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Electronic supporting information

Synthesis and characterization of metallo-supramolecular polymers from thiophene-based unimers bearing pybox ligands

Sviatoslav Hladysh[a*], Daniela Václavková[b], David Vrbata[a], Dmitrij Bondarev[b,c], David Havlíček[d], Jan Svoboda[e], Jiří Vohlídal[a], Jiří Zedník[a]

a) *Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, CZ-12840 Prague 2 , Czech Republic*

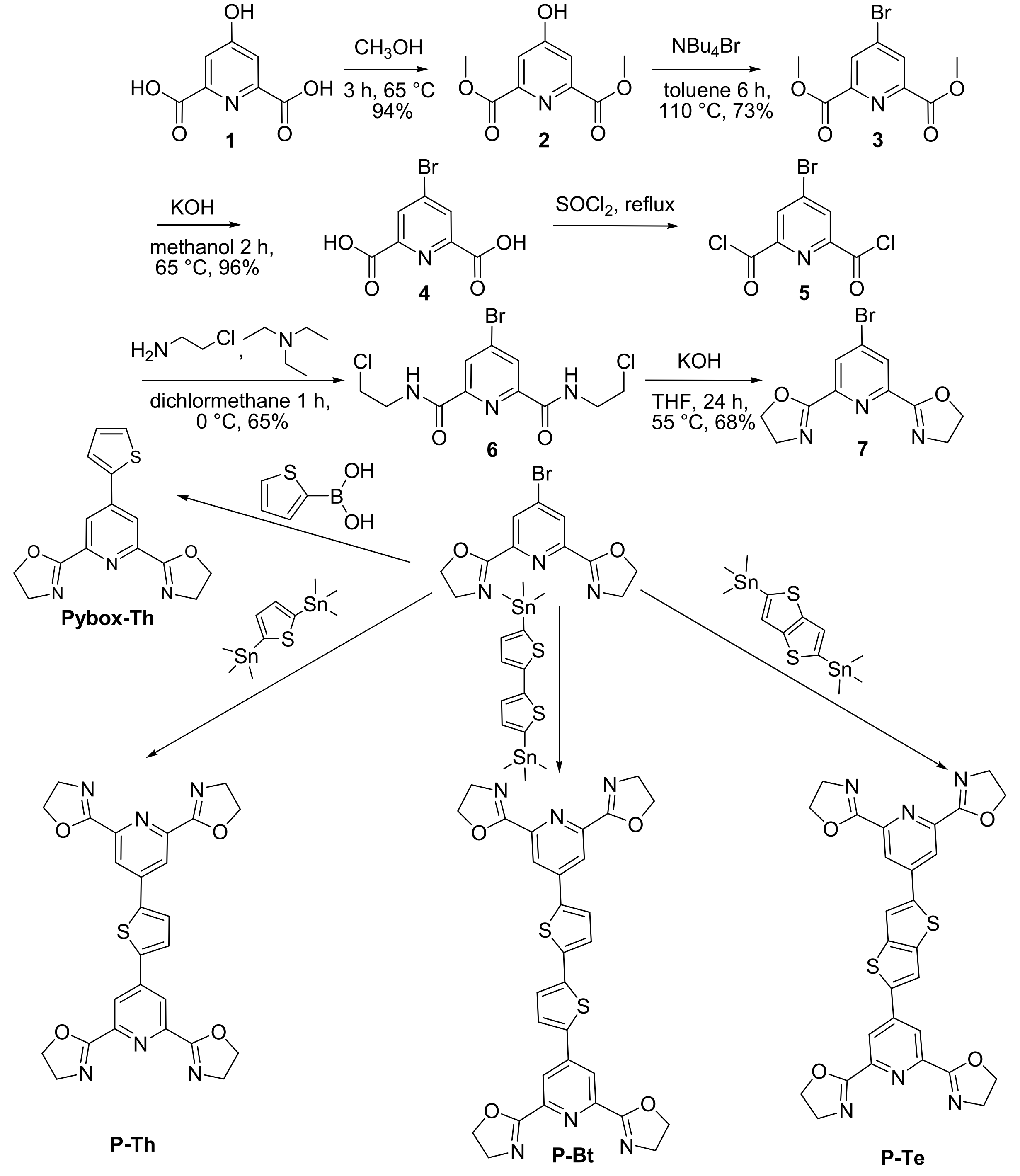
**Corresponding author. E-mail address:* sviatoslavhladysh@gmail.com (S. Hladysh)

b) *Tomas Bata University in Zlín, Faculty of Technology, Department of Polymer Engineering, Vavrečkova 275, CZ-762 72 Zlín, Czech Republic*

c) *Polymer Institute, Slovak Academy of Sciences, Dubravska cesta 9, 845 41 Bratislava, Slovakia*

d) *Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, CZ-12840 Prague 2 , Czech Republic*

e) *Institute of Macromolecular Chemistry AS CR, v.v.i, Heyrovsky Sq. 2, 16206, Prague 6, Czech Republic*



Scheme S1 Synthesis of unimers, **Pybox-Th** ligand and monomer-precursors

Synthesis of starting materials (according to Scheme S1)

Dimethyl 4-hydroxypyridine-2,6-dicarboxylate (**2**)

To a 250 mL round bottle flask charged with chelidamic acid **1** (10 g, 55 mmol), methanol (200 mL) and sulfuric acid (0.2 mL) were added. The mixture was heated to reflux temperature and stirred for 3h. After that the mixture has been cooled and the solvent was removed in *vacuo* to give the white solid. The precipitate was isolated via filtration washed with water (3×50 mL) and dried under vacuum. Yield: 9.4 g, 82%. ^{1}H NMR (300 MHz, DMSO d$_6$, ppm) δ 11.58 (s, OH), 7.57 (s, 2H-pyH), 3.87 [s, 6H-$(OCH_3)_2$].

Dimethyl 4-bromopyridine-2,6-dicarboxylate (**3**)

Tetrabutylammonium bromide of (20 g, 60 mmol) and P_2O_5 (16 g, 113 mmol) were dissolved in toluene (100mL) in a round bottle flask (250 mL) and dimethyl ester of chelidamic acid (5 g, 20 mmol) was slowly added. The mixture was stirred for 6 h at 110 ^{0}C and, upon partial cooling, toluen was removed on a rotary evaporater. The obtained yellow oil was mixed with distilled water (60 mL) and the product extracted with dichloromethane (2×50mL). The organic phase was washed with water (3×40 mL), dried with Na_2SO_4, and the crude product obtained by evaporating dichloromethane was recrystallized from methanol to give a white solid **3** (yield 4.75 g, 73%). ^{1}H NMR (300 MHz, DMSO d$_6$, ppm) δ 8.4 (s, 2H-pyH), 3.92 [s, 6H-$(OCH_3)_2$]. IR (DRIFT), cm^{-1}: 3105 (w), 2950 (w), 7727 (s), 1601 (m), 1445 (s), 1360 (m), 1266 (s), 1129 (m), 988 (m), 780 (m), 645 (w), 466 (s).

4-Bromopyridine-2,6-dicarboxylic acid (**4**)

Dimethyl 4-bromopyridine-2,6-dioate **3** (4 g, 15 mmol) was dissolved in methanol (150 mL) and after that potassium hydroxide (1.79 g, 32 mmol) dissolved in methanol (50 mL) was added. The reaction mixture was heated at 65 °C for 2 h. After cooling to room temperature the solvent was evaporated to get the potassium salt of 4-bromopyridine-2,6-dicarboxylic acid. The salt was dissolved in water (50 mL) and solution obtained was concentrated by aqueous hydrogen chloride solution (37%) in order to get pH=1. The white precipitate formed was filtered off, washed with water (3×50 mL) and dried under vacuum. Yield: 3.4 g, 94%. ^{1}H NMR (300 MHz, DMSO d$_6$, ppm) δ 8.36 (s, 2H-pyH).

4-Bromopyridine-2,6-dicarbonyl dichloride (**5**)

Compound **4** (3 g, 12 mmol) and thionyl chloride (20 g, 168 mmol) were placed into a 100 mL round bottom flask. The resulting mixture was stirred and heated at reflux for 1 h. The residual thionyl chloride was removed in vacuum to give the crude product as a yellow powder. Yield: 3.4 g, 98%.

4-Bromo-N^2,N^6-bis(2-chloroethyl)pyridine-2,6-dicarboxamide (**6**)

To dichlormethane solution of chlorethylamine hydrochloride (3.48 g, 30 mmol) and triethylamine (4.85 g, 48 mmol) was slowly added dichloromethane solution of the crude 4-bromo-2,6-pyridinedicarboxylic acid chloride (3.4 g, 12 mmol) at 0 °C . The mixture was stirred for 1 h at room temperature. Than the solvent was removed by rotary evaporation and water (50 mL) was infused into flask. The mixture was extracted with dichlormethane (3×30 mL). The combined organic extracts were dried over $MgSO_4$. Evaporation of solvent and crystallization from methanol gave the product as a white powder (3.5 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.51 (s, 2H-pyH), 8.12(br s, 2H- NH), 3.84 (m, 4H-CH_2N), 3.75 (t, 4H-CH_2Cl).

4-bromo-2,6-bis(4,5-dihydro-2-oxazolyl)-pyridine (**7**)

The preparation of the key compound 2,2'-(4-bromopyridine-2,6-diyl)bis(4,5-dihydrooxazole) was performed as follows. Briefly: compound **6** (3.5 g, 9.5 mmol) had been dissolved in THF (50 mL) and 25 % water solution of KOH (2.1 g, 38 mmol) was added into THF solution of **6** by a dropping funnel. The mixture was stirred at 50 °C for 48 h. The solvent was evaporated and the residue was purified by recrystallization from ethanol to afford 2.1 g of the desired product as a white solid (68% yield). Analytical data are in good accordance with published results.

2,6-Bis(oxazoline-2-yl)-4-(2-thienyl)pyridine (***Pybox-Th***)

An aqueous solution (10 mL) of K_2CO_3 (2.5 g, 18 mmol) was added to a mixed solution of **7** (0.5 g, 1.7 mmol), 2-thienylboronic acid (0.32 g, 2.5 mmol) and $Pd(PPh_3)_4$ (0.03 g, 0.025 mmol) in distilled THF (40 mL) and the obtained reaction mixture was stirred for 24 h at 80 ^{0}C. Then the mixture was cooled to room temperature, THF distilled off and the obtained dark solution acidified with hydrochloric acid to pH 3-4 to obtain a white precipitate that was subsequently filtered off and recrystallized from propan-2-ol. Yield: 0.33 g, 66%.^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.33 (s, 2H-pyH), 7.65 (d, 1H-Th), 7.47 (d, 1H-Th), 8.33 (t, 1H-Th), 4.55 (t, 4H-CH_2N), 4.14 (t, 4H-CH_2O).

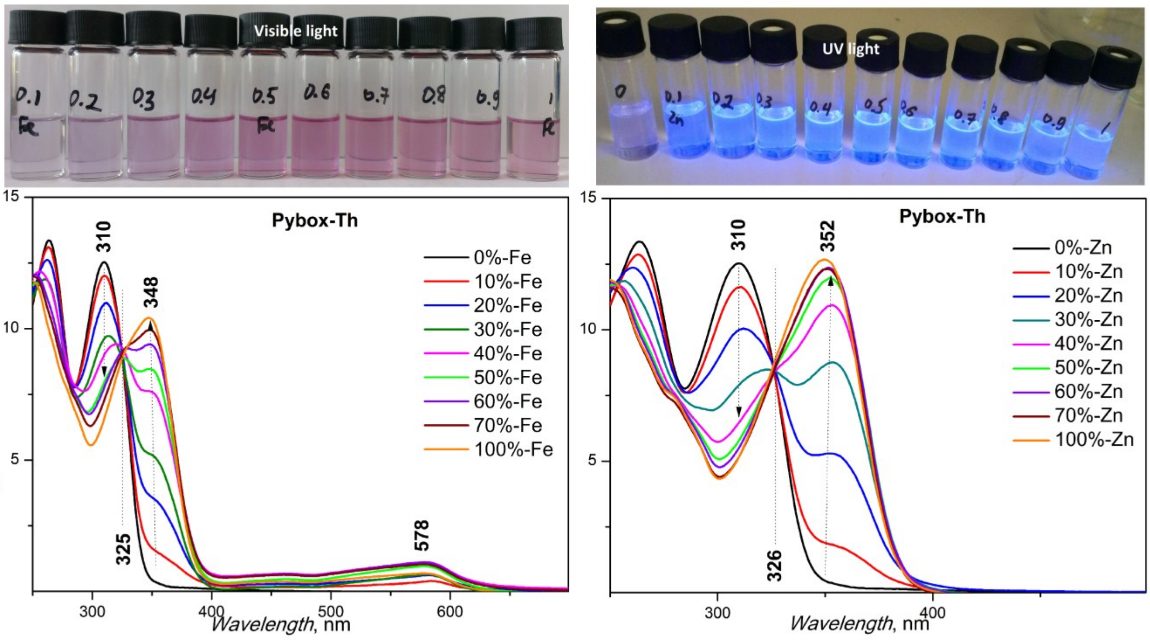


Figure S1 UV/vis titration of Fe^{2+} and Zn^{2+} against **Pybox-Th** ligand in a mixture of chloroform and methanol (1/1 by volume) in different ligand to metal ratios.

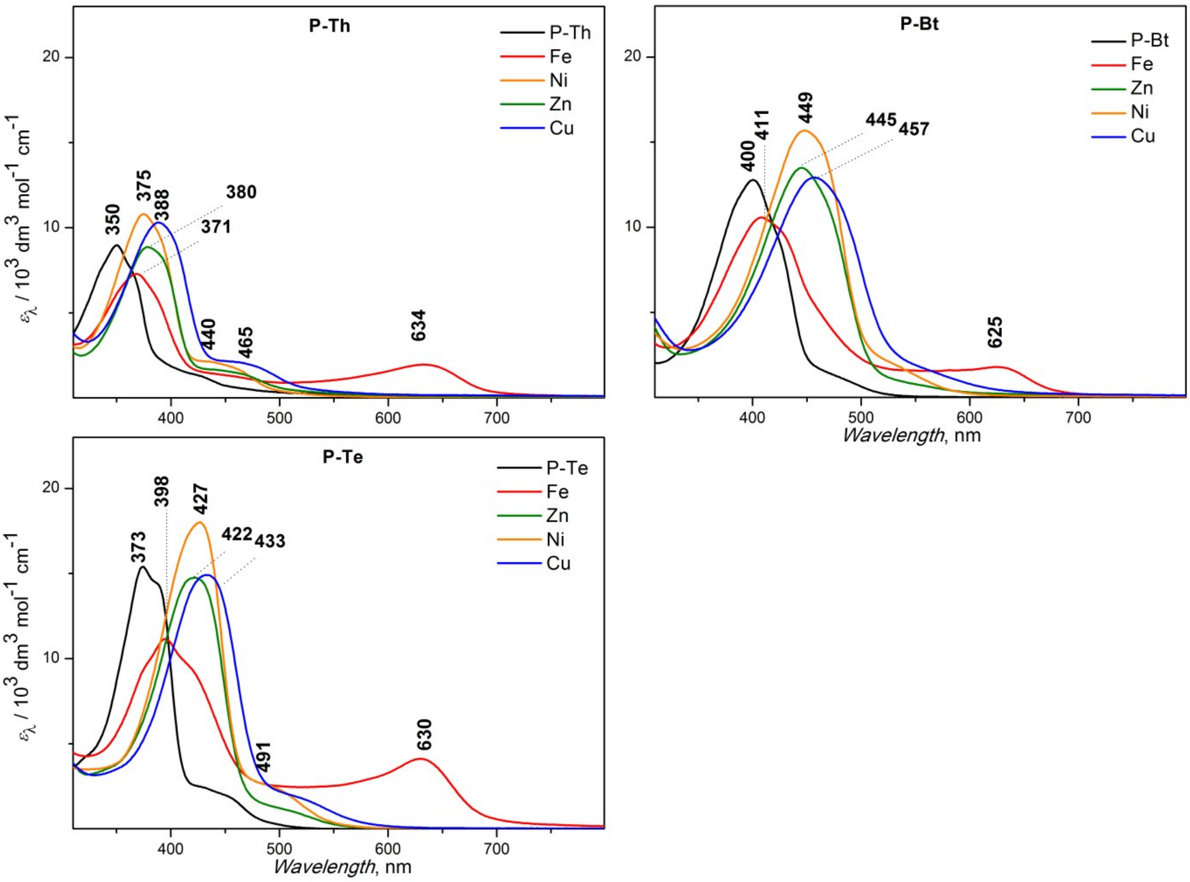


Figure S2 Absorption spectra of **P-Th**, **P-Bt** and **P-Te** with indicated metal ions. A metal-ligand ratio is (1:1).

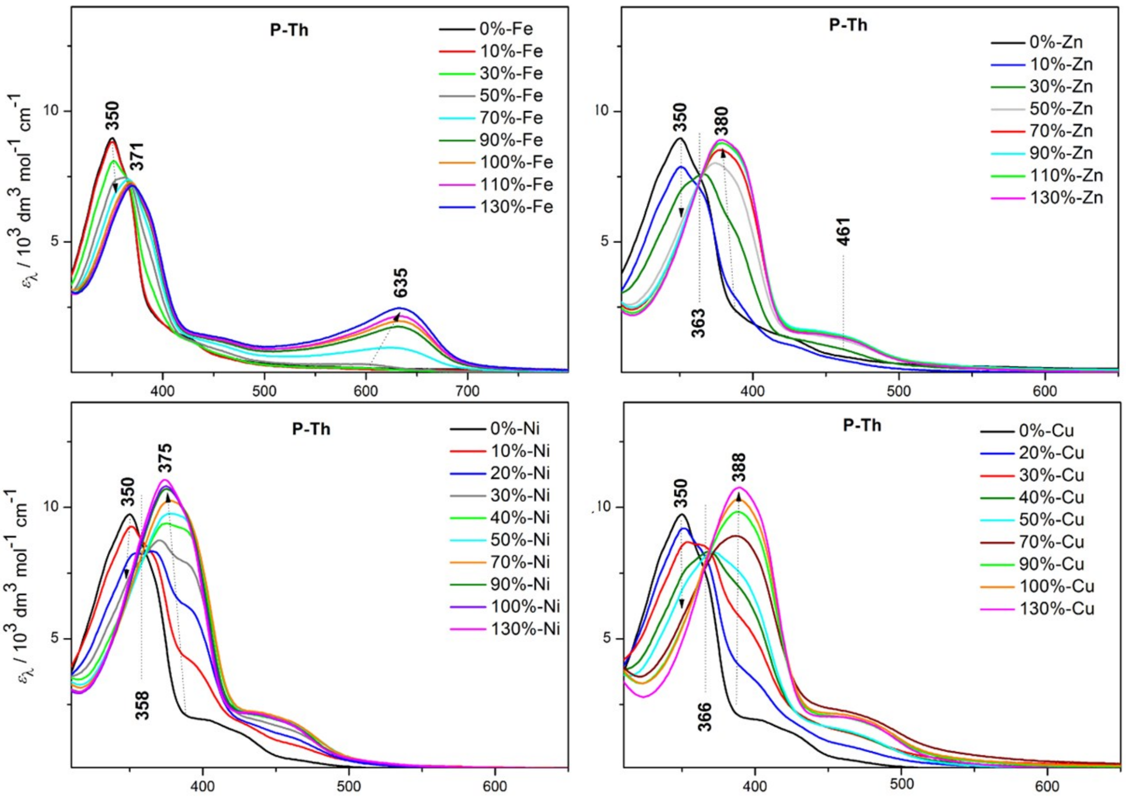


Figure S3 UV/vis titration spectra of **P-Th** (2×10^{-4} M, based on monomer unit) with various metal ions (2×10^{-2} M).

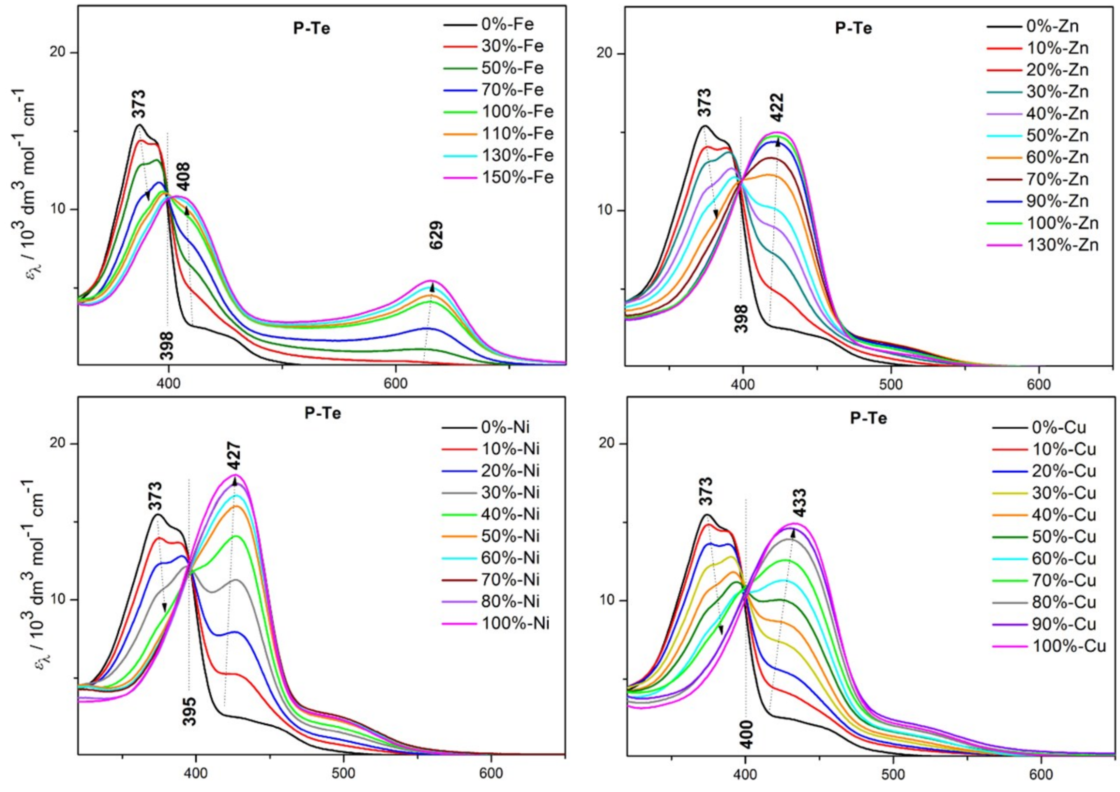


Figure S4 UV/vis titration spectra of **P-Te** (2×10^{-4} M, based on monomer unit) with various metal ions (2×10^{-2} M).

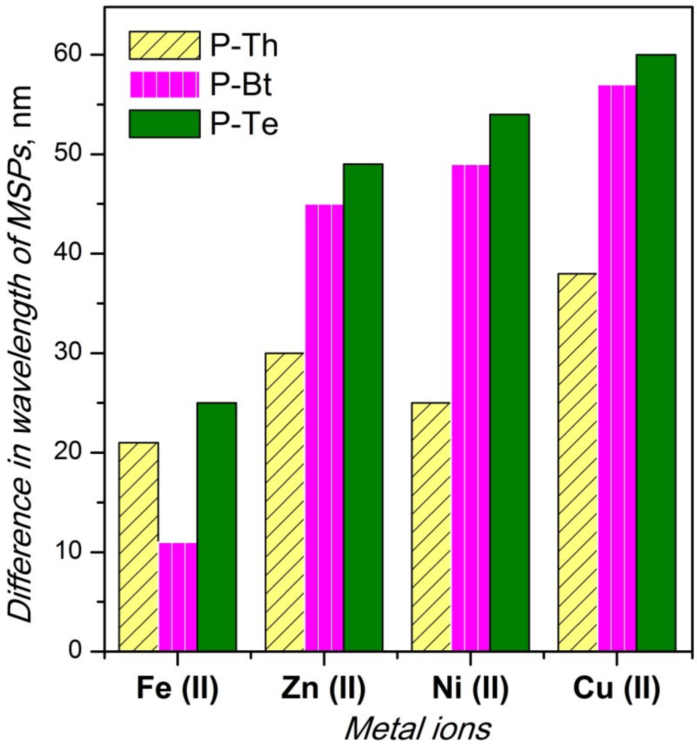


Figure S5 Graphical dependence of redshift differences of (MSP)s based on synthesized unimers and different metal ions. Data are extracted from UV/vis titration experiments of unimers. r = 1

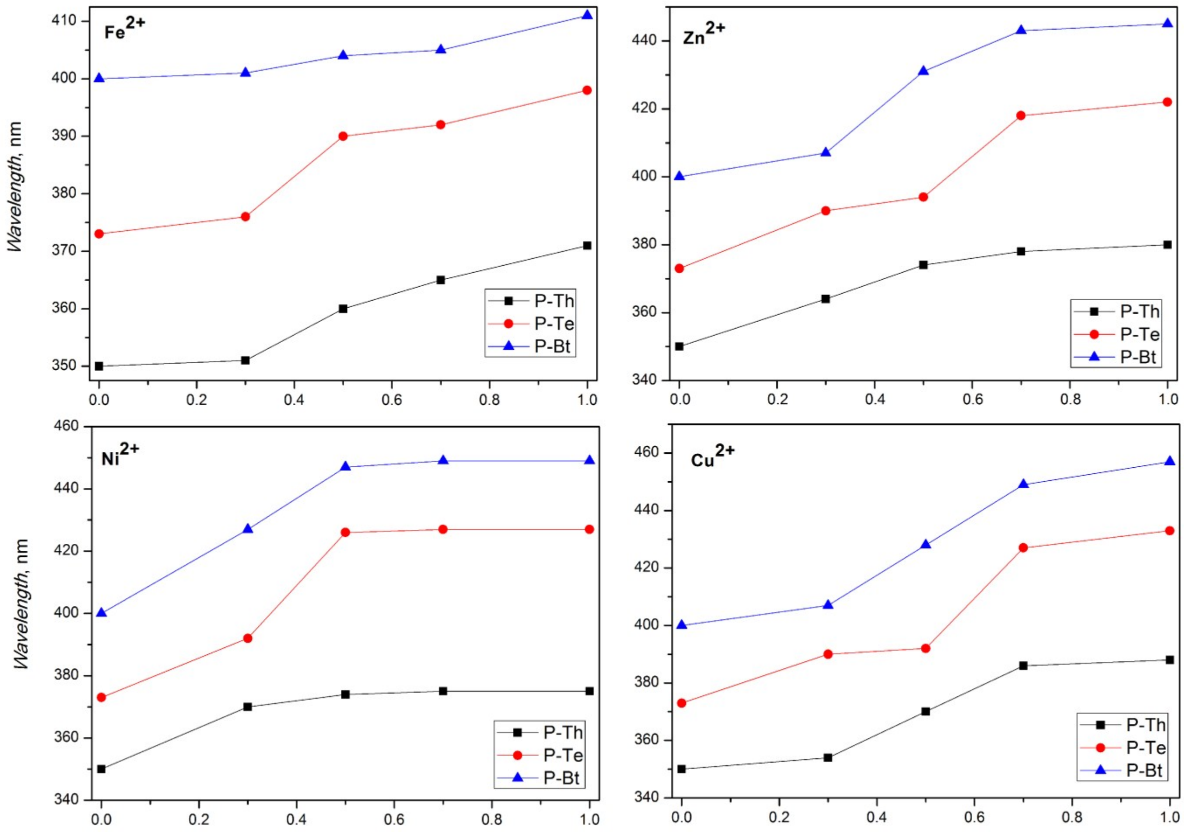


Figure S6 Graphical depiction of redshifts during formation of (MSP)s.

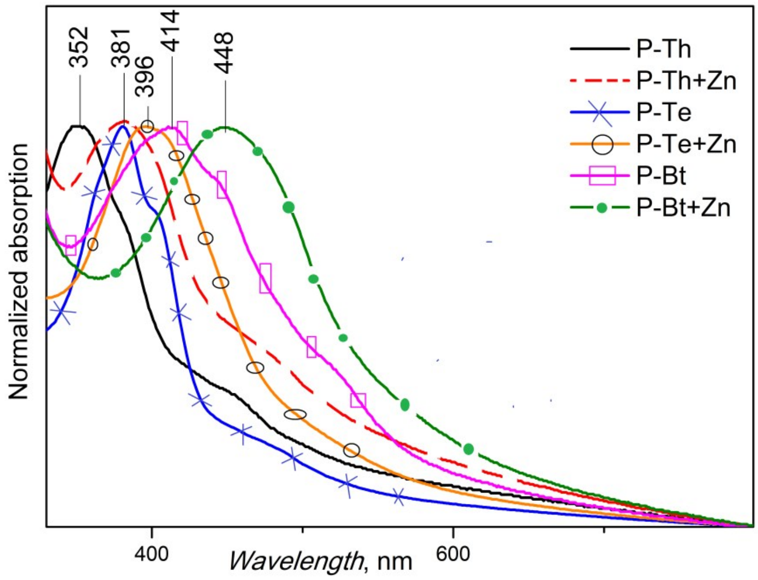


Figure S7 Absorption spectra of solid thin films of **P-Th**, **P-Bt**, **P-Te** and their (MSP)s. Molar ratio between unimer and Zn^{2+} is (1:1).

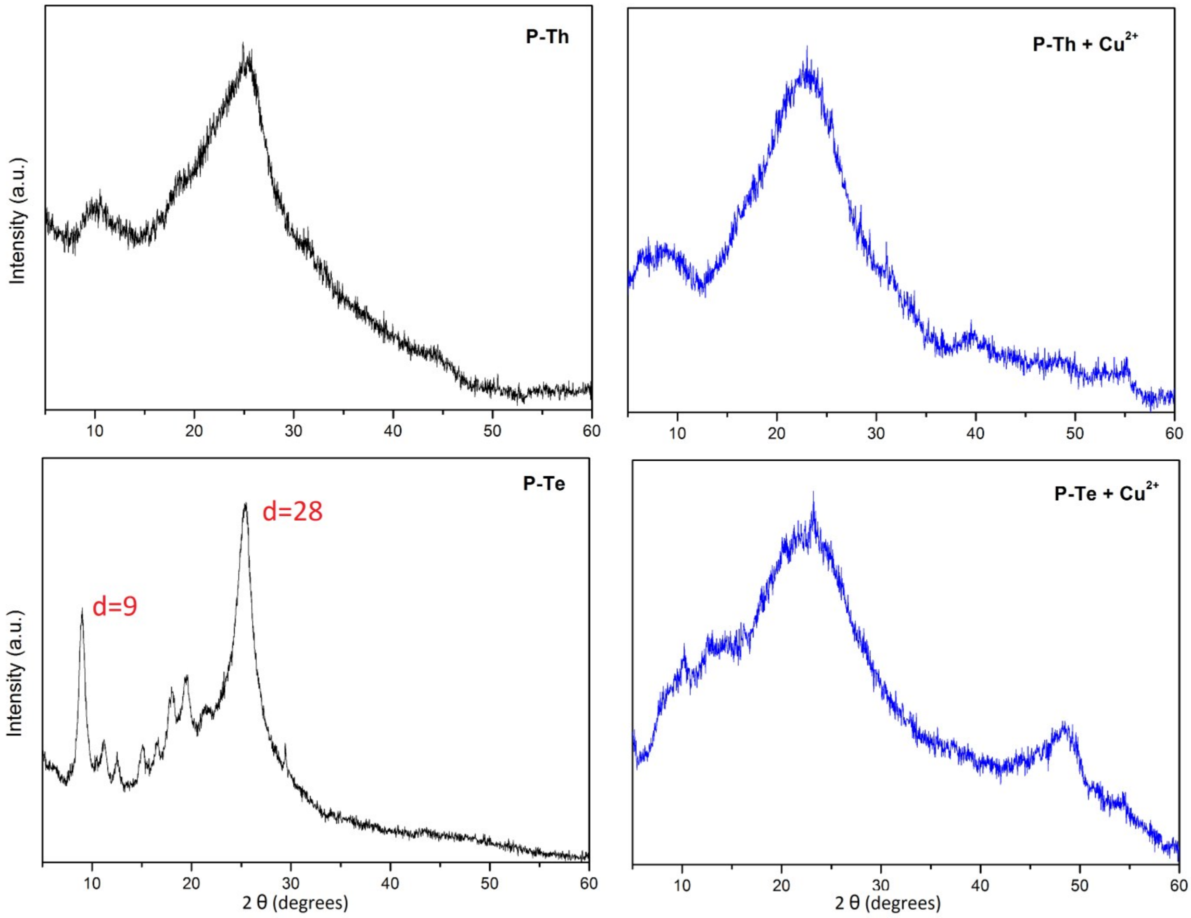


Figure S8 X-ray diffraction patterns of **P-Th**, **P-Te** and their Cu^{2+} based (MSP)s. Molar ratio between unimers and Cu^{2+} is (1:1).

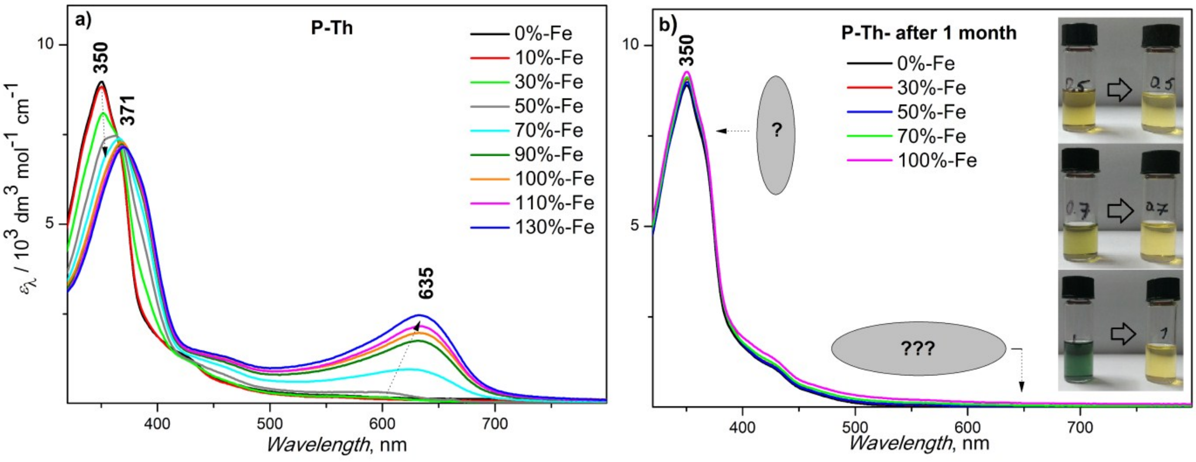


Figure S9 Comparison of UV/vis spectra of **P-Th** after 1 day (a) and 1 month (b).

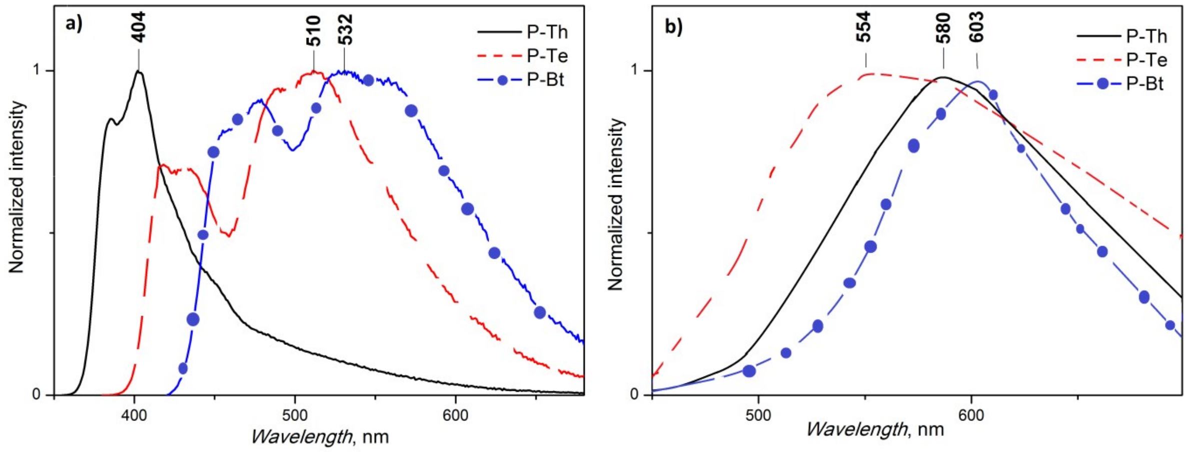


Figure S10 Emission spectra of unimers (**P-Th**, **P-Bt**, **P-Te**) in solution (a) and solid state (b).

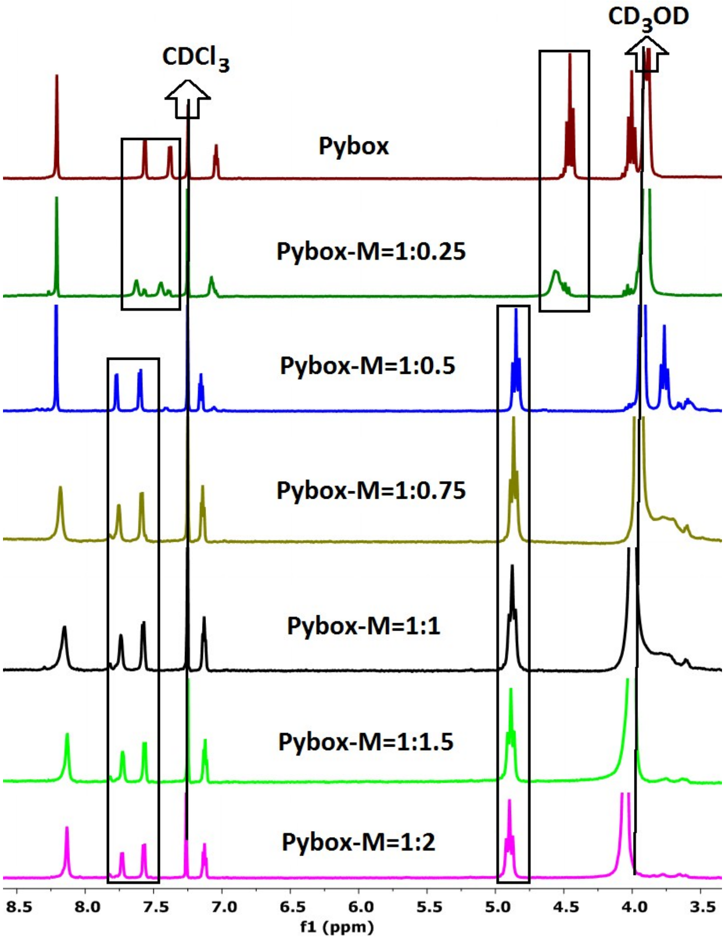


Figure S11 ^{1}H NMR titration of **Pybox-Th** by Zn^{2+} metal ions with different molar ratios in $CDCl_3$ + CD_3OD (1:1)

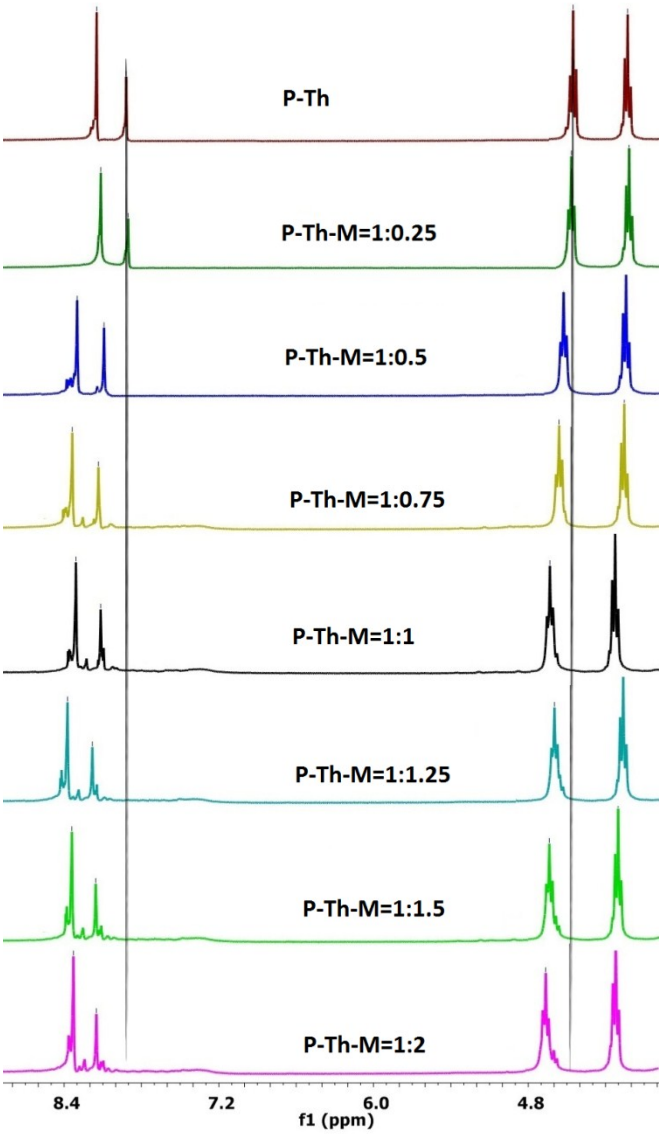


Figure S12 ^{1}H NMR titration of **P-Th** by Zn^{2+} metal ions with different molar ratios in DMSO-d6

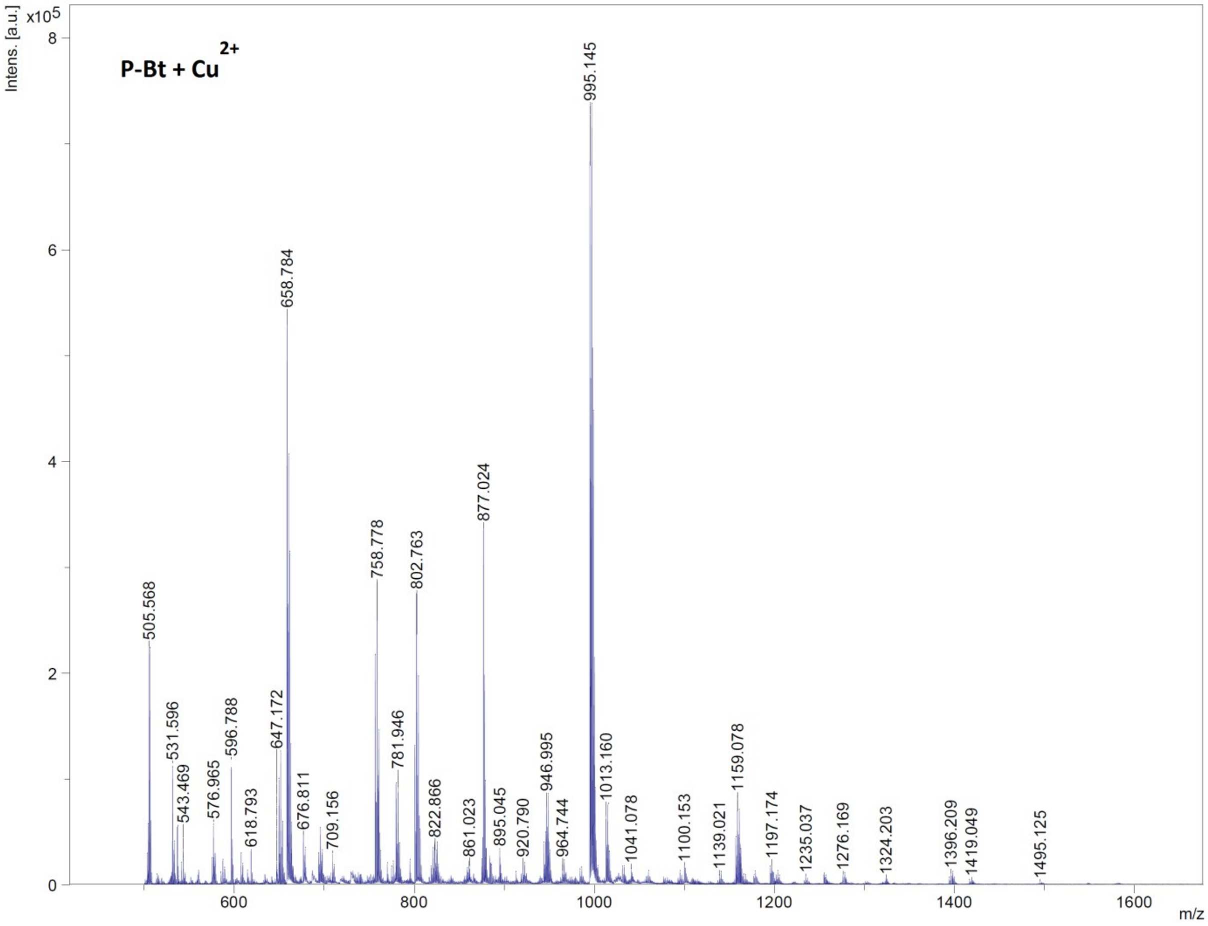
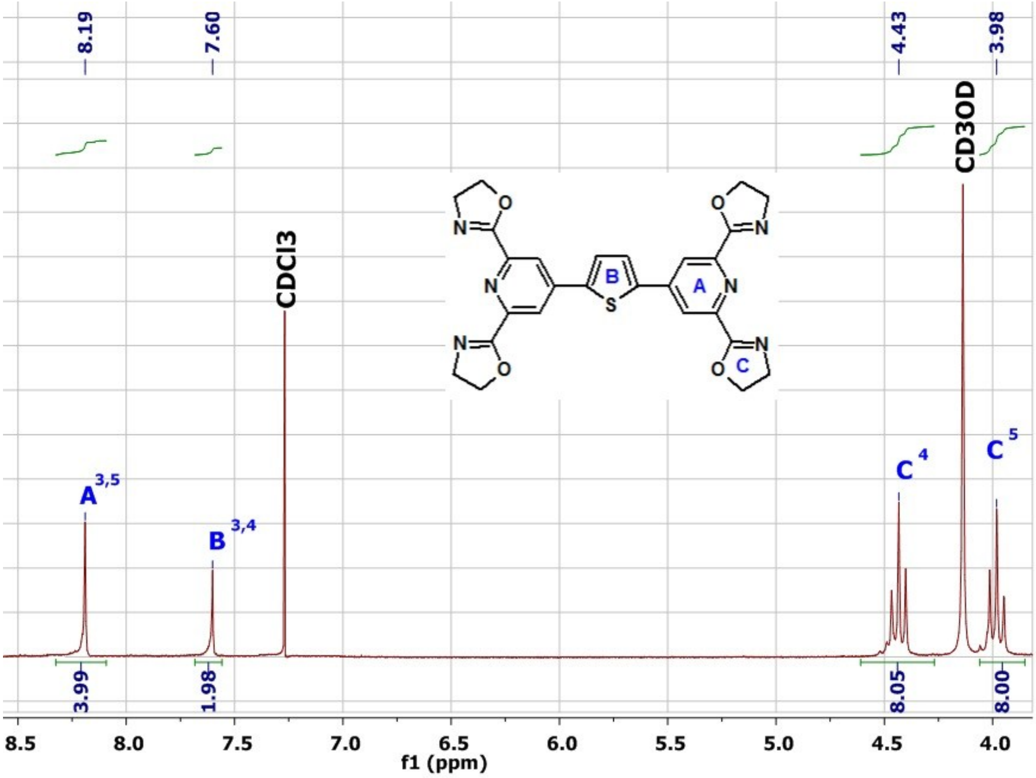


Figure S13 MALDI-TOF spectrum of MSP based on **P-Bt** unimer and Cu^{2+} (IC).

NMR spectra of synthesized unimers



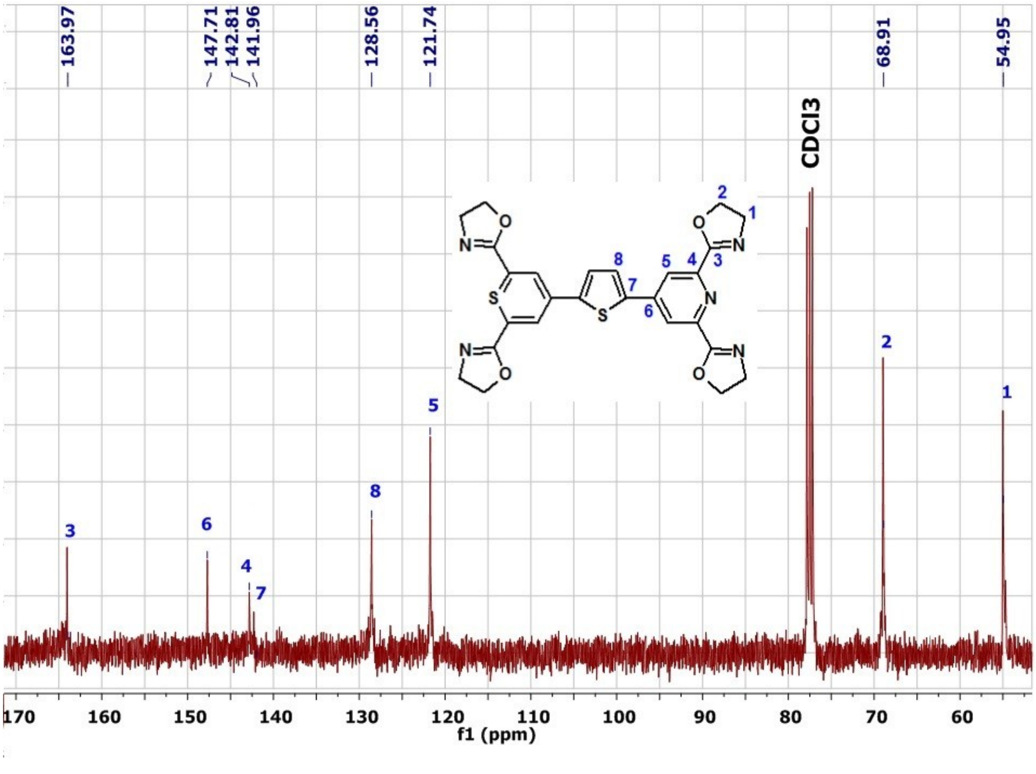


Figure S14 Proton and carbon NMR spectra of **P-Th**

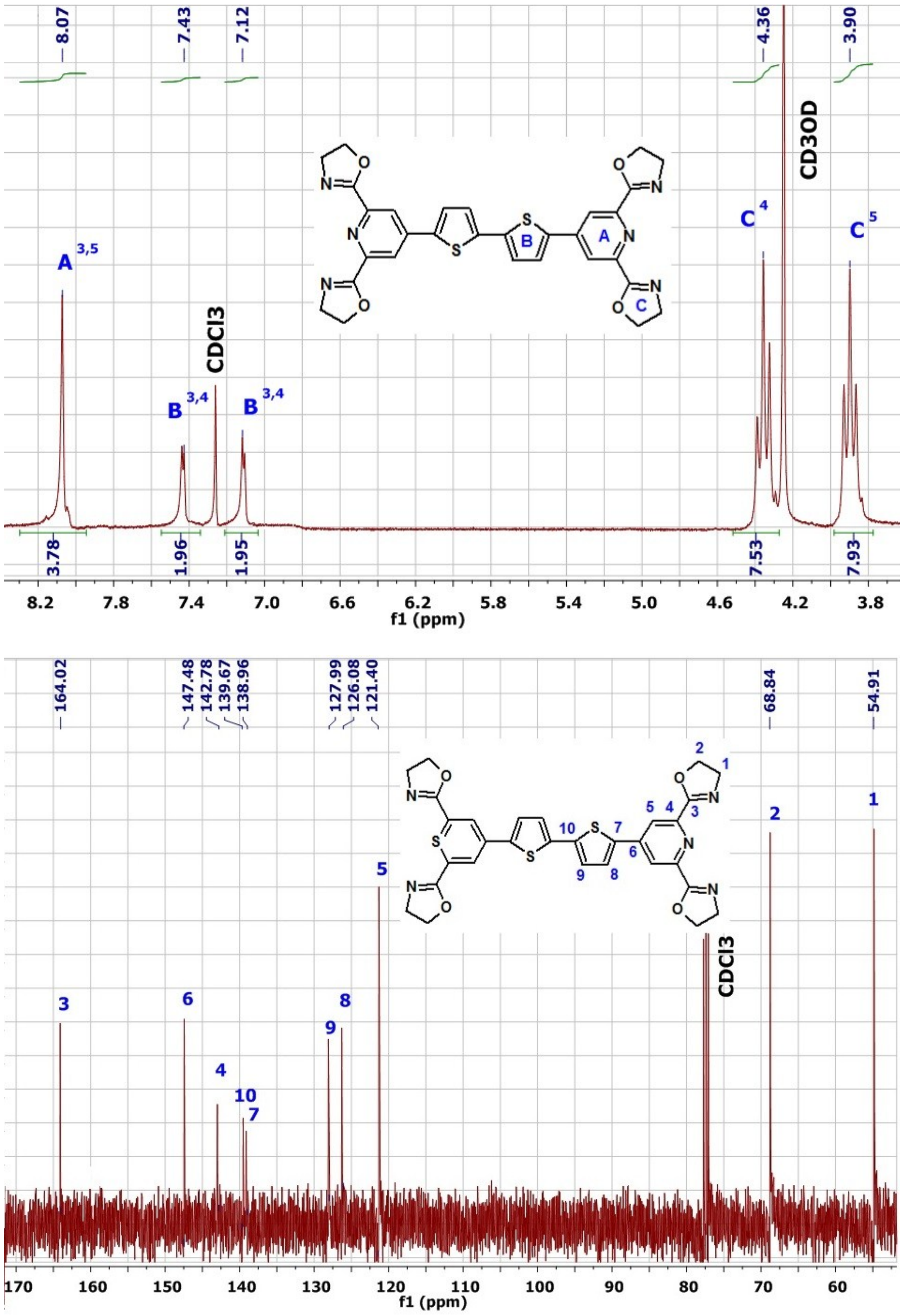


Figure S15 Proton and carbon NMR spectra of **P-Bt**

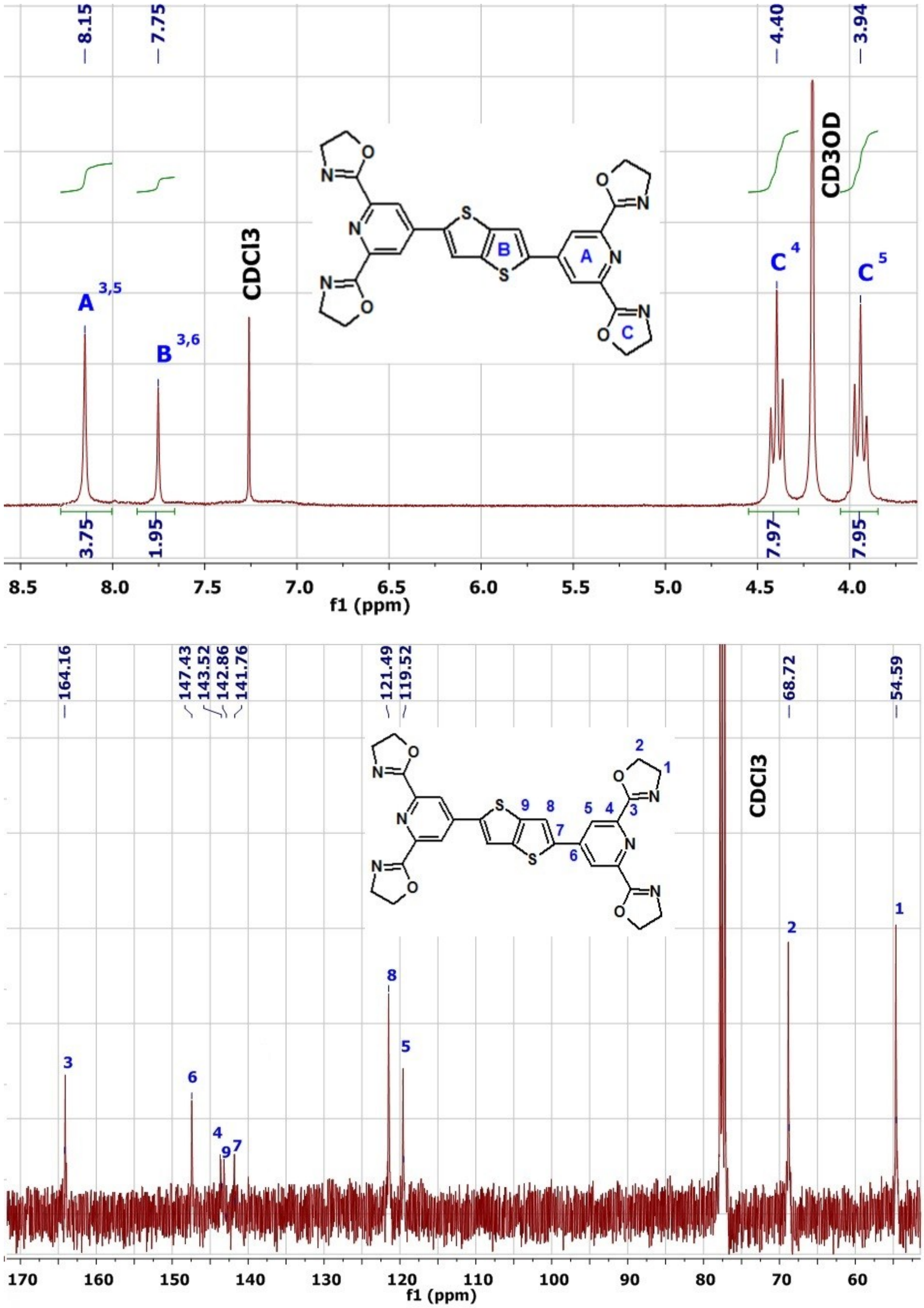


Figure S16 Proton and carbon NMR spectra of **P-Te**