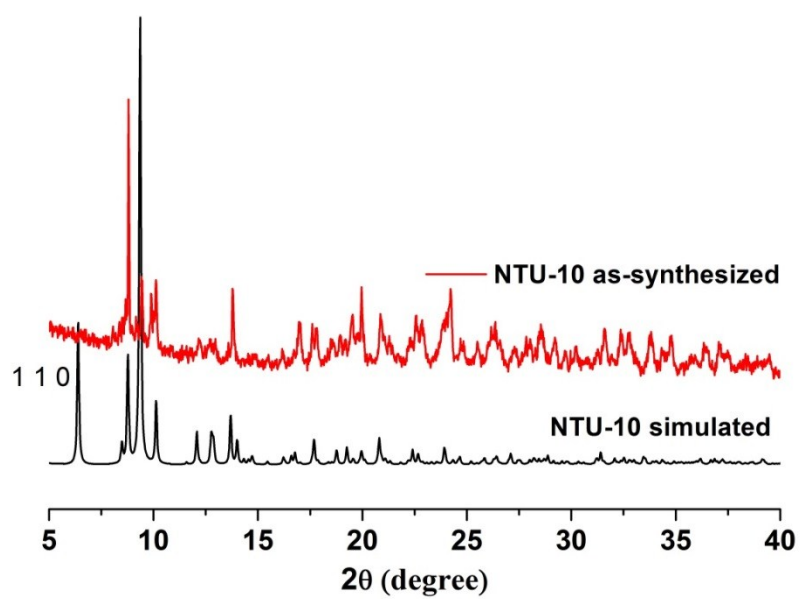


Figure S21 PXRD of NTU-10. Not preferred orientation of crystal growth result in peak absence at (1 1 0) crystal surface.

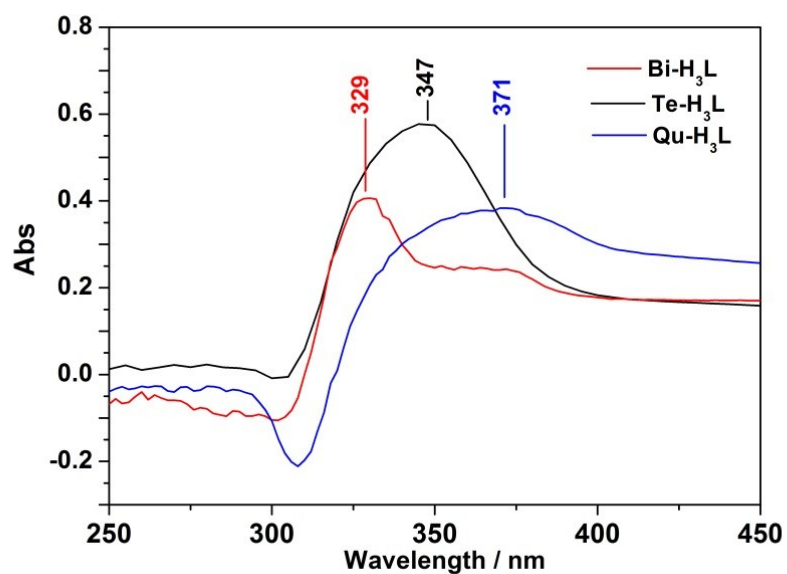


Figure S22 UV absorption spectra of three ligands at solid state.

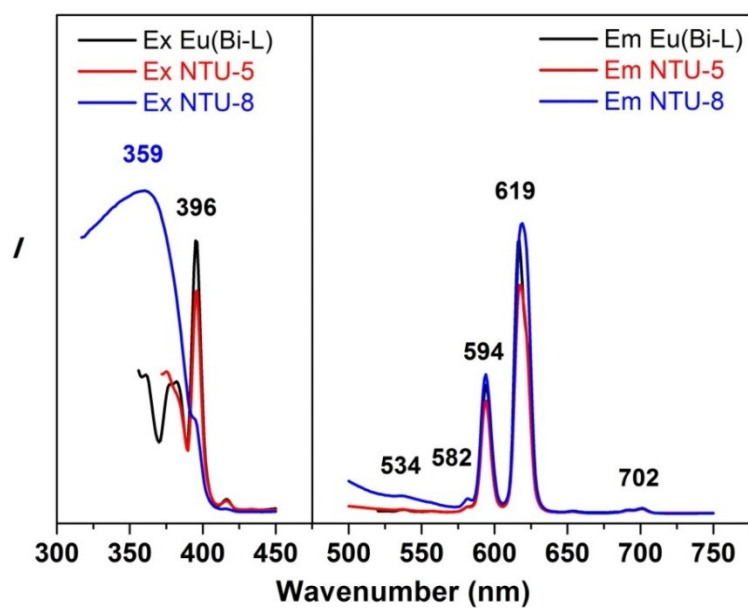


Figure S23 Luminescent spectra of Eu(Bi-L), NTU-5 and NTU-8 in solid state at room temperature

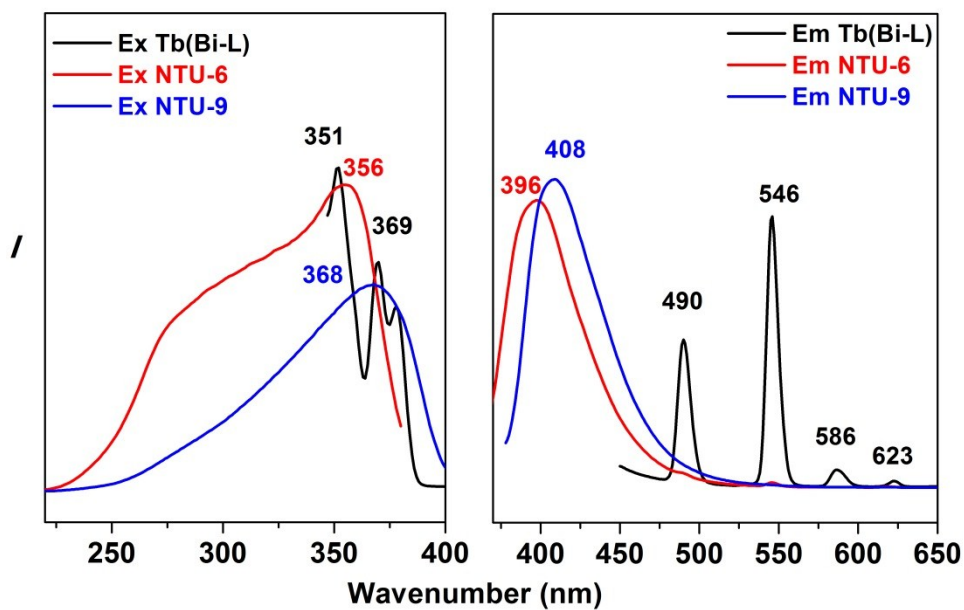


Figure S24 Luminescent spectra of Tb(Bi-L), NTU-6 and NTU-9 in solid state at room temperature.

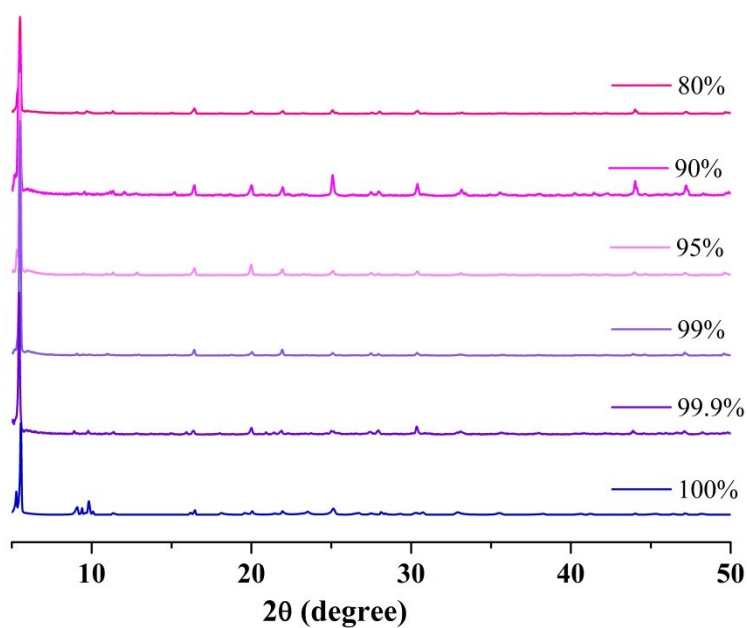


Figure S25 PXRD patterns of series Eu/Tb(Te-L) with varied molar ratio of Eu/Tb ions.

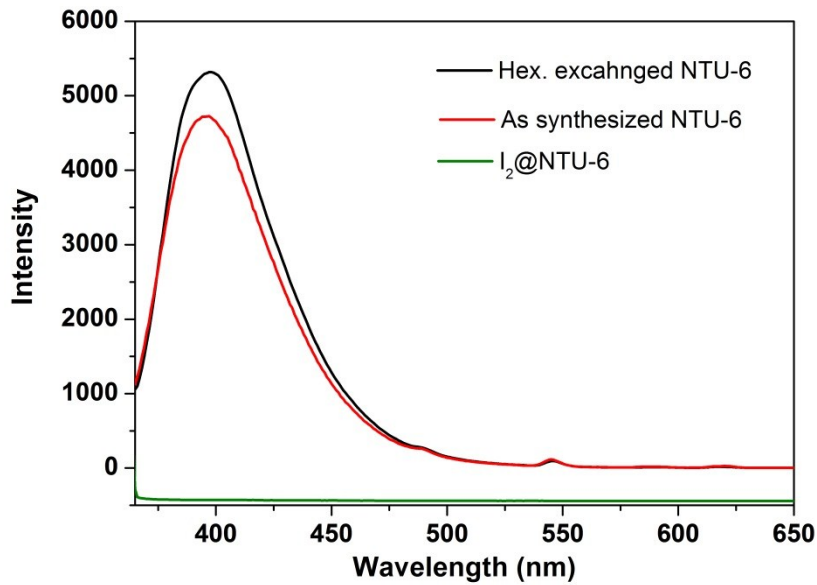


Figure S26 Luminescent spectra of hexane exchanged NTU-6, as synthesized NTU-6 and I₂@NTU-6 in solid state at room temperature.

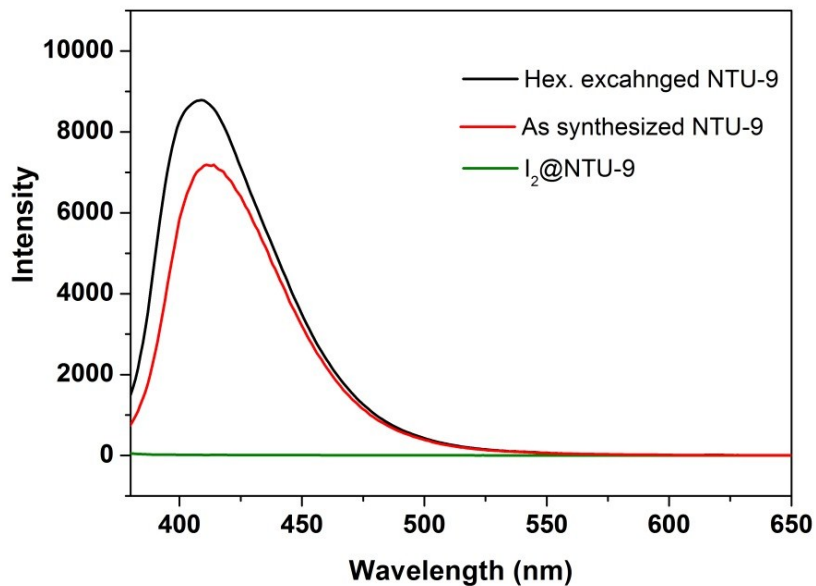


Figure S27 Luminescent spectra of hexane exchanged NTU-9, as synthesized NTU-9 and I₂@NTU-9 in solid state at room temperature.

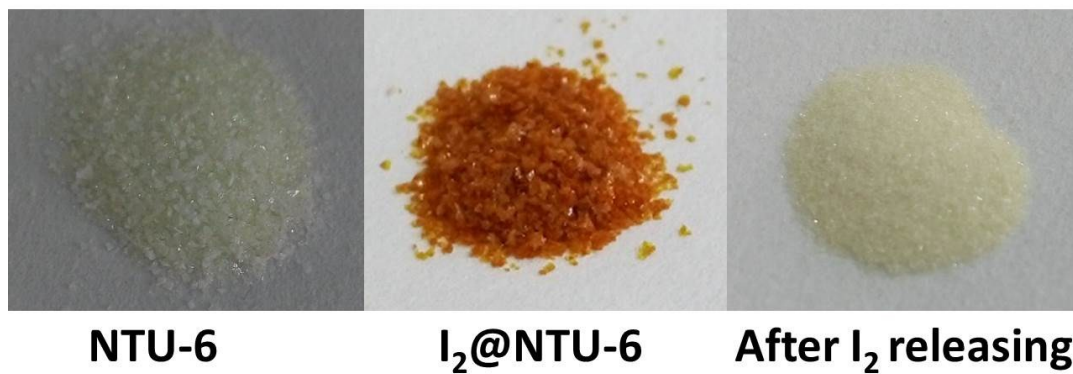


Figure S28 Color change of NTU-6 crystals before and after I₂ releasing.

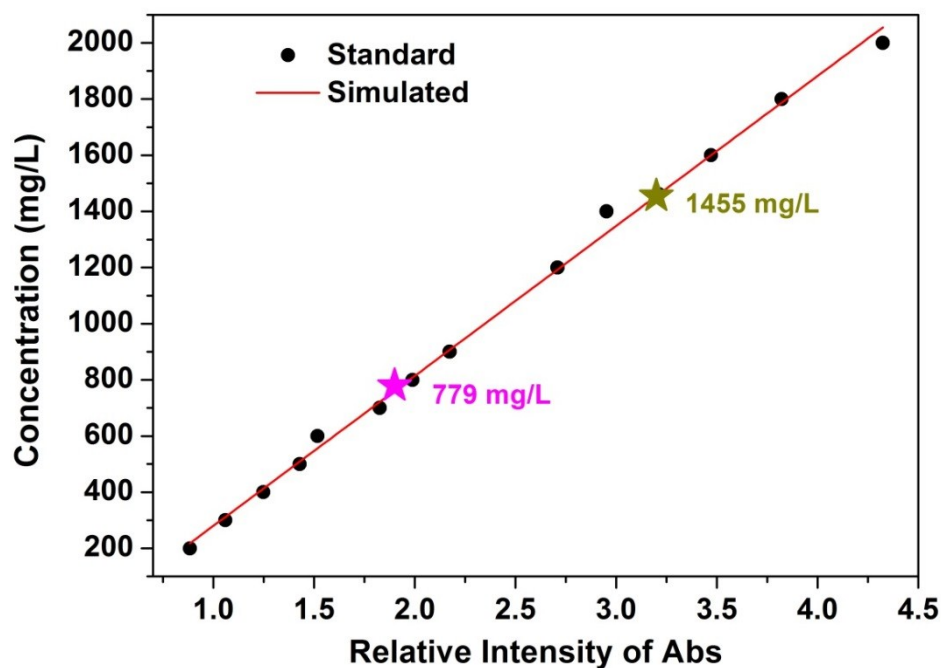


Figure S29 The standard line of I₂ ethanol show very good fitness. I₂@NTU-6 (20 mg) and I₂@NTU-9 (14 mg) were soaked into 2 mL and 2.5 mL ethanol, respectively. About 1h later, we checked the UV-spectrum of the solution only. The intensity of the 290 nm peak locates on the standard line: yellow star for NTU-6 and red purple for NTU-9.

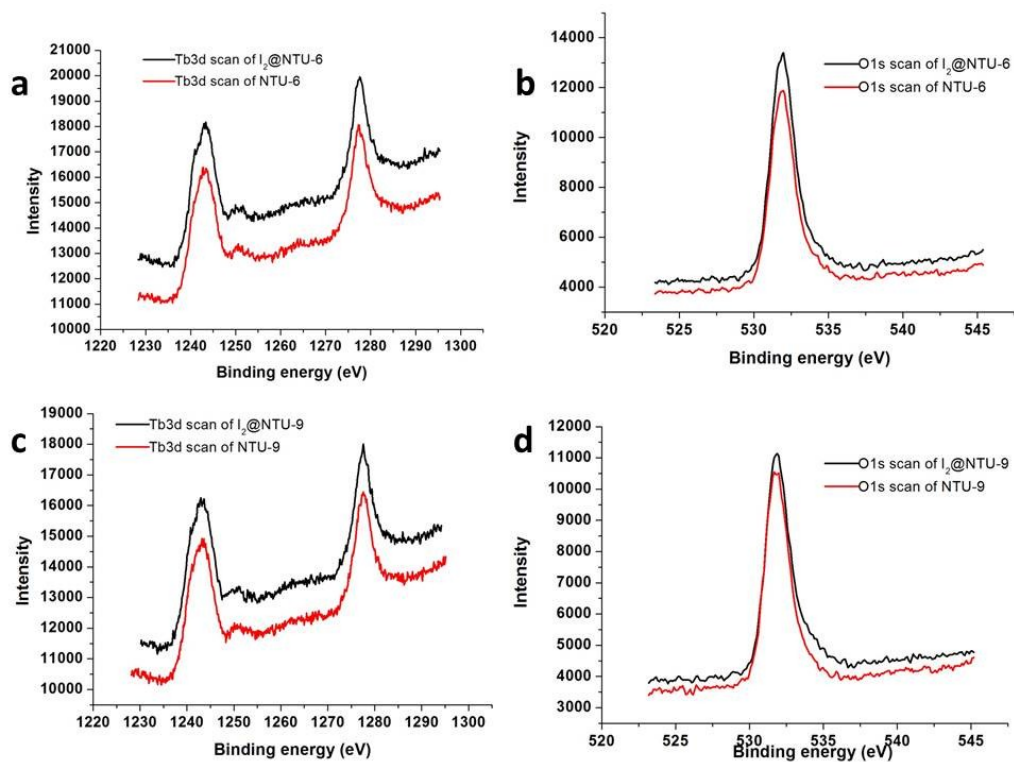


Figure S30 Comparison of XPS of Tb3d and O1s in NTU-6, NTU-9 and their iodine encapsulated phases.

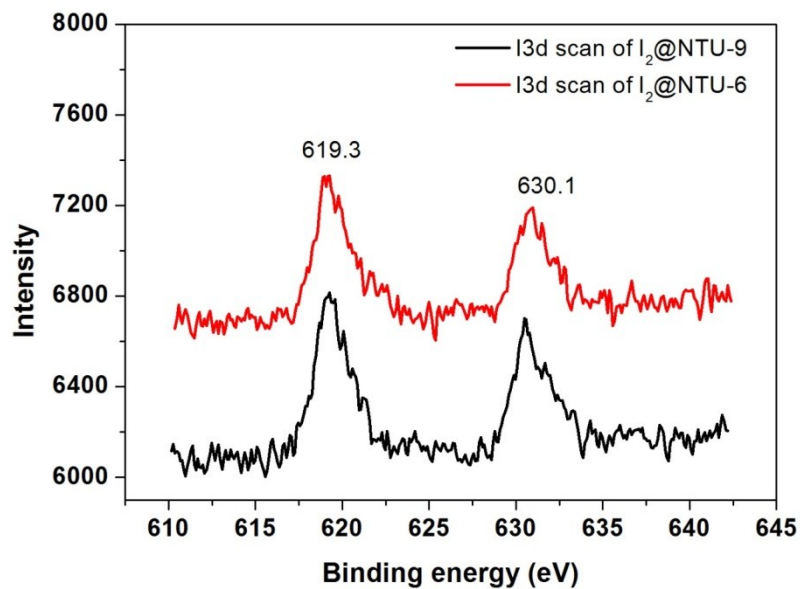


Figure S31 XPS spectrum of I3d scan of I₂@NTU-6 and I₂@NTU-9.

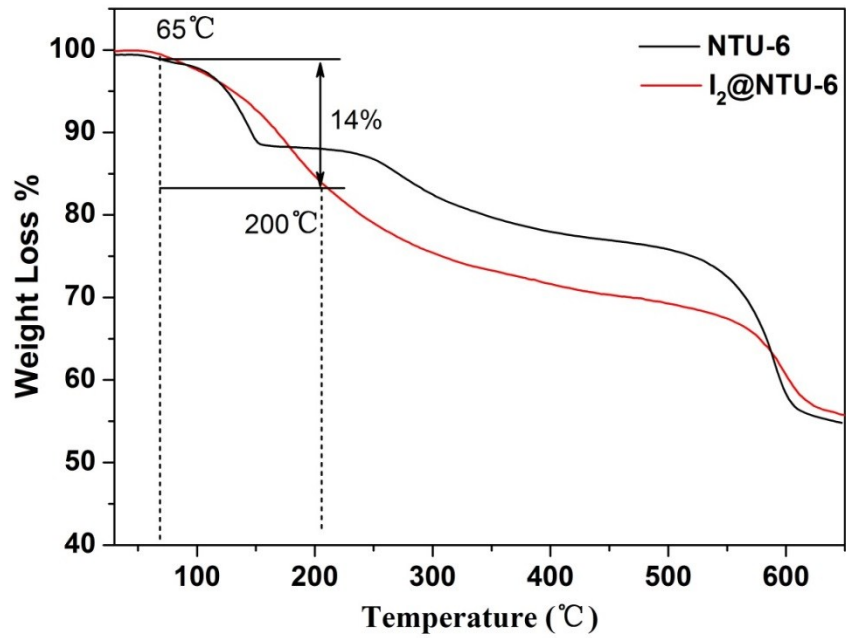


Figure S32 TG of I₂@NTU-6

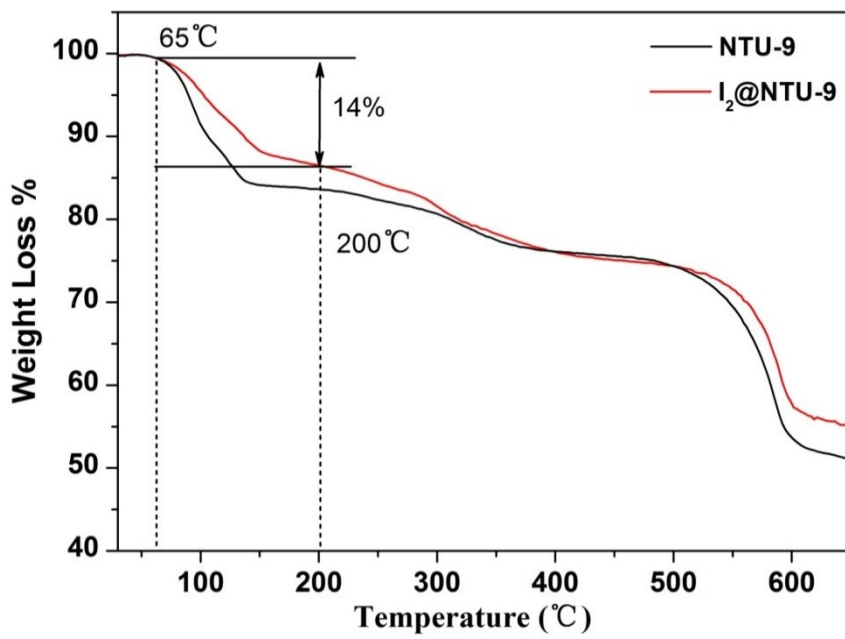


Figure S33 TG of I₂@NTU-9

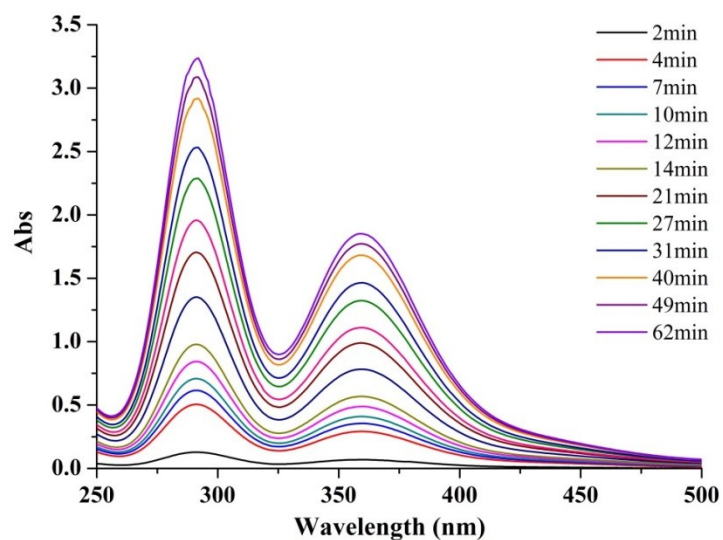


Figure S34 UV spectra of I_2 releasing from $I_2@NTU-5$ (20 mg in 2.0 mL EtOH).

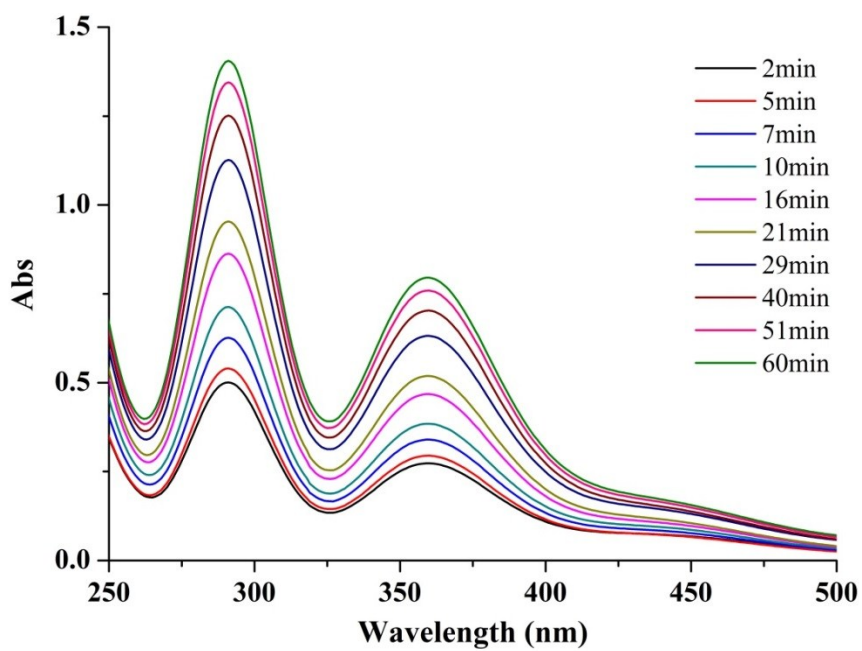


Figure S35 UV spectra of I_2 releasing from $I_2@NTU-7$ (10 mg in 2.5 mL EtOH).

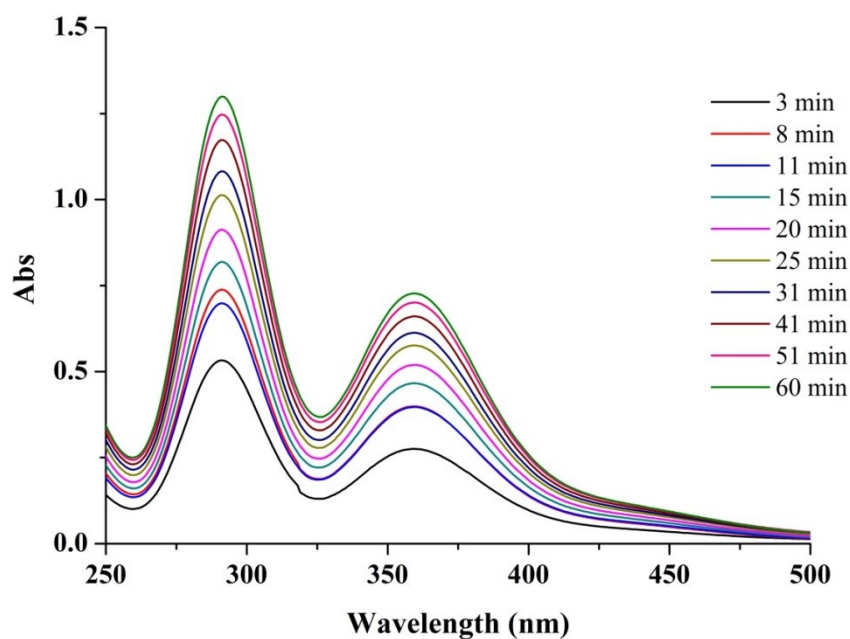


Figure S36 UV spectra of I_2 releasing from $I_2@NTU-8$ (10 mg in 2.5 mL EtOH).

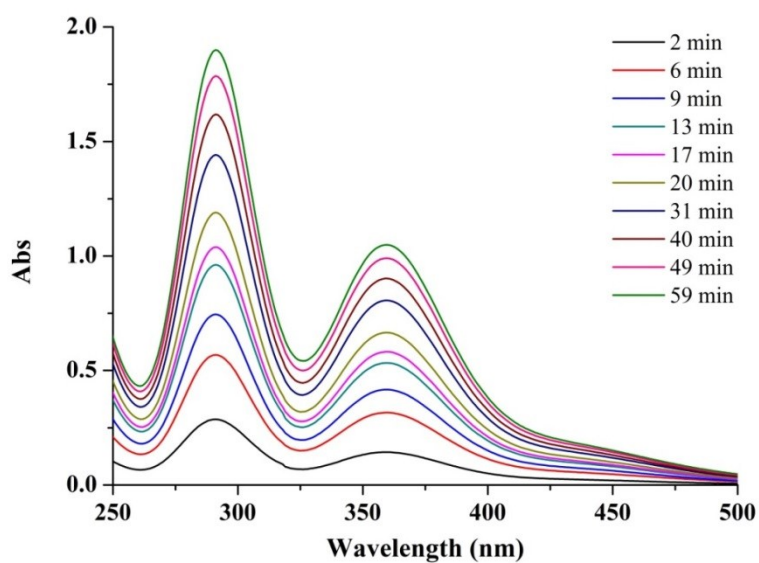


Figure S37 UV spectra of I_2 releasing from $I_2@NTU-10$ (13 mg in 2.5 mL EtOH).

References

- (1) Duan, J. G.; Higuchi, M.; Kitagawa, S. *Inorg. Chem.* **2015**, *54*, 1645.
- (2) Sheldrick, G. M. *Acta Crystallogr. Sec. A* **2008**, *64*, 112.
- (3) Vandersluis, P.; Spek, A. L. *Acta Crystallogr. Sec. A* **1990**, *46*, 194.
- (4) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.