Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information:

Semi-conductive helical homochiral metal−organic frameworks based on enantiomeric proline derivatives

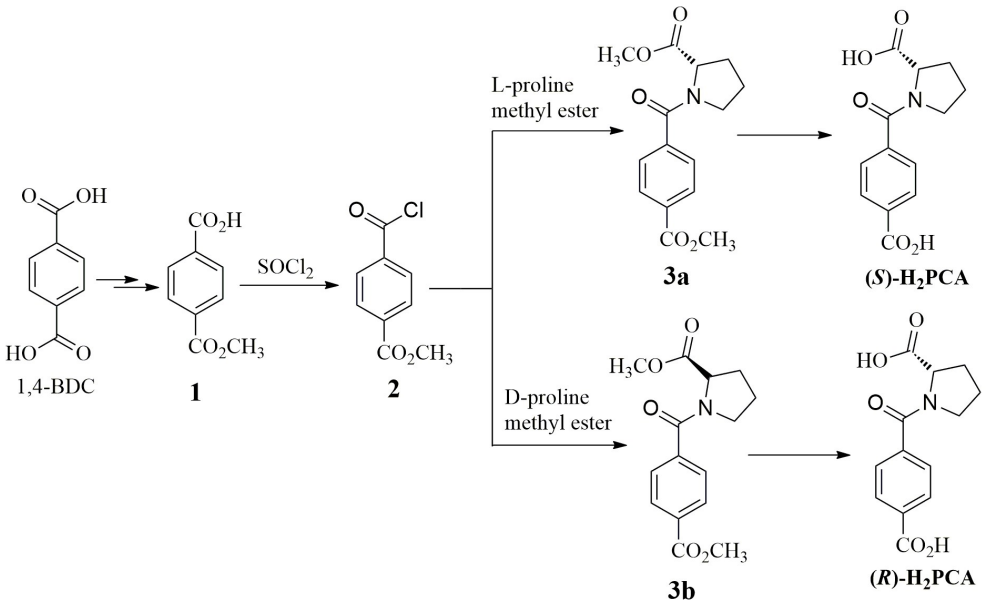
Yu-Lu Ma,[b] Qin Meng[a] and Zhong-Xuan Xu*[a]

[a]School of chemistry and chemical engineering, Zunyi Normal College, Zunyi, Guizhou 563002, P.R China

[b]School of Pharmaceutical Sciences and Yunnan Key Laboratory of Pharmacology for Natural Products, Kunming Medical University, Kunming, 650500, P.R China.

E-mail: xuzhongxuan4201@163.com

1. Synthesis of (*S*)-H_2PCA and (*R*)-H_2PCA



Scheme S1. Synthetic routes to the compounds (*S*)-H_2PCA and (*R*)-H_2PCA

1.1 Synthesis of methyl 1-(4-(methoxycarbonyl)benzoyl)pyrrolidine-2-carboxylate (**3**)

Compound 1 (1.8g, 10mmol), freshly distilled $SOCl_2$ (20 mL) and dimethyl-formamide (0.1 mL) were added in a round-bottomed flask under a nitrogen atmosphere. After the reaction mixture was heated at 90 °C for three hours, the excess $SOCl_2$ was removed under in vacuo, giving compound 2 as a colorless liquid. Compound 2 in dry CH_2Cl_2 (15 mL) was added dropwise into a solution of methyl ester of L-proline or D-proline (1.6 g, 12 mmol) in the dry CH_2Cl_2 (50 mL) and triethylamine (2.2 g, 22 mmol) under a nitrogen atmosphere and ice-water bath. The reaction mixture was washed with 1.0 M HCl (2 × 150 mL) and saturated NaCl (2 × 15 mL), then dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue was purified by flash column chromatography (EtOAc: petroleum ether = 1:2) to give compound **3** as a white solid (2g, 68%). ^{1}HNMR (400 MHz, CDCl3), δ (ppm): 8.11−8.06 (2H, d), 7.65−7.63 (2H, d), 3.94 (3H, s), 3.79 (3H, s),

3.65−3.61 (1H, m), 3.52−3.46 (1H, m), 2.35−2.33(1H, m), 2.01−1.90(3H, m), ^{13}C NMR (100 MHz, $CDCl_3$), δ(ppm): 172.46, 168.97, 165.49, 140.46, 131.75, 129.86, 127.45, 58.83, 52.40, 49.52, 29.36, 24.78; LRSM (ESI): Mass calcd for $C_{15}H_{17}NO_5$ $[M+H]^+$, 292.3; found 292.3.

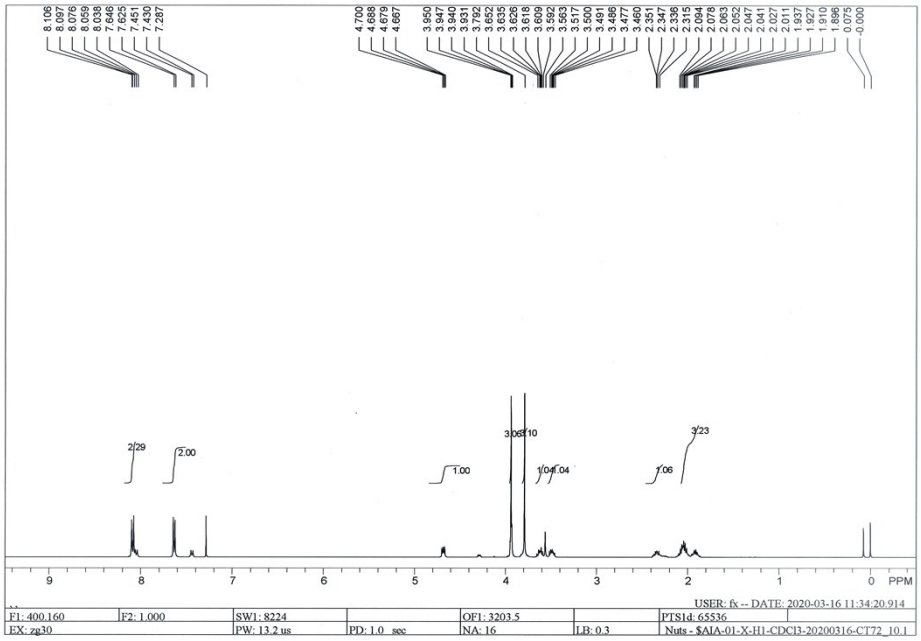


Figure S1. ^{1}HNMR of compound **3** in $CDCl_3$

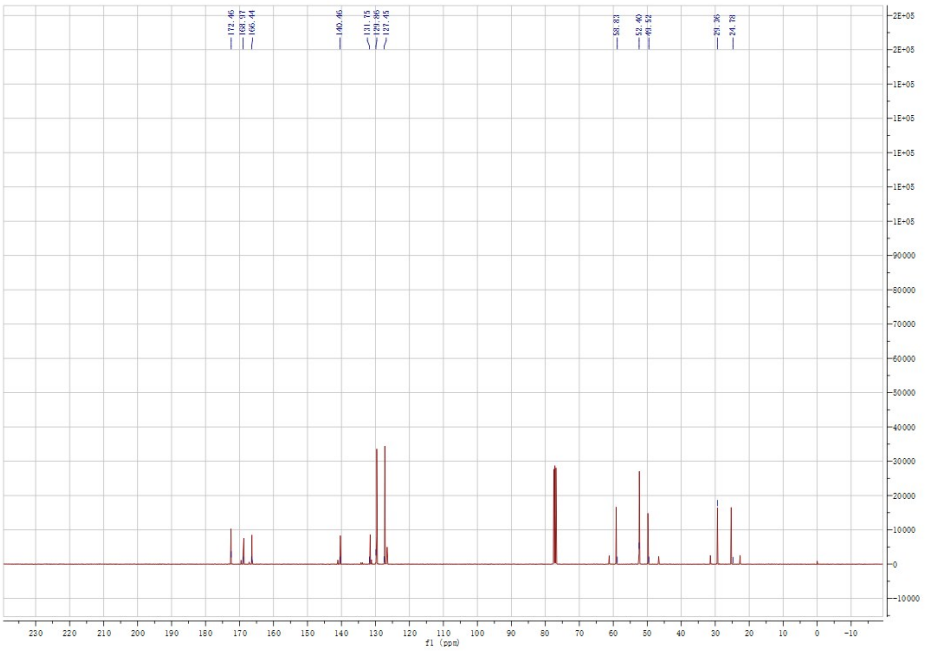
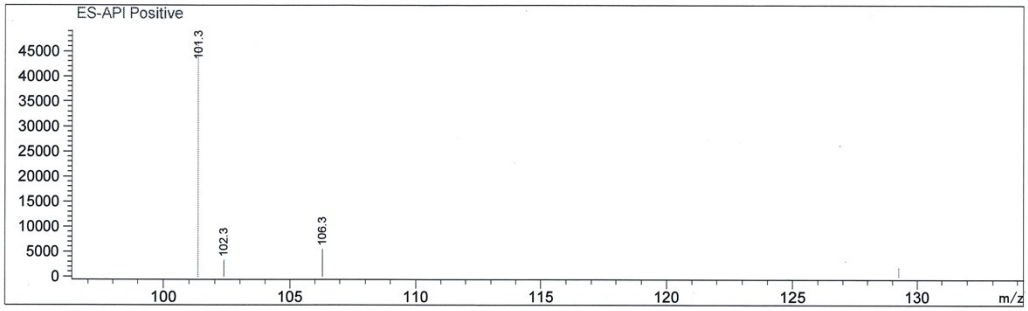


Figure S2. ^{13}CNMR of compound **3** in $CDCl_3$

Ret. Time: 1.69 <<<< POSITIVE SPECTRA >>>>



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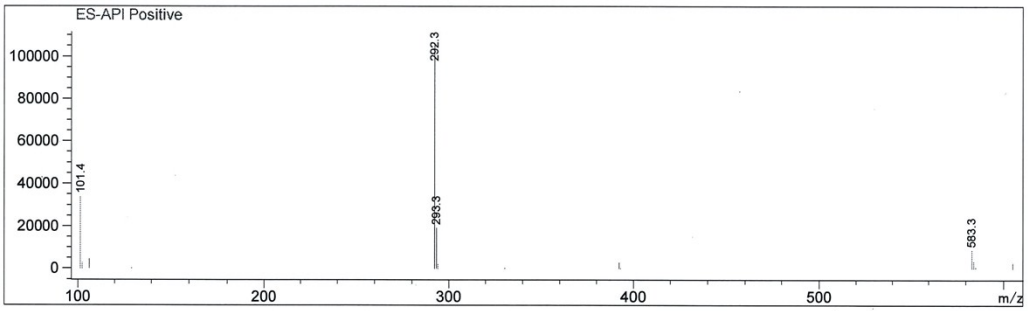

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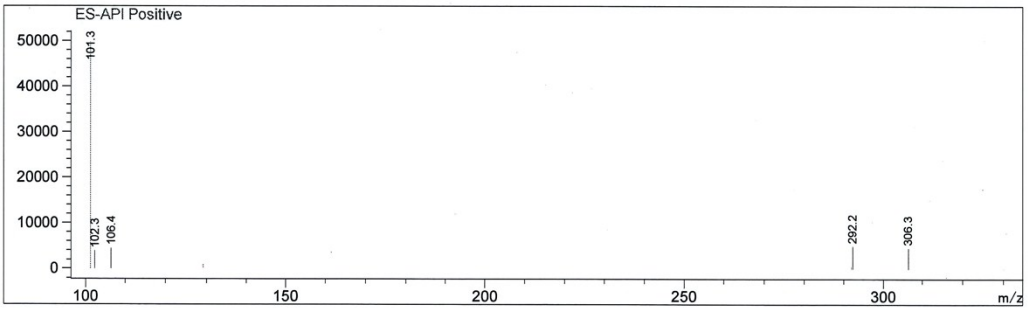

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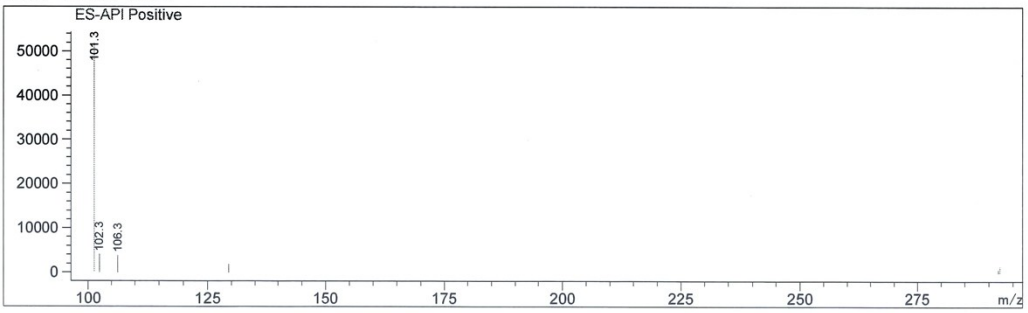

Figure S3. The LRSM of compound **3**

1.2 Synthesis of (*S*)-H_2PCA and (*R*)-H_2PCA

Compound **3** (1.45g, 5mmol), CH_3OH (10 mL), H_2O (20 mL) and sodium hydroxide (0.8 g, 20 mmol) were added to a 50mL flask with a stirring bar. After the reaction mixture was stirred and heated at 50 °C for 6 h, the result solution was slowly acidified to pH 1−2 in an ice bath. The (*S*)-H_2PCA ((*R*)-H_2PCA) was obtained as a white solid: ^{1}H NMR (400 MHz, CD_3OD), δ (ppm): 8.12−8.10 (2H, d), 7.67−7.65 (2H, d), 4.61−4.58 (2H, q), 3.61−3.50 (2H, m), 2.41−2.38 (1H, m), 2.01−1.90 (3H, m), ^{13}C NMR (100 MHz, CD_3OD), δ(ppm): 173.25, 167.72, 167.06, 140.72, 132.57, 129.79, 127.64, 59.12, 49.51, 29.42, 25.07; LRSM (ESI): Mass calcd for $C_{13}H_{13}NO_5$ $[M+H]^+$, 264.3; found 264.3.

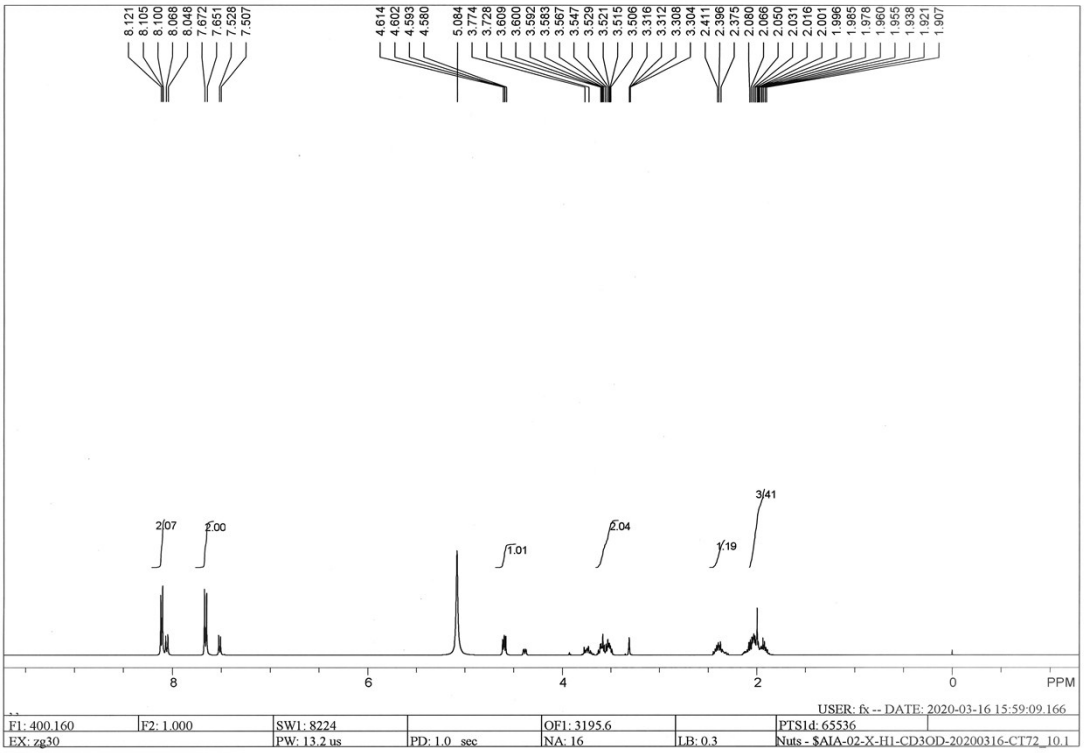

Figure S4. ^{1}H NMR of H_2PCA in CD_3OD

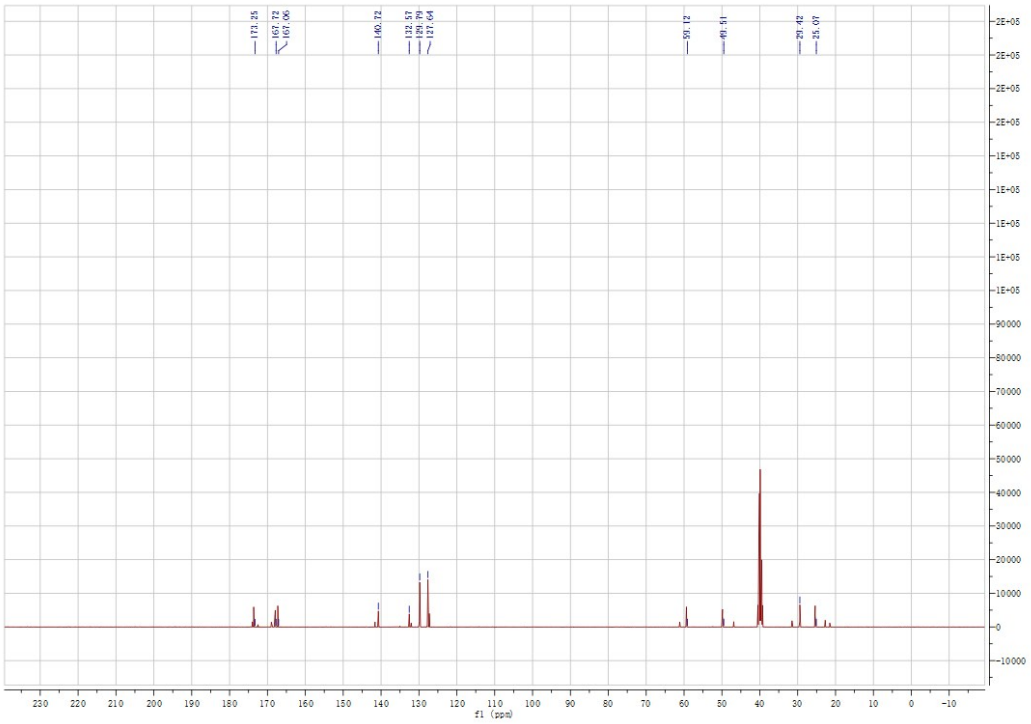

Figure S5. ^{13}C NMR of H_2PCA in CD_3OD

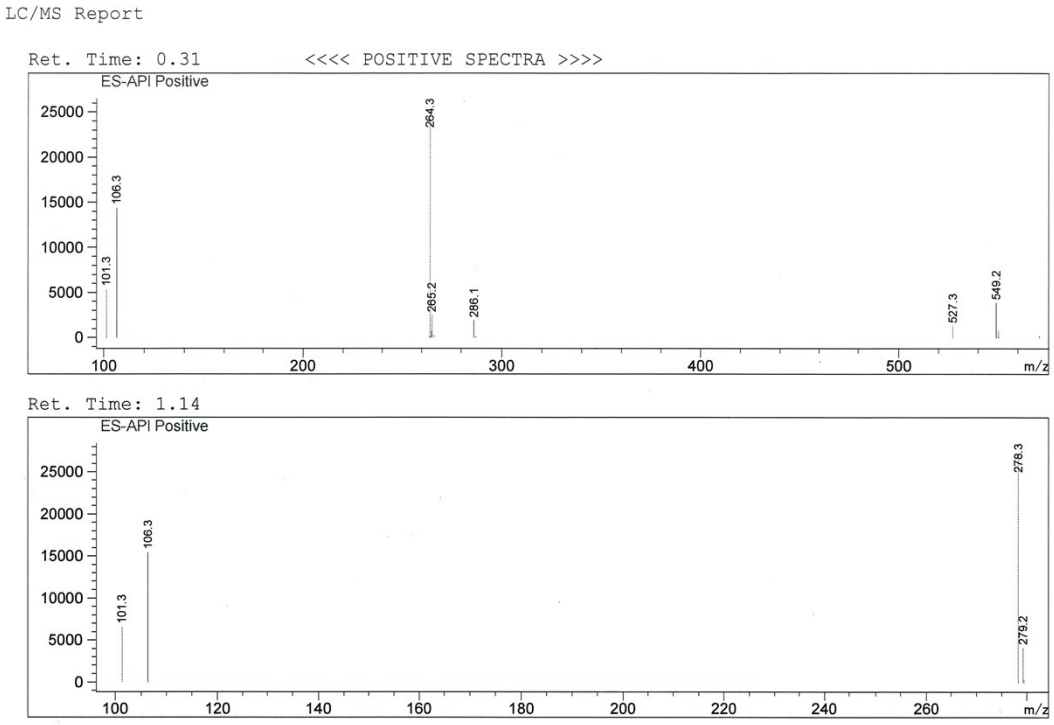

Figure S6. The LRMS of H_2PCA

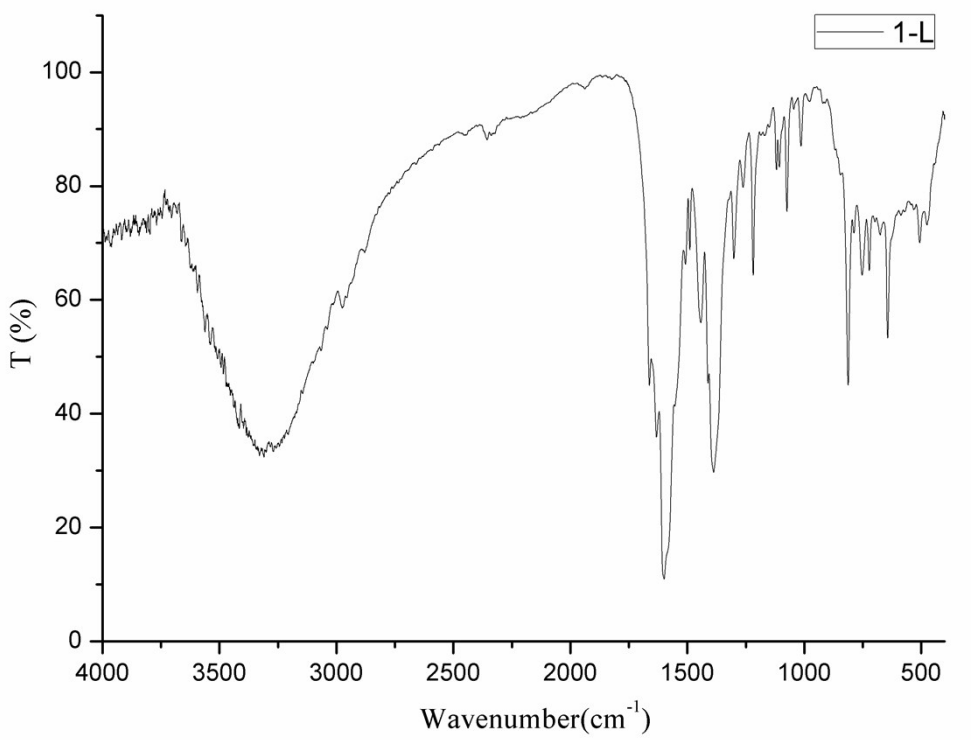

Figure S7. The IR spectra of **1-L**

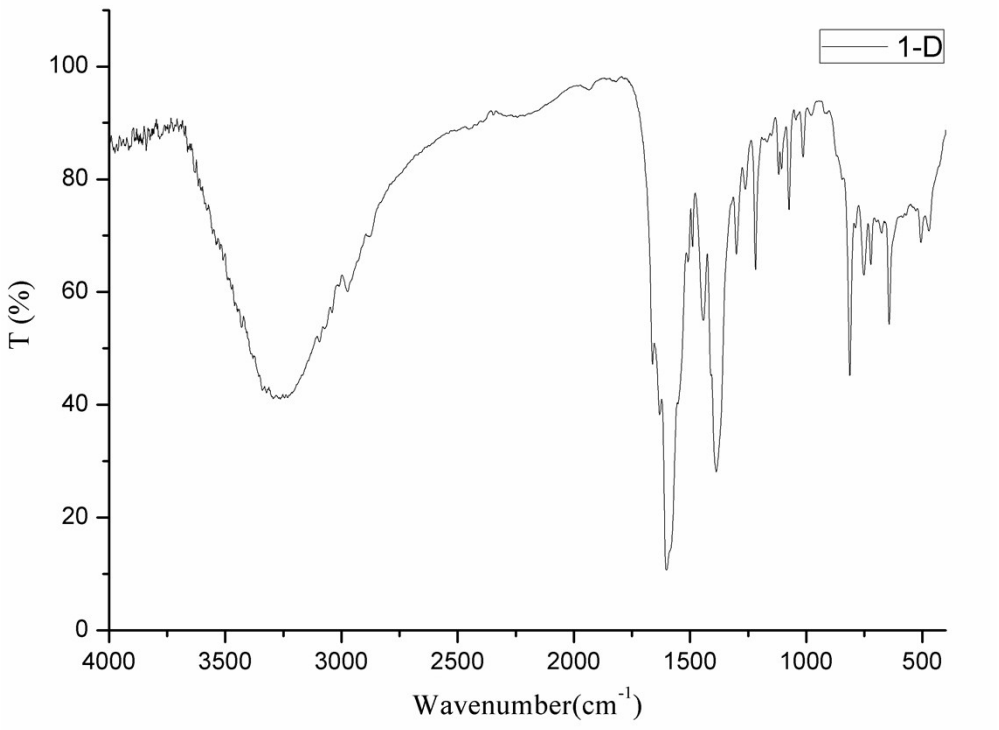

Figure S8. The IR spectra of **1-D**

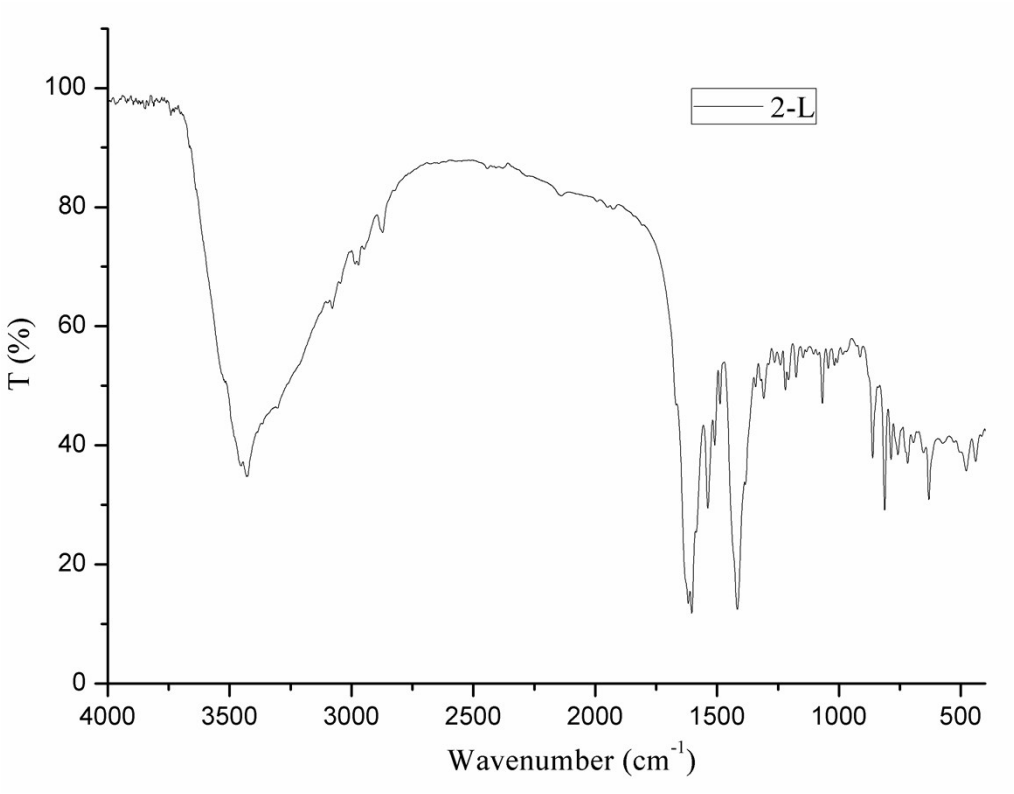

Figure S9. The IR spectra of **2-L**

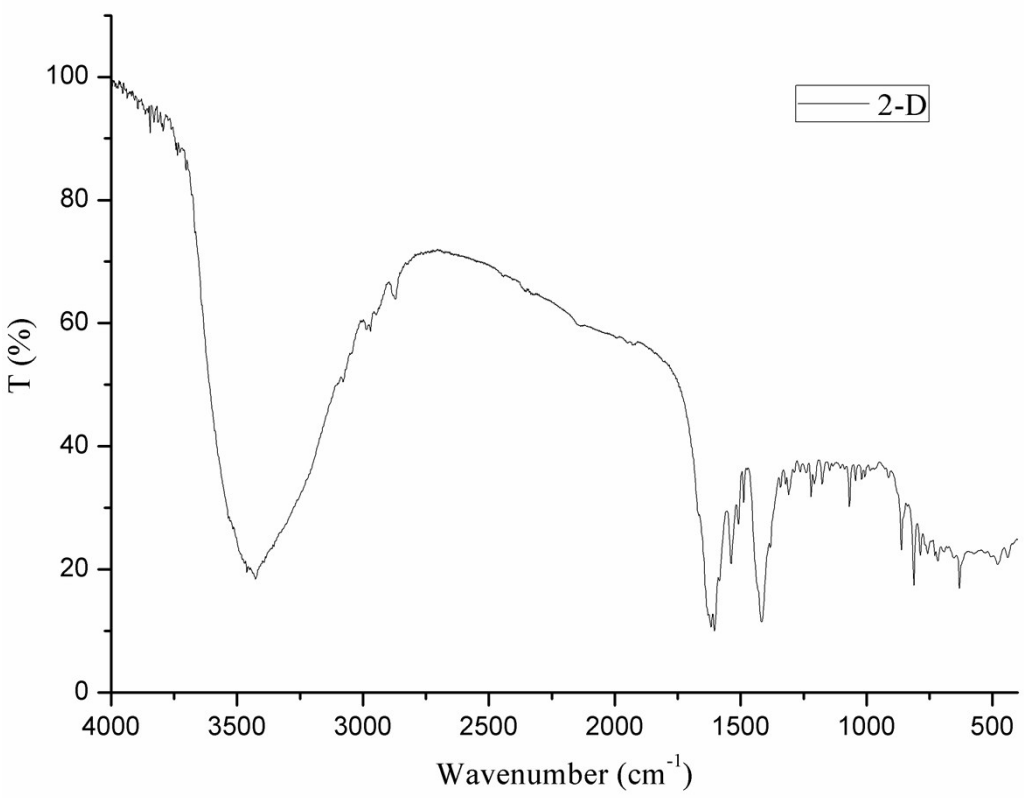

Figure S10. The IR spectra of **2-D**

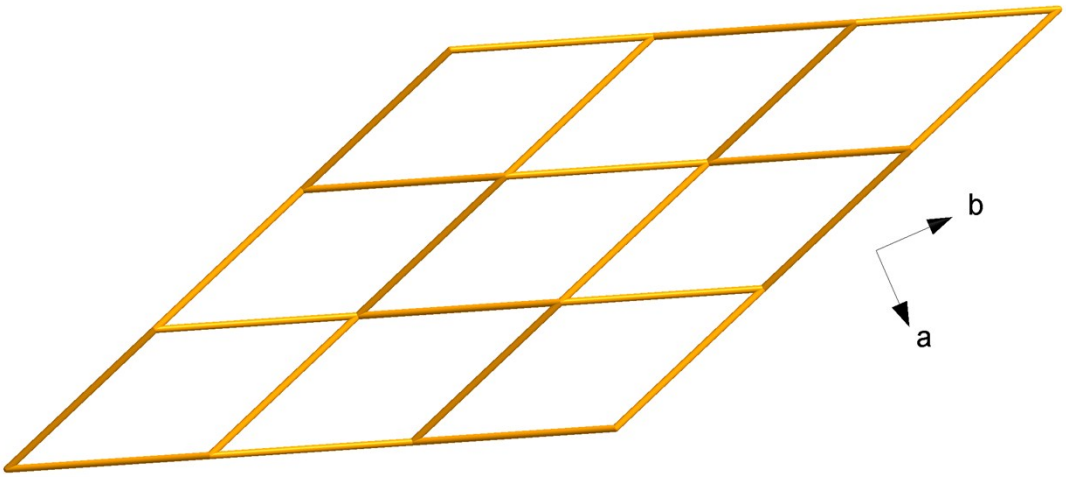

Figure S11. The *sql* net of Cu-(*S*)-PCA layer in compound **1-L**

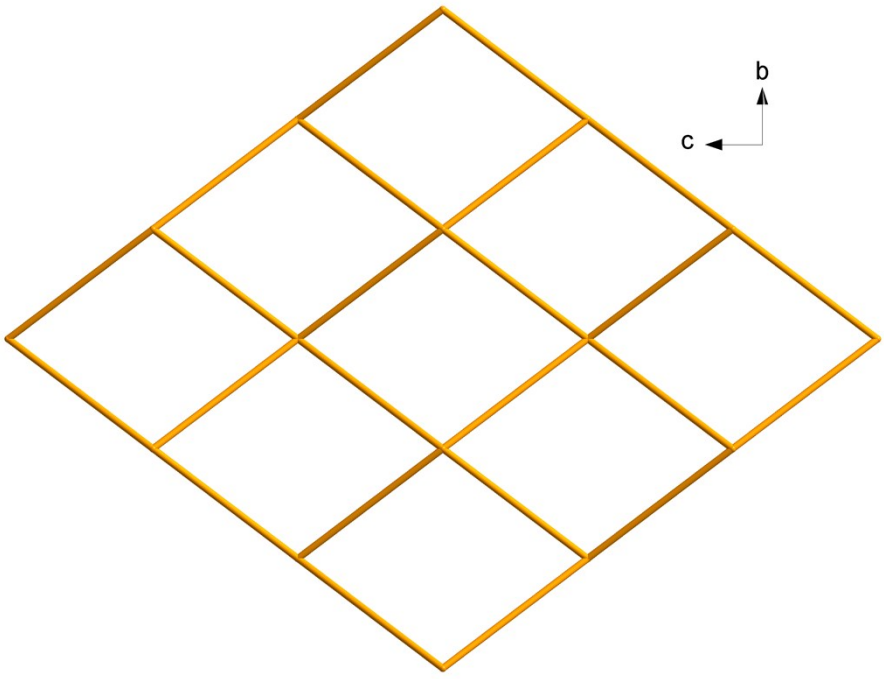

Figure S12. The *sql* net of Co-(*S*)-PCA layer in compound **2-L**

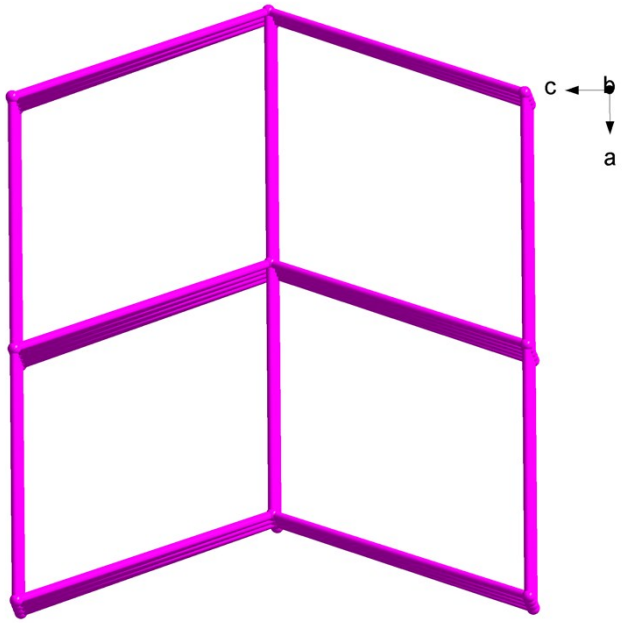

Figure S13. The 6-Connected *pcu* net of **2-L**

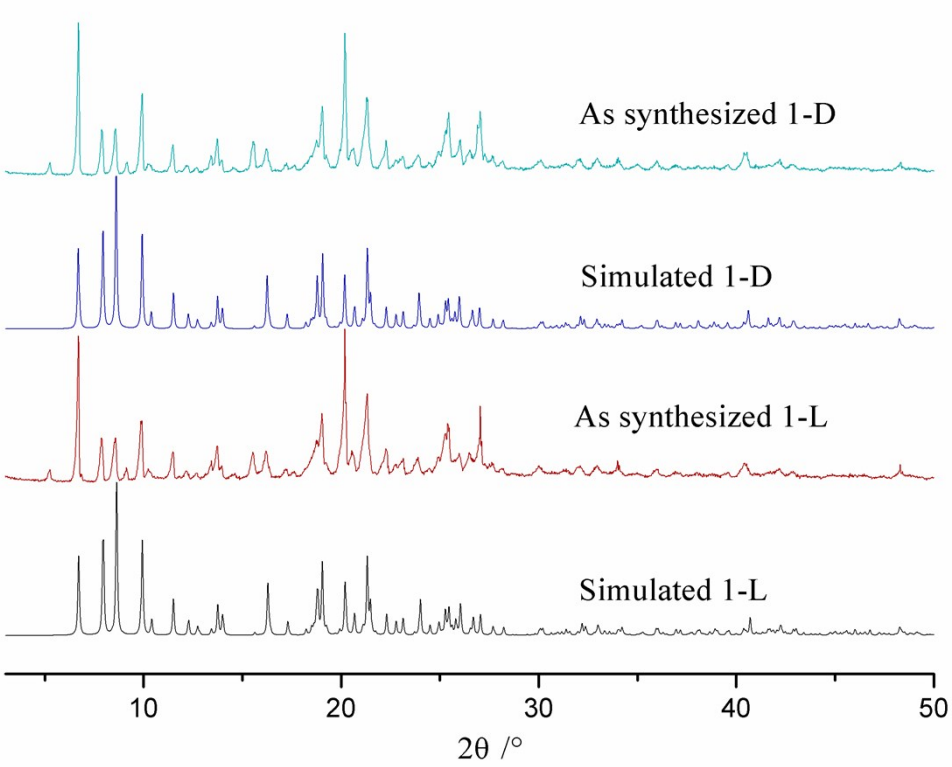

Figure S14. PXRD patterns of **1-D** and **1-L**

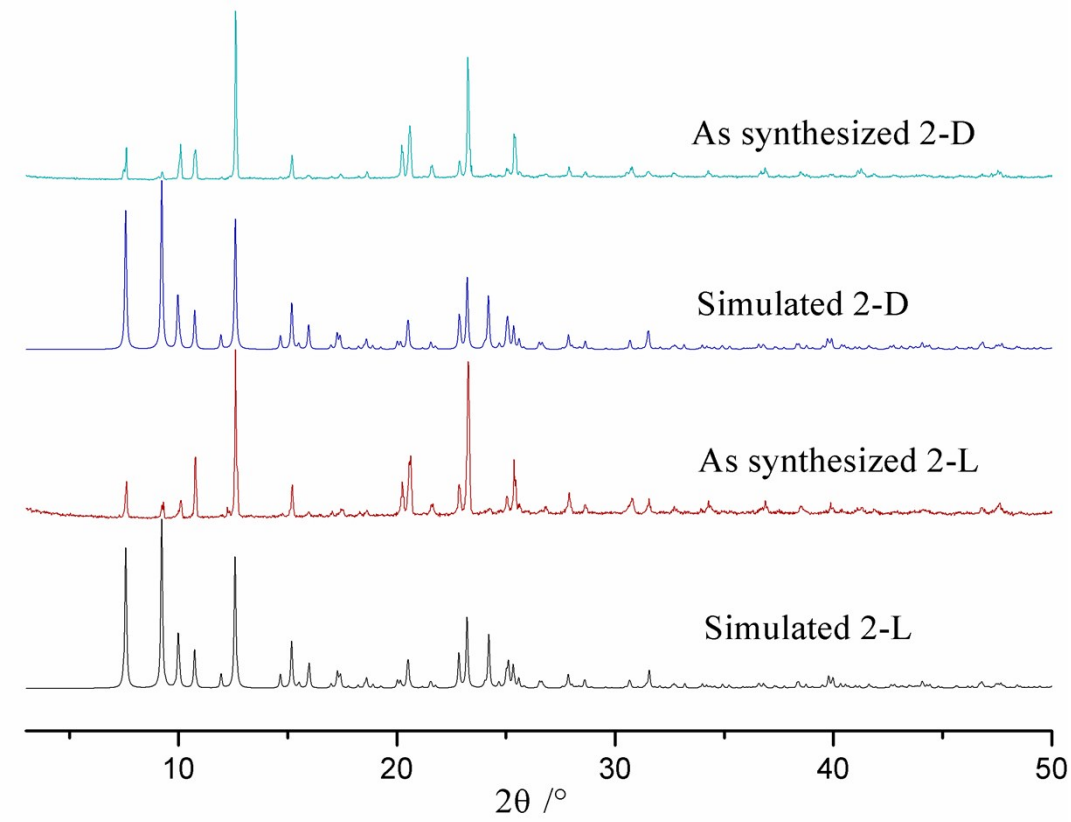

Figure S15. PXRD patterns of **2-D** and **2-L**

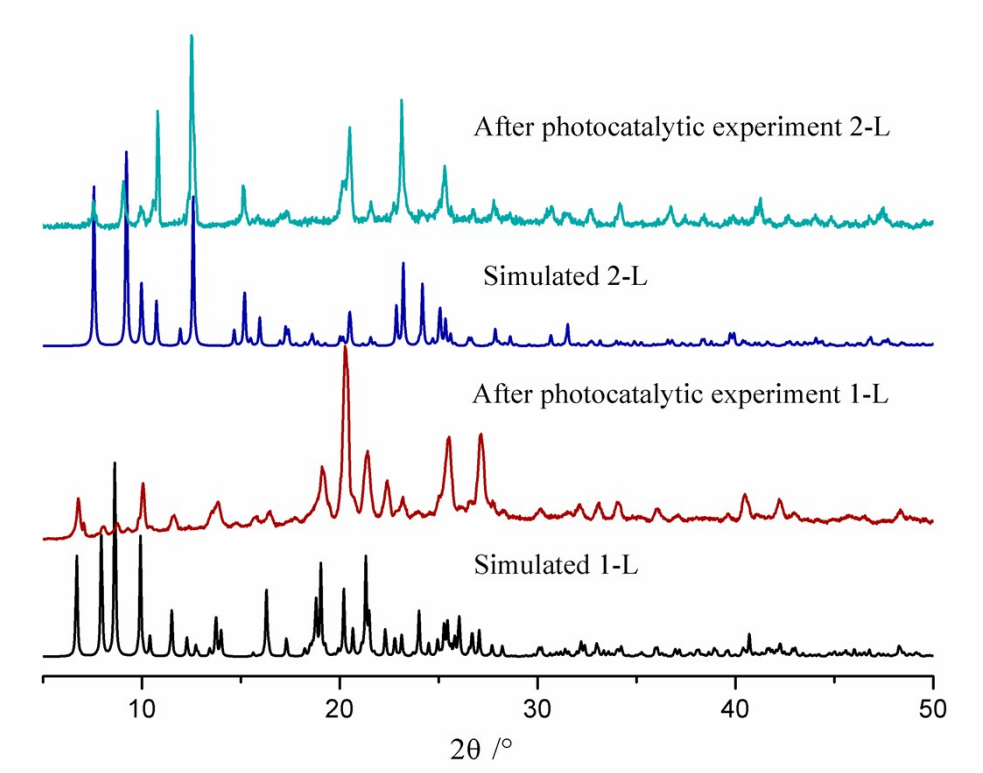

Figure S16. PXRD patterns of **1-L** and **2-L** after photocatalytic experiments

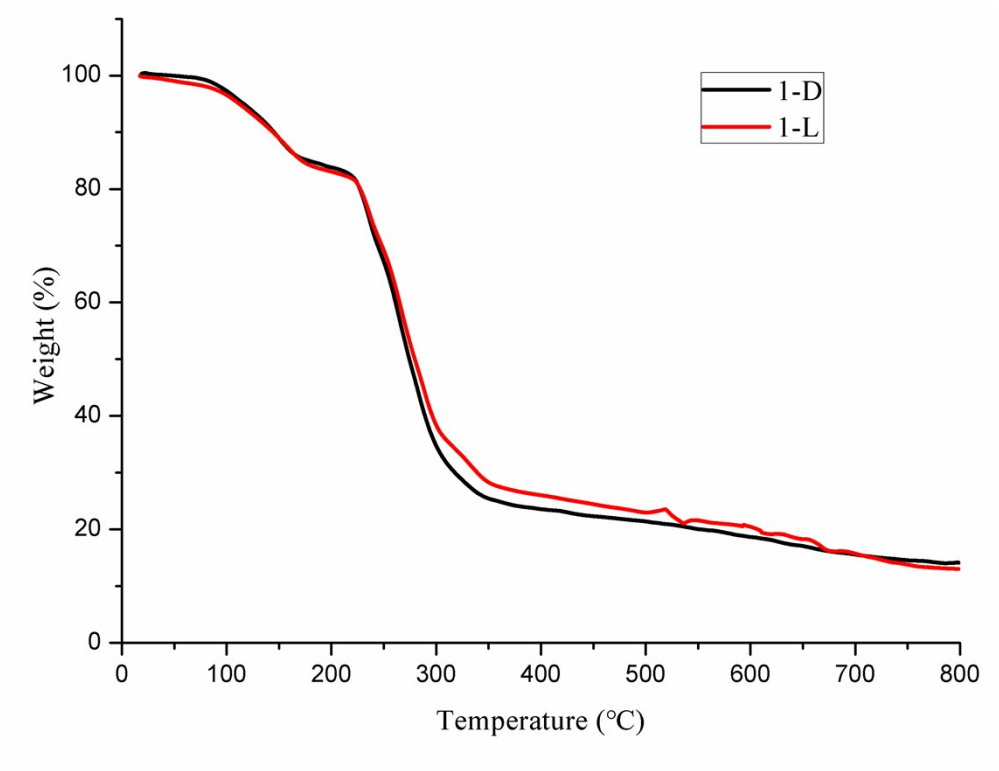

Figure S17.TGA curves of **1-L** and **1-D**

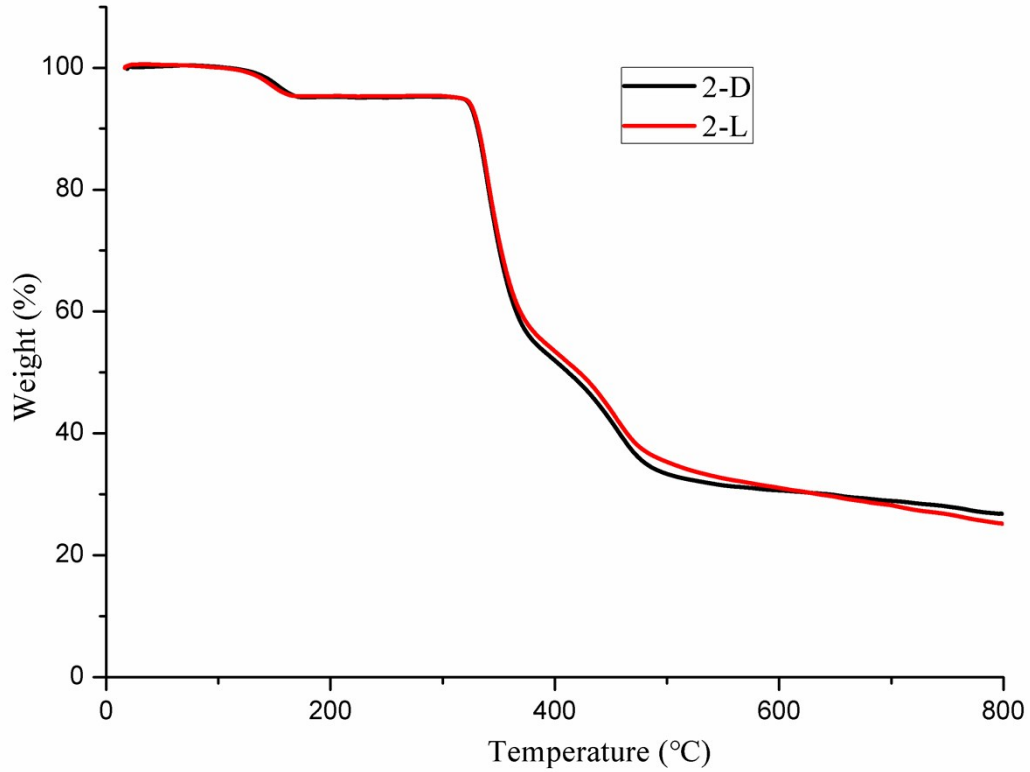

Figure S18.TGA curves of **2-L** and **2-D**

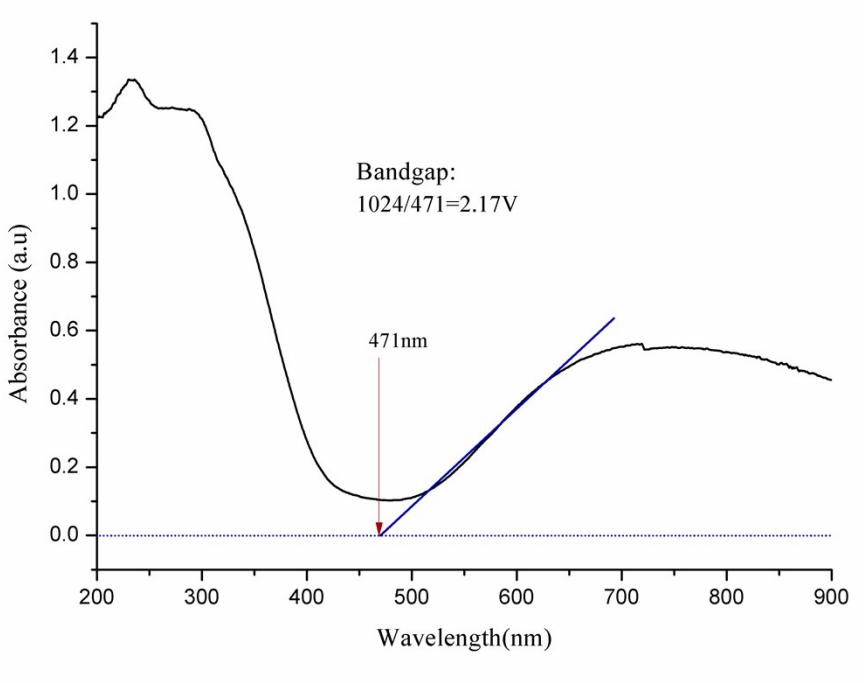

Figure S19. The bandgap of **1-L** from solid UV-vis absorption spectrum according to KM method

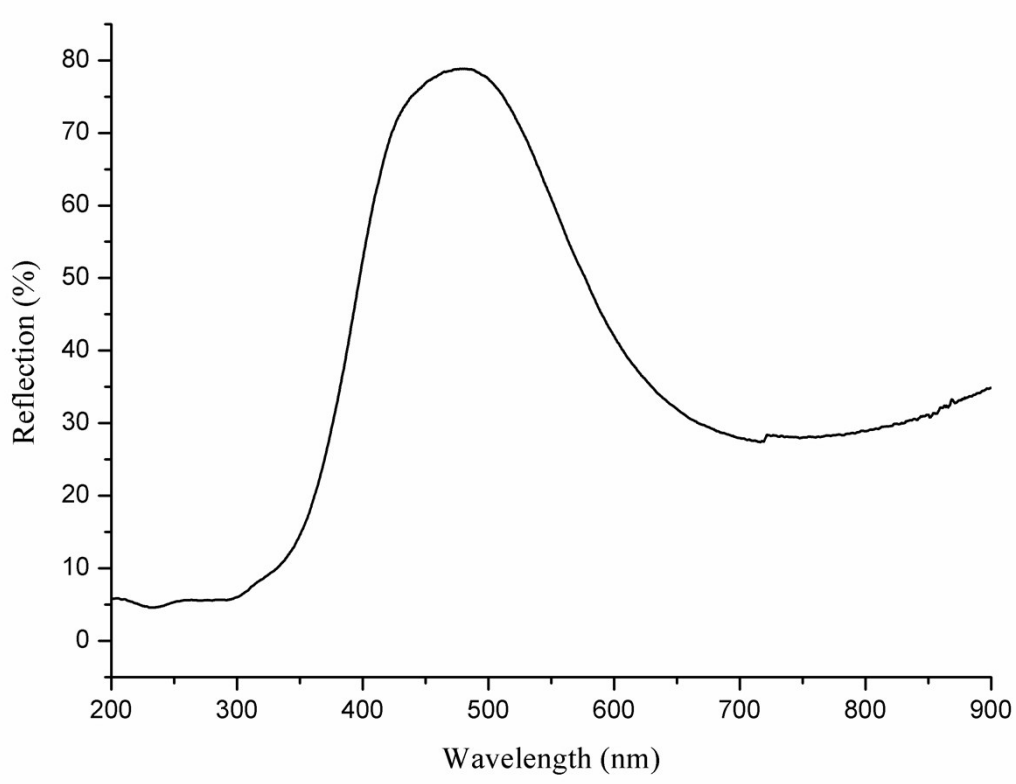

Figure S20. Solid UV-vis reflection spectrum of **1-L**

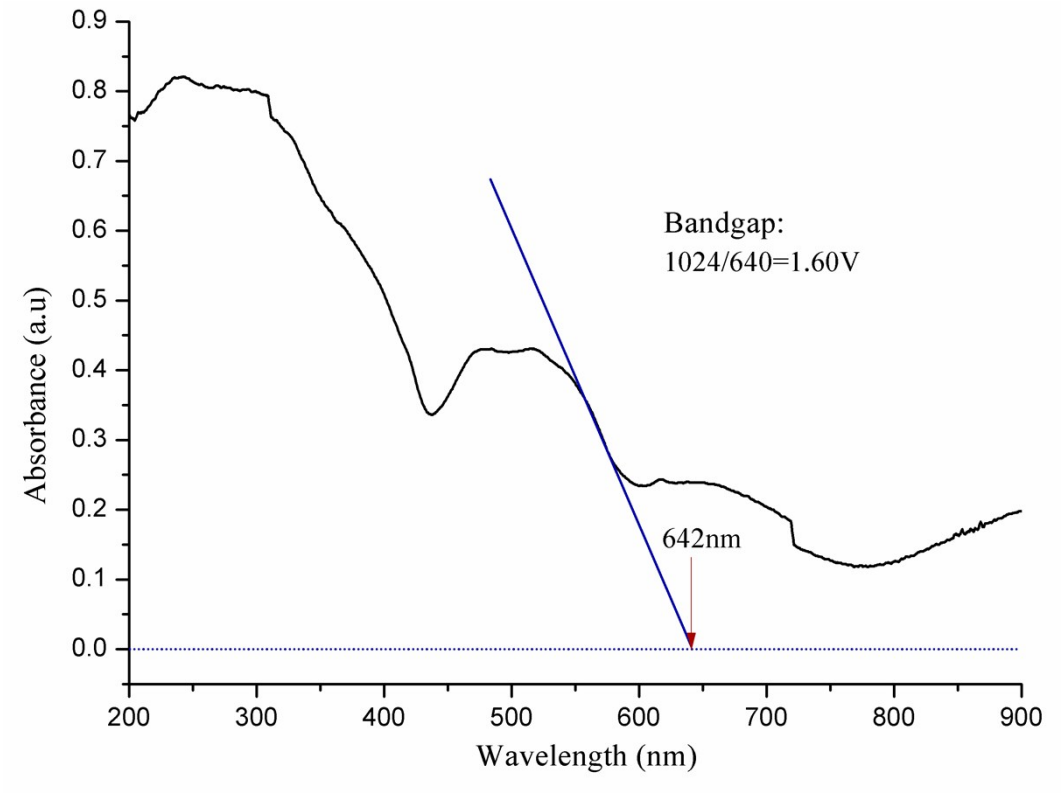

Figure S21. The bandgap of **2-L** from solid UV-vis absorption spectrum according to KM method

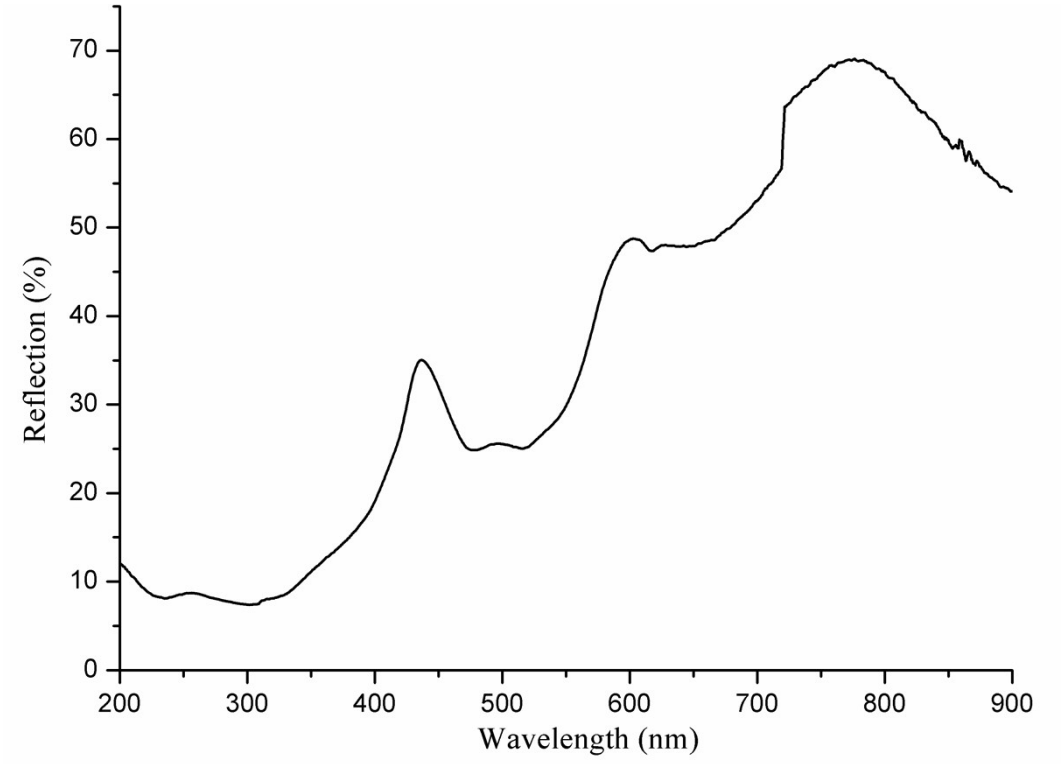

Figure S22. Solid UV-vis reflection spectrum of **2-L**

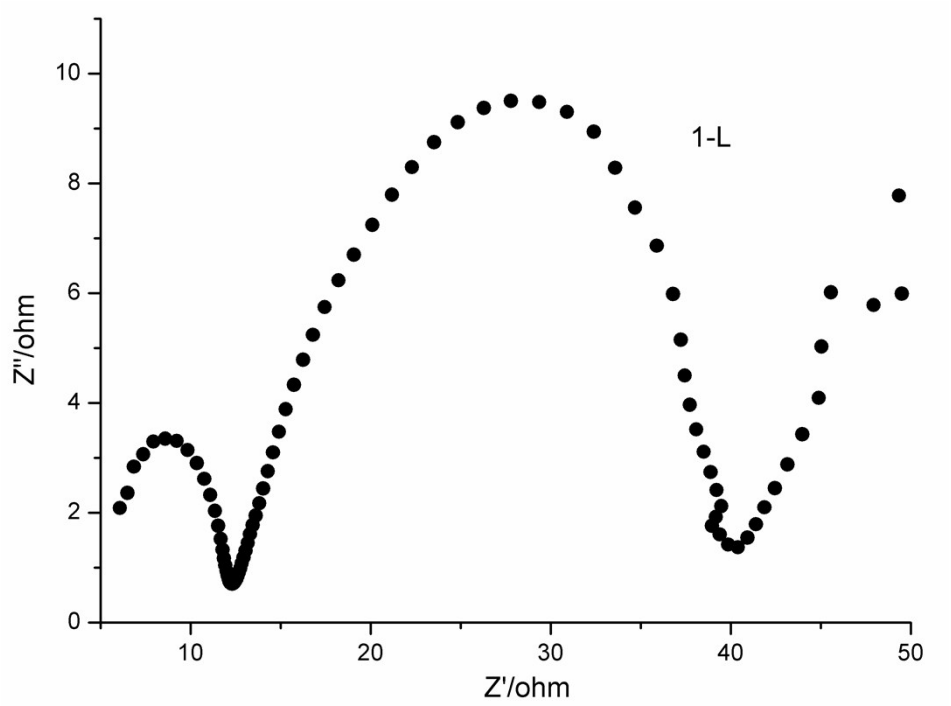

Figure S23. EIS plot of **1-L**

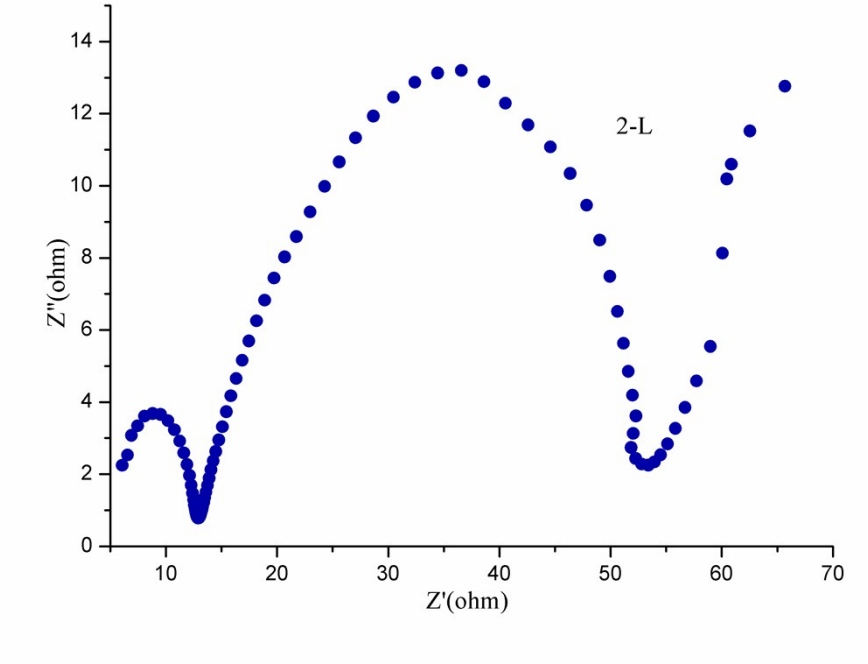

Figure S24. EIS plot of **2-L**

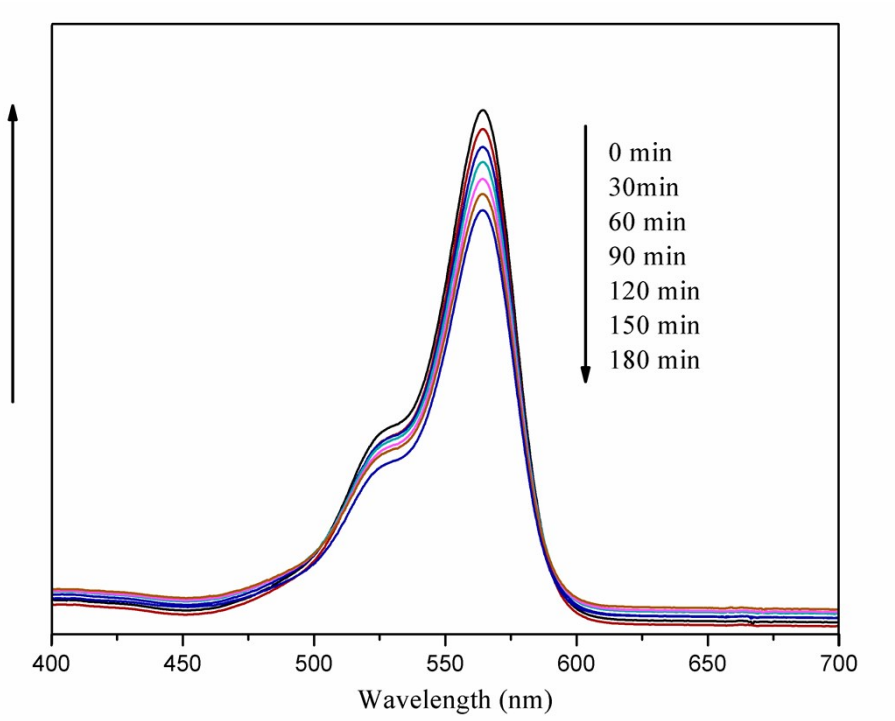

Figure S25. Photocatalytic degradation of RhB solution under UV irradiation without catalyst