Supporting Information

Tetraphenylethene-decorated Functional Polybenzoxazines: Post-polymerization Synthesis *via* Benzoxazine-isocyanide Chemistry and Application in Probing and Catalyst Fields

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Contents

Synthesis of 4, 4'-(1, 2-diphenylethene-1, 2-diyl)dianiline (1)

4, 4'-(1, 2-diphenylethene-1, 2-diyl)dianiline (1) was synthesized according to the reported procedure[1]. Into a 50 mL flask with two necks, 4-aminobenzophenone (1.0 g, 5.1 mmol) and zinc power (1.326 g, 20.4 mmol) were dissolved in 20 mL of dry THF under N_2 atmosphere. The mixture was cooled in ice bath at 0 °C, and $TiCl_4$ (1.13 mL, 10.2 mmol) was added dropwise. After reacting for 30 min, the mixture was warmed to room temperature and refluxed overnight. 20 mL of 10 wt % K_2CO_3 solution was added to quench the reaction. The mixture was extracted with ethyl acetate, and the organic phase was washed with water then dried over with anhydrous $MgSO_4$. After solvent evaporation, the product was purified by Al_2O_3 column using ethyl acetate/petroleum ether (1:1 v/v, with 1 vol % of triethylamine) as eluent to get yellow solid (434 mg, 47 %) (with the content of little amount of unknown impurity). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.15-6.86 (m, 10H), 6.64-6.55 (d, 4H), 6.32-6.23 (d, 4H), 5.11-4.99 (s, 4H).

Synthesis of 1, 1, 2, 2-tetrakis(4-aminophenyl)ethene (5)

1, 1, 2, 2- tetrakis(4-aminophenyl)ethene (**5**) was synthesized by following previously reported procedure[2]. Into a 50 mL Schlenk tube, **4** (240 mg, 0.46 mmol) was dissolved in 5 mL of THF. Raney nickel (~1.0 g) and hydrazine monohydrate (0.385 mL, 6.2 mmol) were added to the solution and the mixture was refluxed for 12 h. The mixture was cooled down to room temperature, and the nickel was filtered off carefully. The solvent was removed under reduced pressure to afford a dark-red solid of compound **5** (156 mg, 85%). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 6.57 (d, 8H),

6.25 (d, 8H), 4.84 (s, 8H).

Table S1. Fluorescence quantum yields of **P1**, **P2-1**, **P2-2** and **P2-3** in solution and solid state.

Polymer	$\Phi_{solution}$ (%)[a]	Φ_{solid} (%)[b]
P1	0.05	2.0
P2-1	4.0	17.2
P2-2	6.2	17.4
P2-3	3.3	16.5

[a]: $\Phi_{solution}$=fluorescence quantum yield in THF/water mixture with 90 vol % water content, measured by using quinine sulfate as standard. [b]: Φ_{solid}=absolute fluorescence quantum yield in solid state.

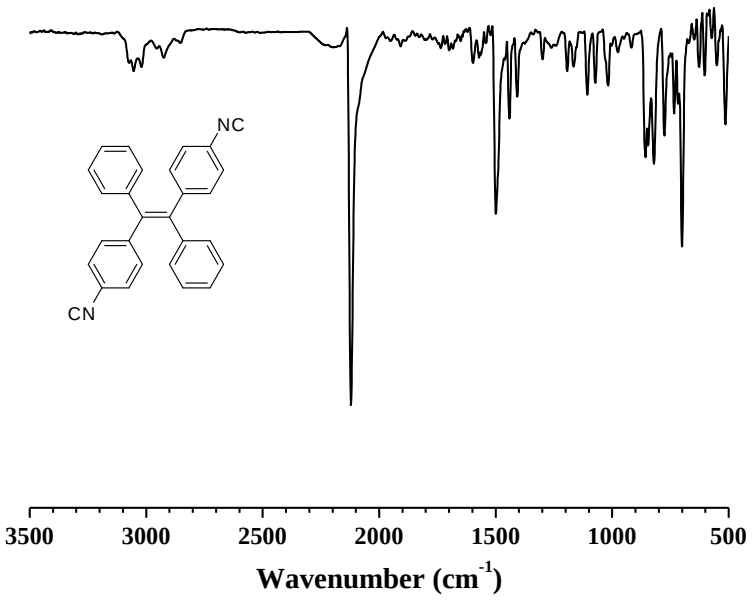

Figure S1. FT-IR spectrum of **M1**.

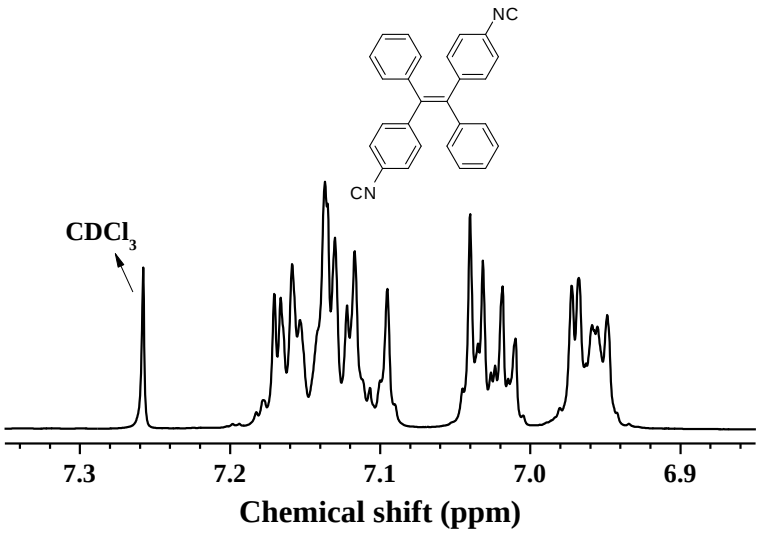

Figure S2. ^{1}H NMR spectrum of **M1**.

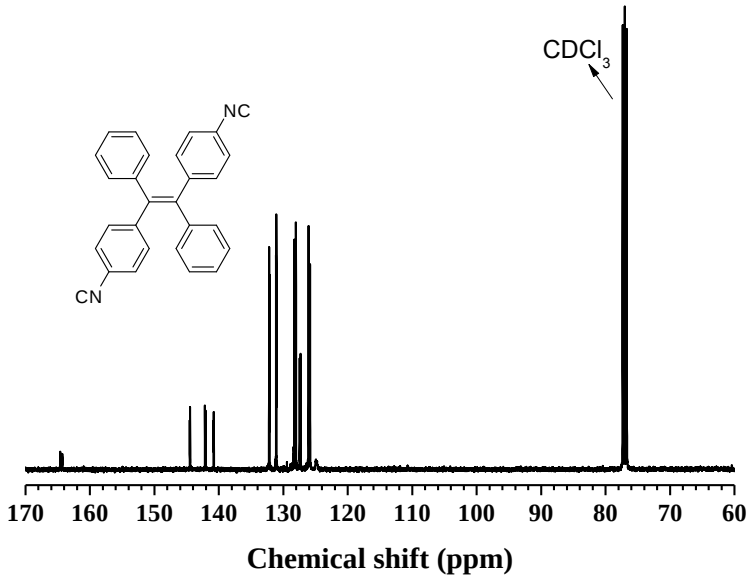

Figure S3. ^{13}C NMR spectrum of **M1**.

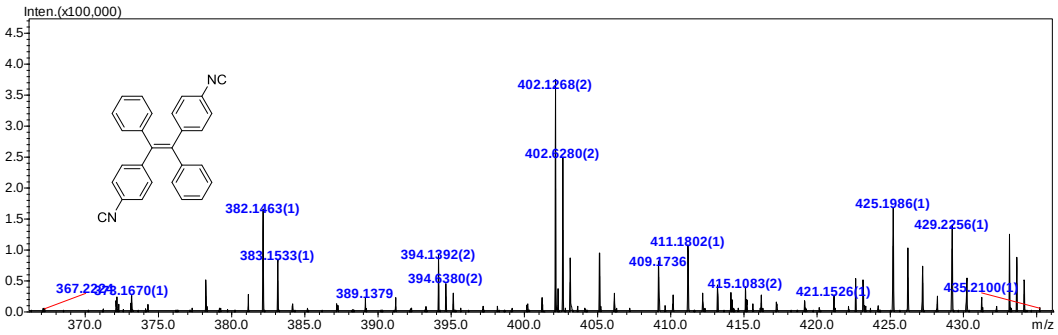

Figure S4. TOF-MS spectrum of **M1**.

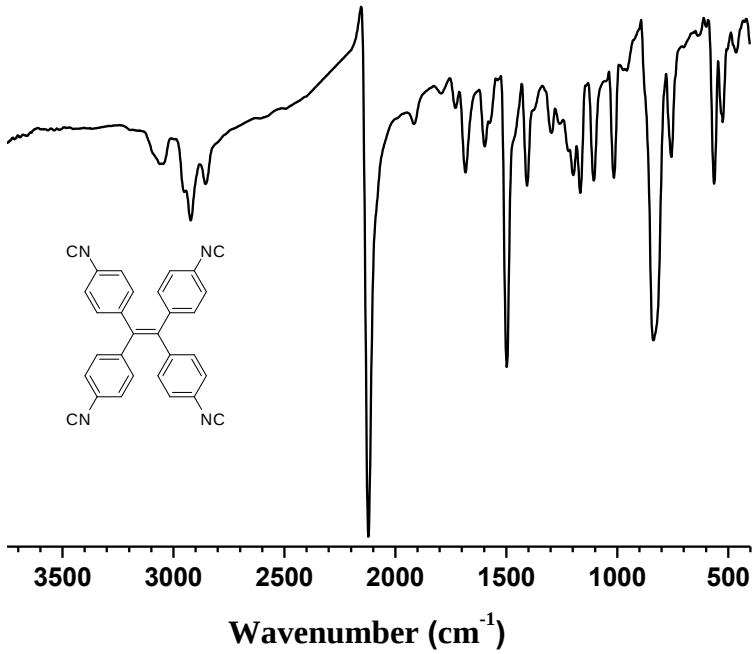

Figure S5. FT-IR spectrum of **M2**.

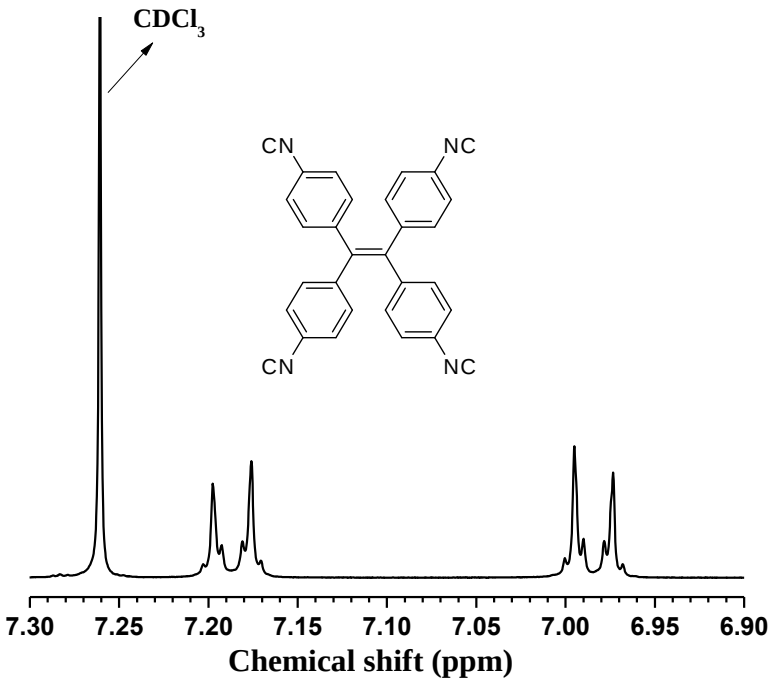

Figure S6. ^{1}H NMR spectrum of **M2**.

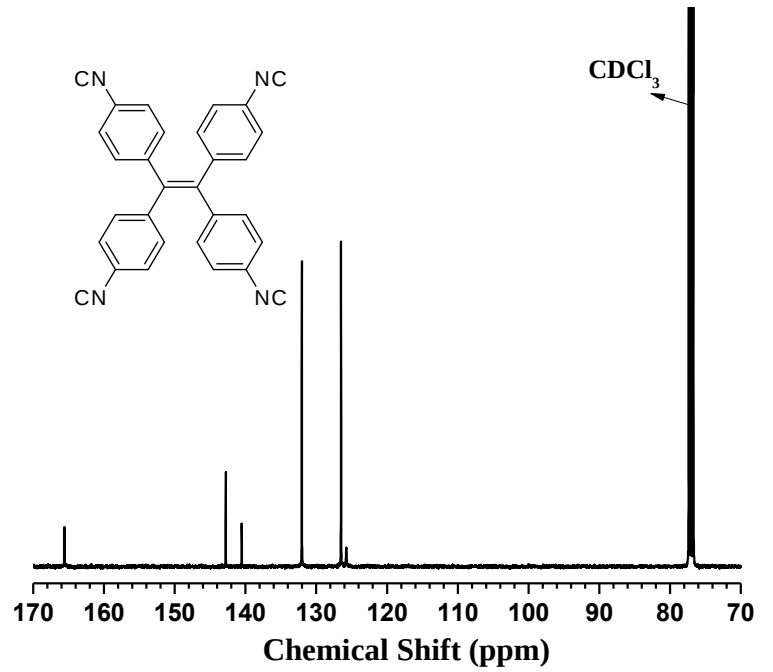

Figure S7. ^{13}C NMR spectrum of **M2**.

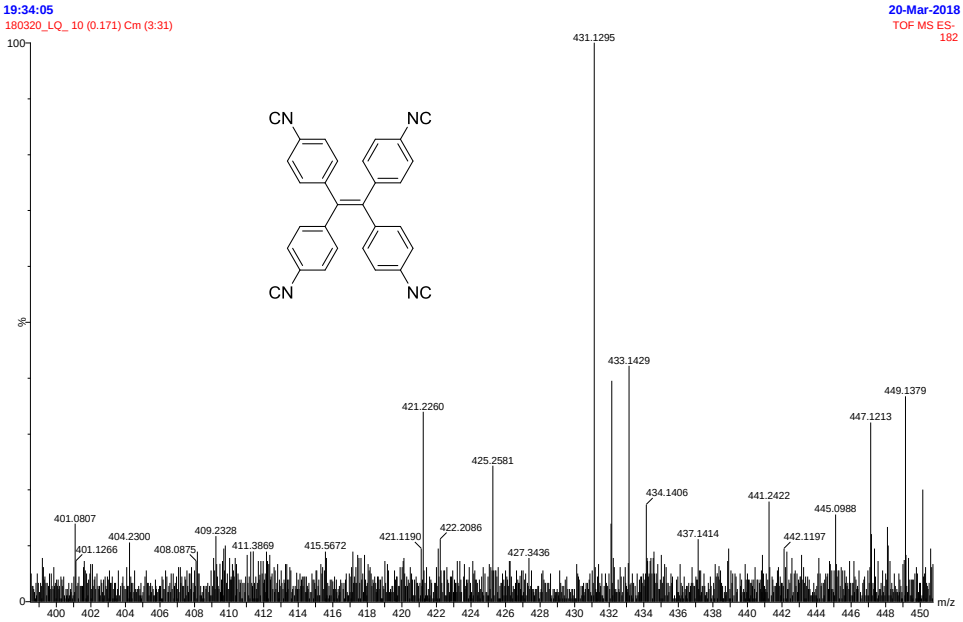

Figure S8. TOF-MS spectrum of **M2**.

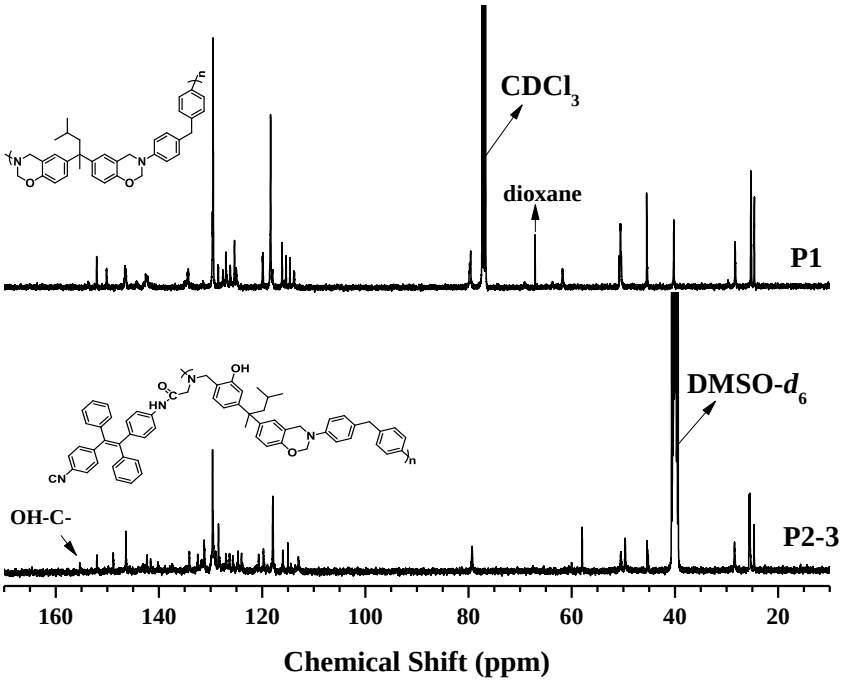

Figure S9. ^{13}C NMR spectra of **P1 (**upper**)** and **P2-3 (**bottom**)**.

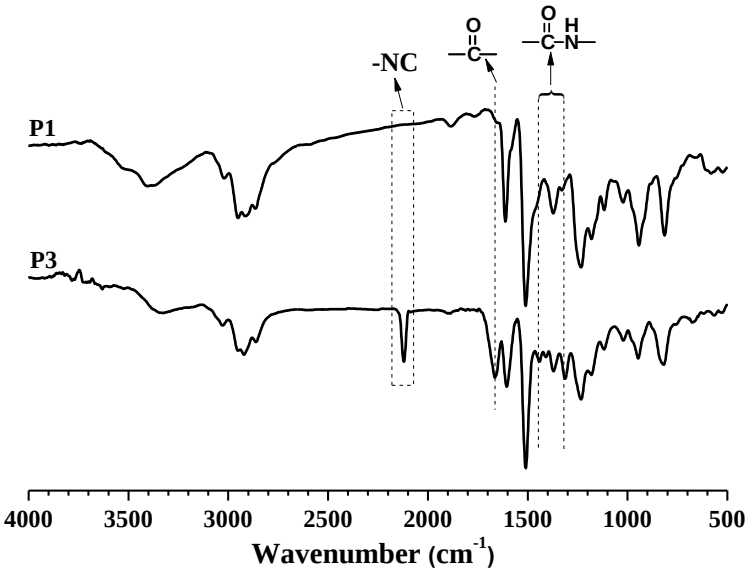

Figure S10. FT-IR spectra of **P1** and **P3**.

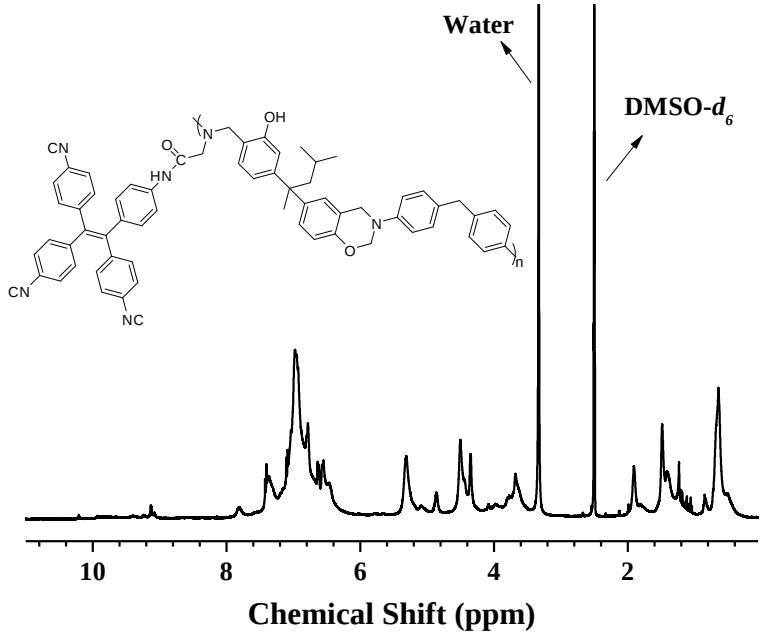

Figure S11. ^{1}H NMR spectrum of **P3**.

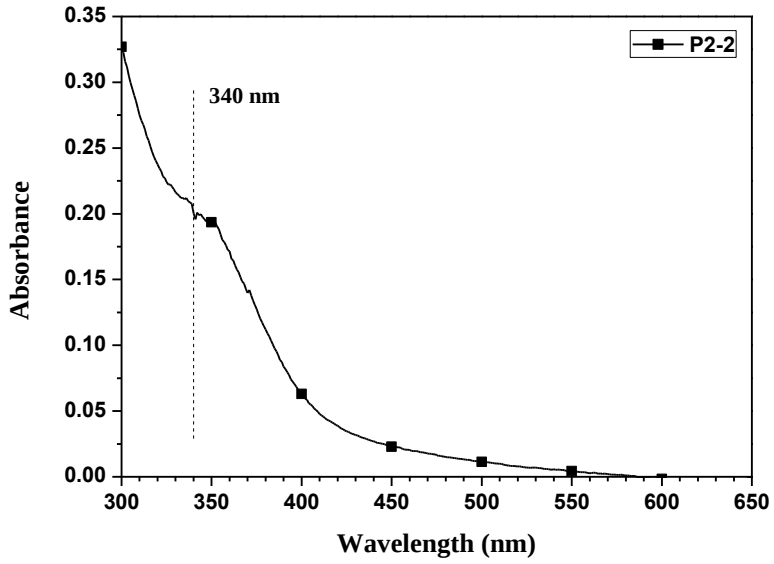

Figure S12. UV-vis absorption spectrum of **P2-2**.

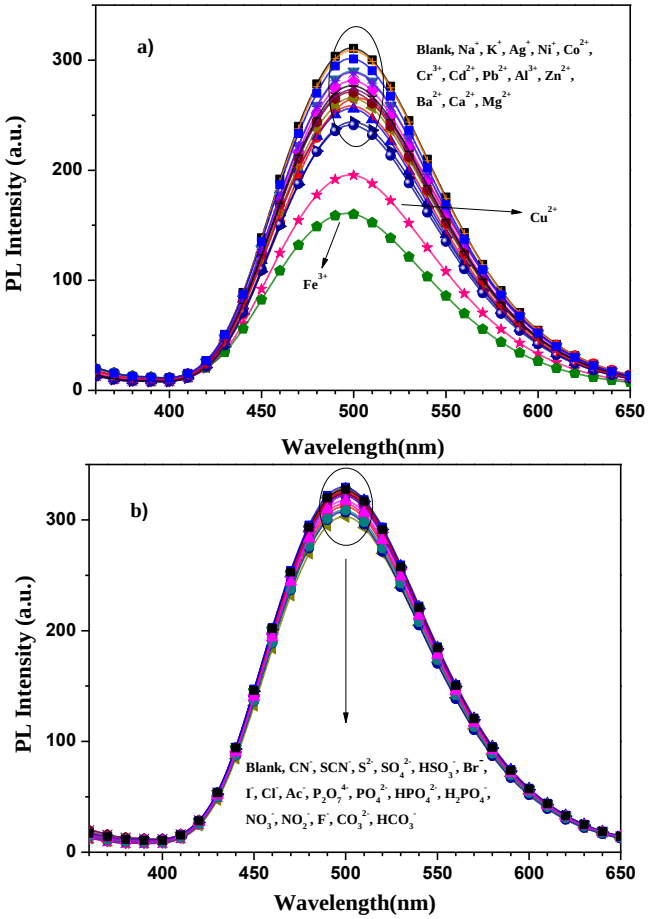

Figure S13. PL spectra of **P2-2** in the presence of common a) cations (1×10^{-4} M) and b) anions (1×10^{-4} M) in THF/water (f_w% = 90 %, stabilized by **SDS** (8×10^{-3} M), excited by 340 nm).

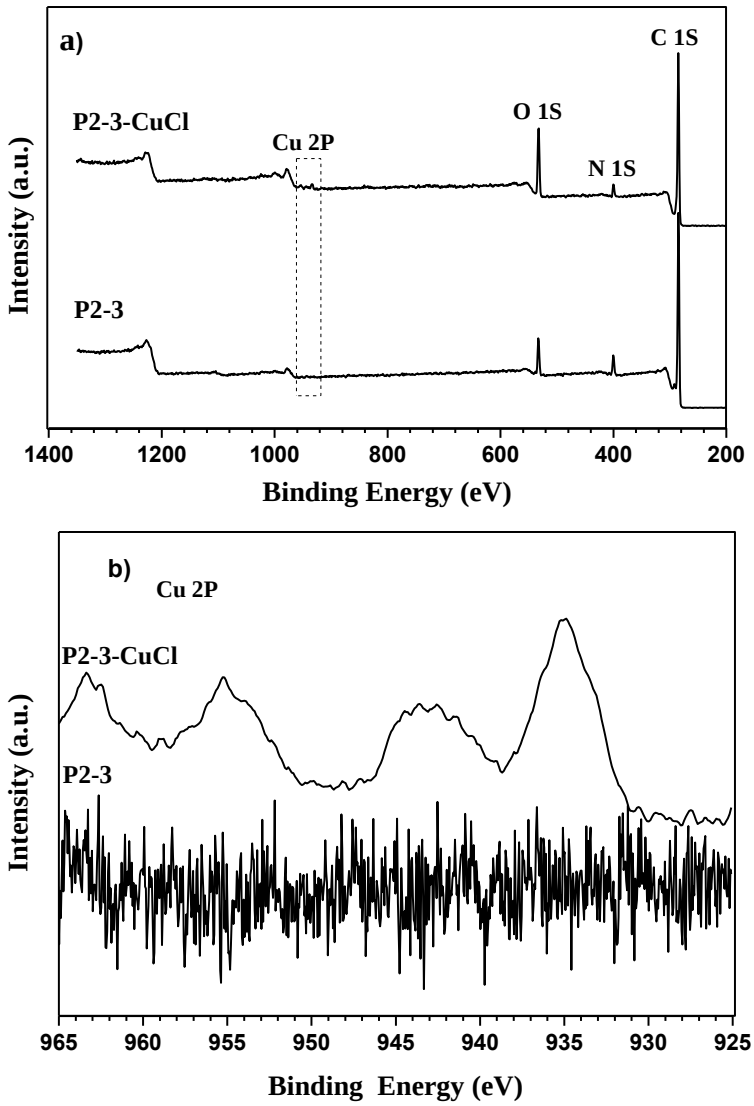

Figure S14. a) XPS spectra of **P2-3** and **P2-3-CuCl**; b) corresponding Cu 2P XPS spectra.

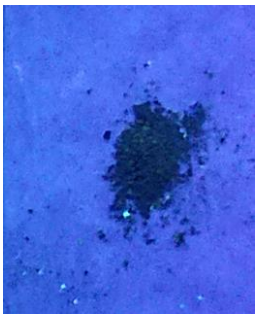

Figure S15. Visual fluorescence photograph of **P2-3-CuCl** under 365 nm UV lamp.

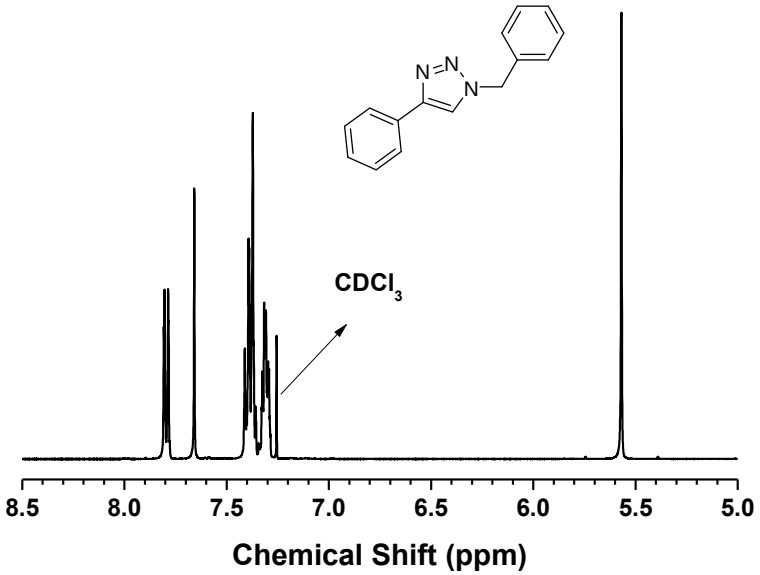

Figure S16. ^{1}H NMR spectrum of **M3**.

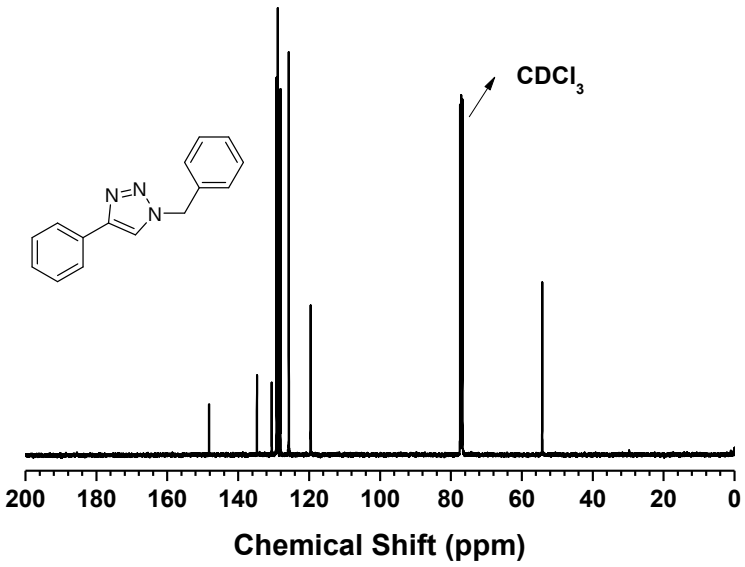

Figure S17. ^{13}C NMR spectrum of **M3**.

References

1. H.-Q. Peng, X. Zheng, T. Han, R. T. K. Kwok, J. W. Y. Lam, X. Huang and B. Z. Tang, *J. Am. Chem. Soc.*, 2017, **139**, 10150-10156.
2. Y. Lin, X. Jiang, S. T. Kim, S. B. Alahakoon, X. Hou, Z. Zhang, C. M. Thompson, R. A. Smaldone and C. Ke, *J. Am. Chem. Soc.*, 2017, **139**, 7172-7175.