

## Electronic Supporting Information

for

### Catalytic Hydrolysis of Paraoxon by Immobilized Copper(II) Complexes of 1,4,7-Triazacyclononane Derivatives

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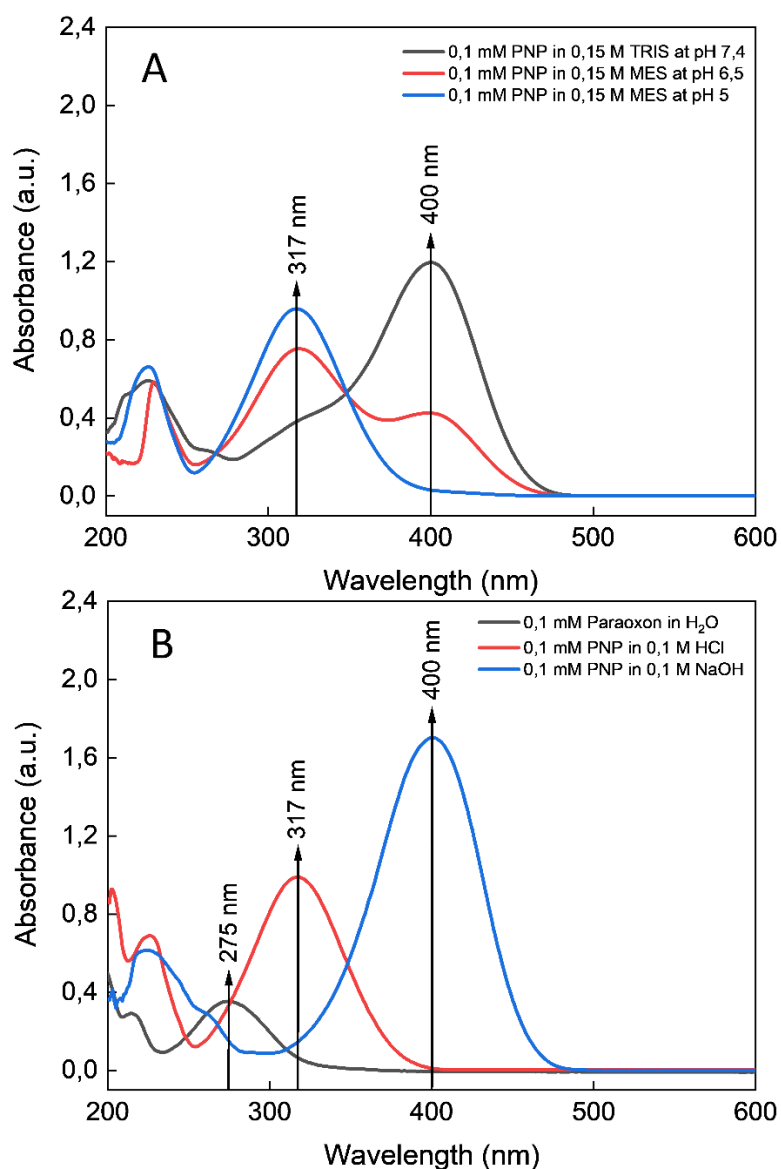


Figure S1: (A) UV-Vis spectra of 4-nitrophenol in selected buffers at various pH: 5 (MES, blue), 6.5 (MES, red) and 7.4 (TRIS, black). (B) UV-Vis spectra of Paraoxon (black), 4-nitrophenol (red) and 4-nitrophenolate (blue).

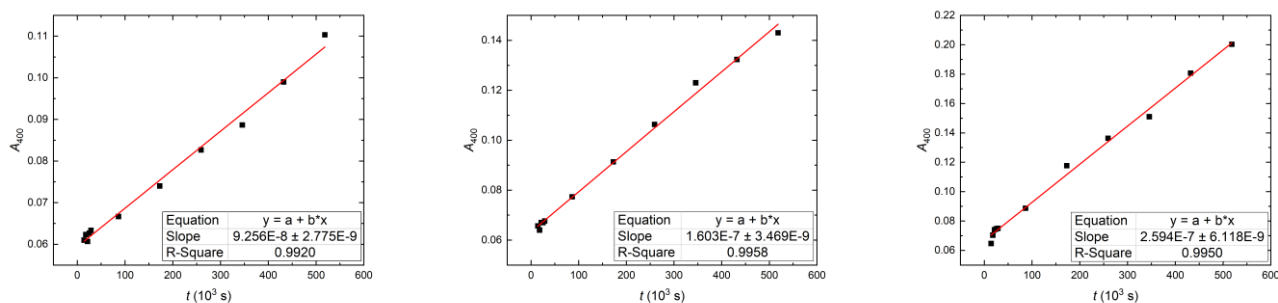


Figure S2: First-order kinetic plots of spontaneous (uncatalyzed) Paraoxon hydrolysis at various temperatures. Conditions:  $c(\text{Paraoxon}) = 1.0 \text{ mM}$ ;  $c(\text{MES}) = 0.15 \text{ M}$  (pH 6.5), temperature (from left to right) 23, 37 and 50 °C, respectively.

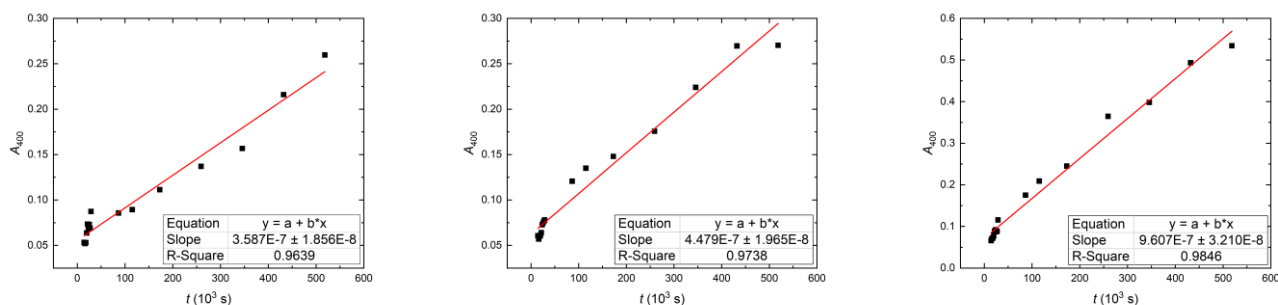


Figure S3: First-order kinetic plots of spontaneous (uncatalyzed) Paraoxon hydrolysis at various temperatures. Conditions:  $c(\text{Paraoxon}) = 1.0 \text{ mM}$ ;  $c(\text{TRIS}) = 0.15 \text{ M}$  (pH 7.4), temperature (from left to right) 23, 37 and 50 °C, respectively.

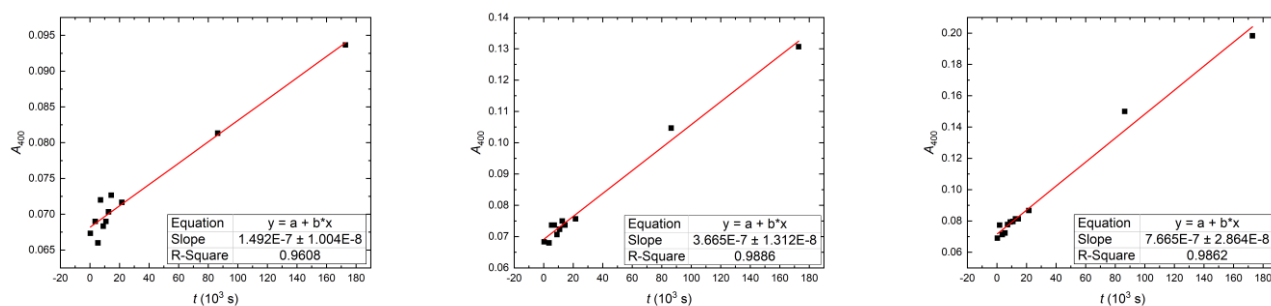
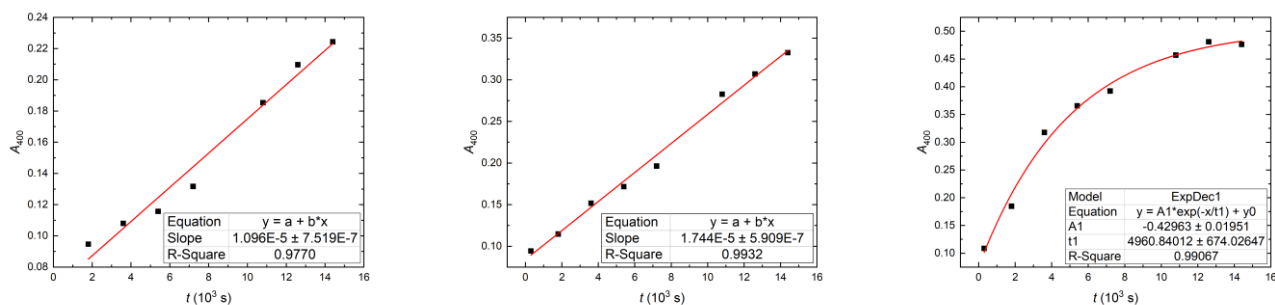
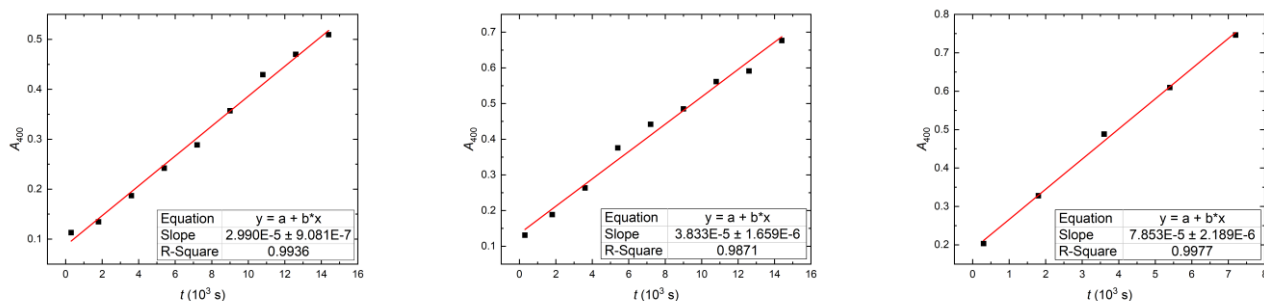


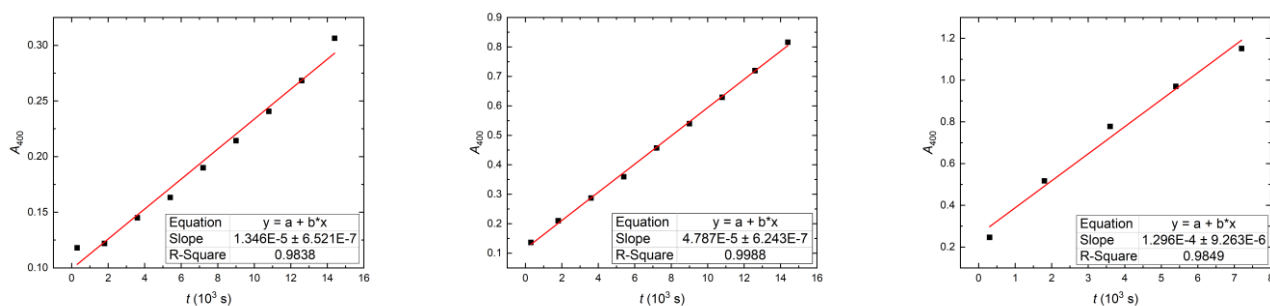
Figure S4: First-order kinetic plots of Paraoxon hydrolysis in the presence of  $\text{CuSO}_4$  at various temperatures. Conditions:  $c(\text{Paraoxon}) = 1.0 \text{ mM}$ ;  $c(\text{CuSO}_4) = 10 \text{ mM}$ ;  $c(\text{TRIS}) = 0.15 \text{ M}$  (pH 7.4), temperature (from left to right) 23, 37 and 50 °C, respectively.



**Figure S5:** First-order kinetic plots of Paraoxon hydrolysis in the presence of Cu-L1 at various temperatures. Conditions:  $c(\text{Paraoxon}) = 1.0 \text{ mM}$ ;  $c(\text{Cu-L1}) = 10 \text{ mM}$ ,  $c(\text{TRIS}) = 0.15 \text{ M}$  (pH 7.4), temperature (from left to right) 23, 37 and 50 °C, respectively.



**Figure S6:** First-order kinetic plots of Paraoxon hydrolysis in the presence of Cu-L2 at various temperatures. Conditions:  $c(\text{Paraoxon}) = 1.0 \text{ mM}$ ;  $c(\text{Cu-L2}) = 10 \text{ mM}$ ,  $c(\text{MES}) = 0.15 \text{ M}$  (pH 6.5), temperature (from left to right) 23, 37 and 50 °C, respectively.



**Figure S7:** First-order kinetic plots of Paraoxon hydrolysis in the presence of Cu-L2 at various temperatures. Conditions:  $c(\text{Paraoxon}) = 1.0 \text{ mM}$ ;  $c(\text{Cu-L2}) = 10 \text{ mM}$ ,  $c(\text{TRIS}) = 0.15 \text{ M}$  (pH 7.4), temperature (from left to right) 23, 37 and 50 °C, respectively.

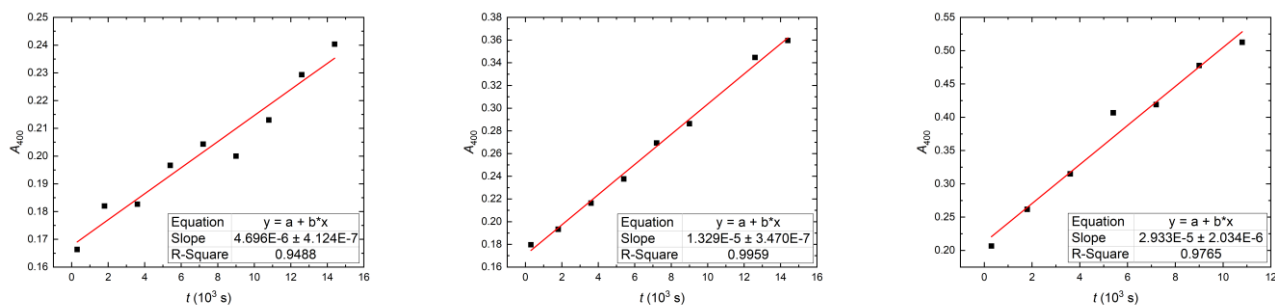


Figure S8: First-order kinetic plots of Paraoxon hydrolysis in the presence of Cu-L2 at various temperatures in EtOH:H2O 3:1 (v:v). Conditions:  $c(\text{Paraoxon}) = 1.0 \text{ mM}$ ;  $c(\text{Cu-L2}) = 10 \text{ mM}$ ,  $c(\text{TRIS}) = 0.15 \text{ M}$  (pH 7.4), temperature (from left to right) 23, 37 and 50 °C, respectively.

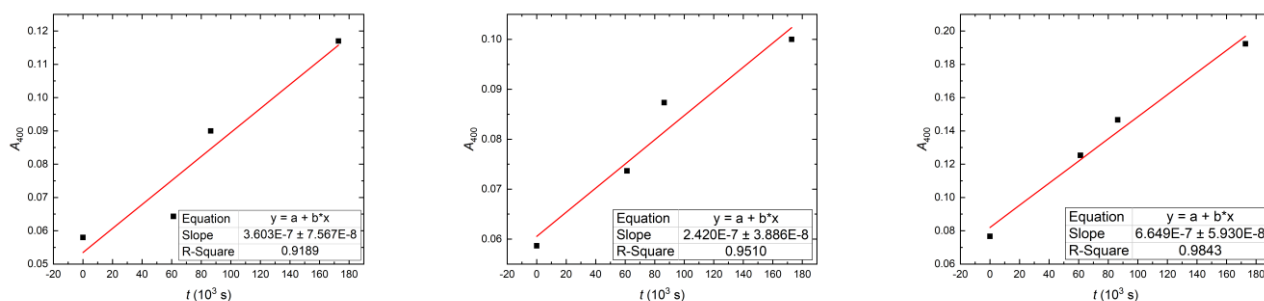
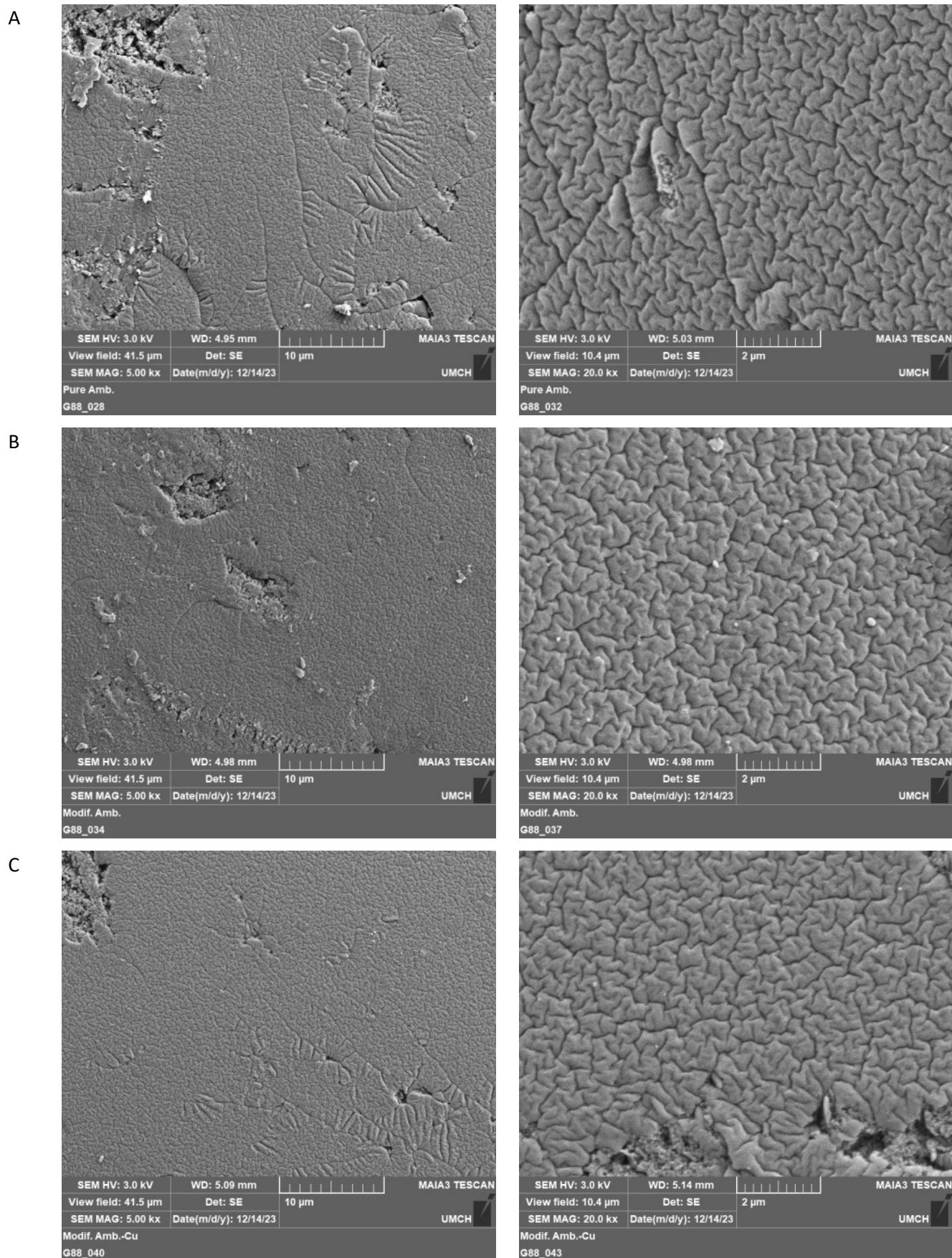


Figure S9: First-order kinetic plots of Paraoxon hydrolysis at 50 °C in the presence of (from left to right): Amberlite beads, Amberlite beads covered with metal-free 2,2'-dithiophene-L1 co-polymer and Amberlite beads covered with 2,2'-dithiophene-L1 co-polymer loaded with Cu(II) ions, respectively. Conditions:  $c(\text{Paraoxon}) = 1.0 \text{ mM}$ ;  $m(\text{beads}) = 30 \text{ mg}$ ,  $c(\text{TRIS}) = 0.15 \text{ M}$  (pH 7.4), temperature 50 °C, volume of the reaction mixture 1 mL.



*Figure S10:* Morphology of materials studied by scanning electron microscopy. A) Native Amberlite beads. B) Amberlite beads covered with 2,2'-dithiophene–**L1** co-polymer. C) Final material after loading with Cu(II).

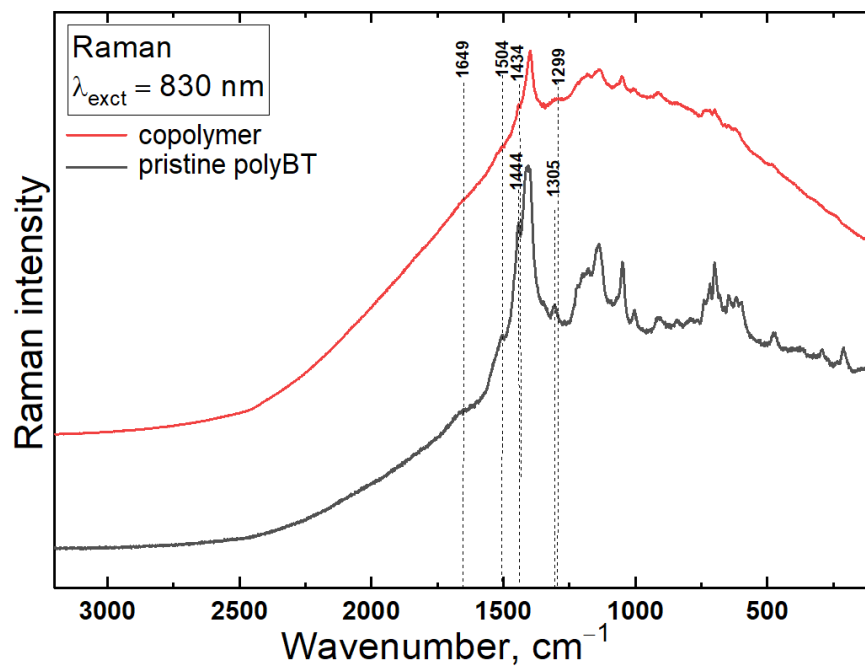


Figure S11. Raman spectra of pristine poly-2,2'-dithiophene and 2,2'-dithiophene-L1 copolymer measured with 830 nm laser excitation.

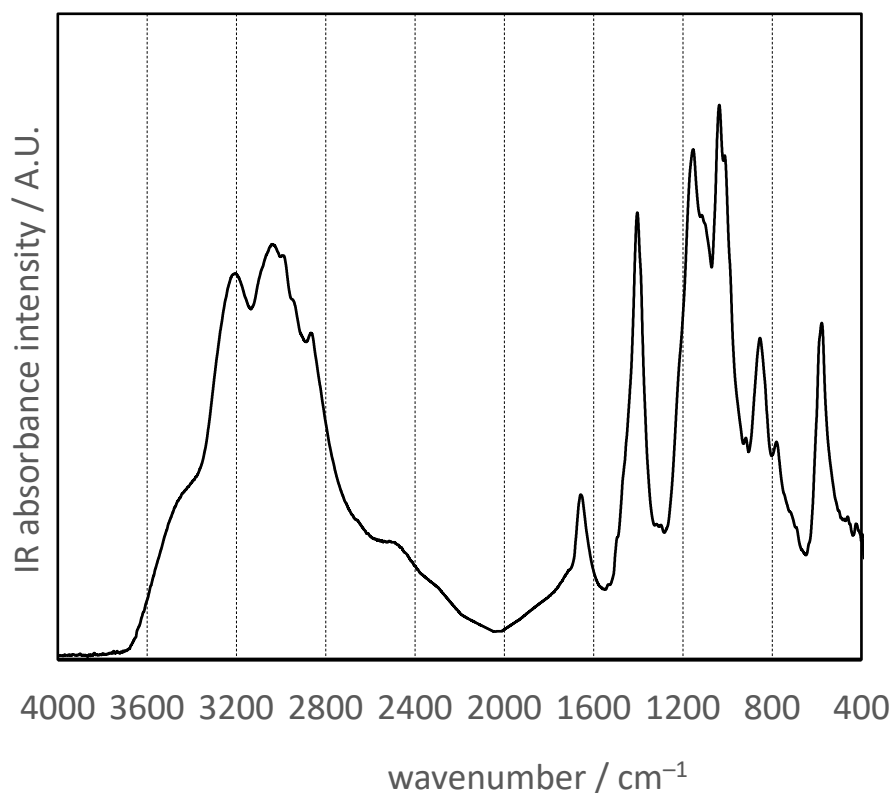
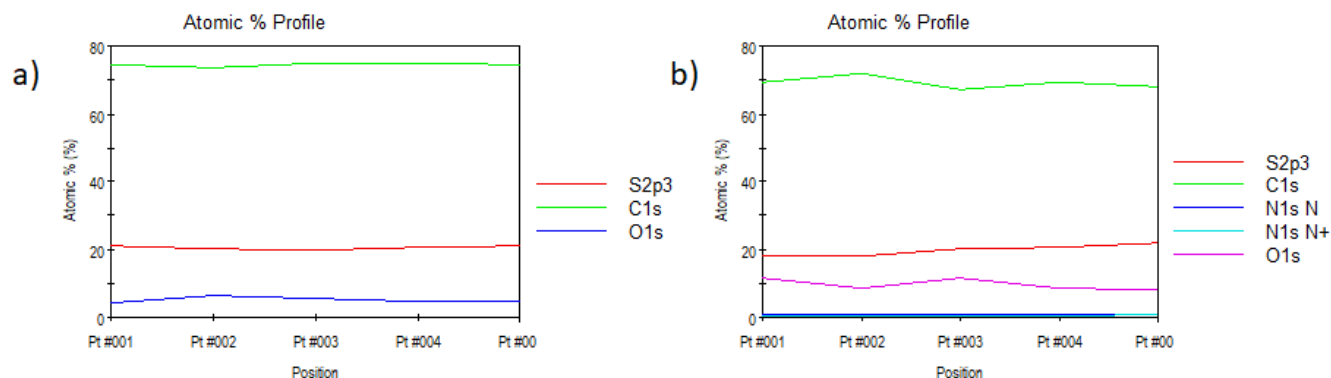


Figure S12. FTIR ATR spectrum of the 2,2'-dithiophene-L1 copolymer. Band at 2850–2880  $\text{cm}^{-1}$  indicates presence of aliphatic C–H bonds due to successful incorporation of L1 into the copolymer.



**Figure S13.** Graphical representations of the results of XPS measurements of a) pristine poly-2,2'-dithiophene and b) 2,2'-dithiophene-L1 copolymer. Five different areas in the individual samples were measured. Source data are listed in Table S1.

**Table S1.** Compilation of XPS results (Atomic %) obtained for pristine poly-2,2'-dithiophene and 2,2'-dithiophene-L1 copolymer. Five different areas in the individual samples were measured.

pristine poly-2,2'-dithiophene					
atom/orbital	sample 1	sample 2	sample 3	sample 4	sample 5
S2p3	21.1495	20.0058	19.838	20.4728	20.9493
C1s	74.5181	73.3673	74.727	74.6528	74.3025
O1s	4.33241	6.62687	5.43502	4.87444	4.74814

2,2'-dithiophene-L1 copolymer					
atom/orbital	sample 1	sample 2	sample 3	sample 4	sample 5
S2p3	18.0892	17.9351	20.0409	20.838	21.9588
C1s	69.0679	71.6147	67.1985	69.0517	68.0765
N1s N	0.791331	1.02867	0.836626	1.05083	0.987052
N1s N+	0.606294	0.620065	0.525804	0.535162	0.746058
O1s	11.4453	8.80146	11.3982	8.52434	8.23168