

Supporting Information for

A TpyRu²⁺-based *bis*metallopolymer and its performance in catalytic water oxidation (Tpy=2,2':6',2''-terpyridine)

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Materials and Methods:

¹H and ¹³C NMR spectra were recorded on a Bruker ADVANCE 500 NMR Spectrometer. ¹H NMR chemical shifts are reported in ppm downfield from Me₄Si (TMS, as an internal standard) using the specified deuterated solvent. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer. Absorption spectra were measured with Hitachi (Model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell. Cyclic voltammetry (CV) was performed with a Zahner IM6 electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, and a Hg/Hg₂Cl₂ electrode, as the reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) was dissolved in MeCN and employed as the supporting electrolyte. The plot includes the signal of the ferrocene, as an internal potential marker.

X-ray crystallography Diffraction data of **TpyRu-Ag Polymer** was recorded on a Bruker CCD diffractometer with monochromatized Mo-K radiation ($\lambda = 0.71073 \text{ \AA}$). The collected frames were processed with the software SAINT. Data collection and reduction were carried out using CrysAlisPro program. Absorption correction was performed using SADABS built-in the CrysAlisPro program suite. Structure was solved by direct methods and refined by full-matrix least-squares on F² using the SHELXTL-97 software package. Atomic positions of non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were introduced at their geometric positions and refined as riding atoms.

Oxygen Measurements

All catalyst in 100 μ L of acetonitrile was respectively introduced into a solution containing 500 equiv of ceric ammonium nitrate as a sacrificial oxidant. During the first 50 min of reaction, the initial rate of oxygen evolution was measured by a Clark electrode (YSI 5331) immersed in the solution by a YSI 5300A Biological Oxygen Monitor.

Ce (IV) - driven water catalytic oxidation were achieved in acidic conditions (pH 1.0, adjusted by CF₃SO₃H). The turnover number (TON) was determined on Shimadzu GC-2014C. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. A Thummel-type mono-Ru catalyst^{S1} as a catalytic water oxidative comparison or standard had been synthesized according to the literature procedure.

A single point reset was performed for each catalytic run. A round bottom flask equipped with T bore Teflon plugs was used to purge the flask and facilitate oxidant injection and also played the O₂ probe. The total working volume is 34 ml. The gas tight vessel was equipped with a stir bar and placed in a temperature controlled water bath (28 °C) containing the CeIV-

pH=1 (CF₃SO₃H). In a typical experiment, the flask was charged with aqua-CF₃SO₃H and the headspace was purged with Argon for ca. 20 min until a stable reading was obtained followed by the injection of a degassed aqueous solutions of aqua-ruthenium complex injection.

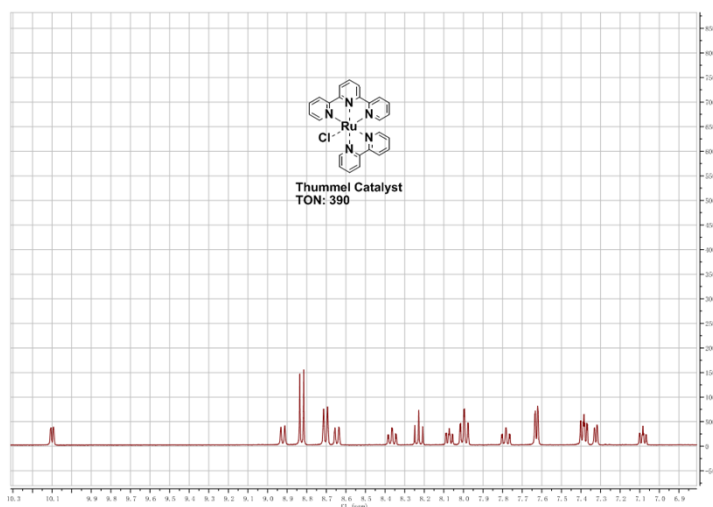


Figure S1: ¹H NMR spectrum of synthesized Thummel Catalyst^{S1}

Detected curves of monomer 2 and polymer 3 analyzed by GC-TCD.

GC-TCD 0.5 ml headspace gas analyze of all complexes with CAN (2.736mmol) in 10 ml of H₂O reaction. Mole of complexes: metallo-organic monomer 2 (1.0×10^{-4} mmol) and metallo-polymer 3 (1.2×10^{-4} mmol), Thummel standard (3.14×10^{-4} mmol).

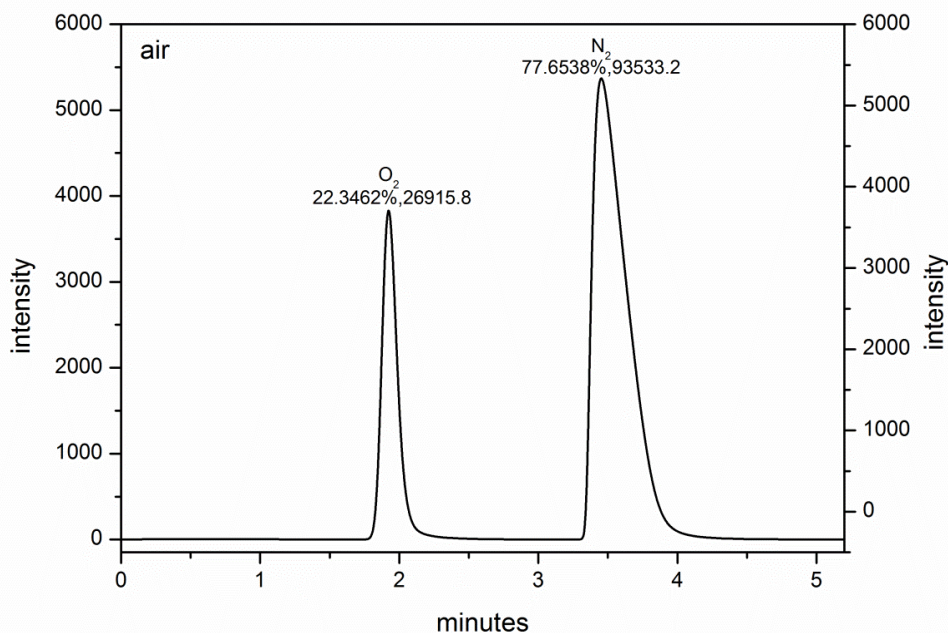


Figure S2: GC-TCD measured O₂ and N₂ peaks from air.

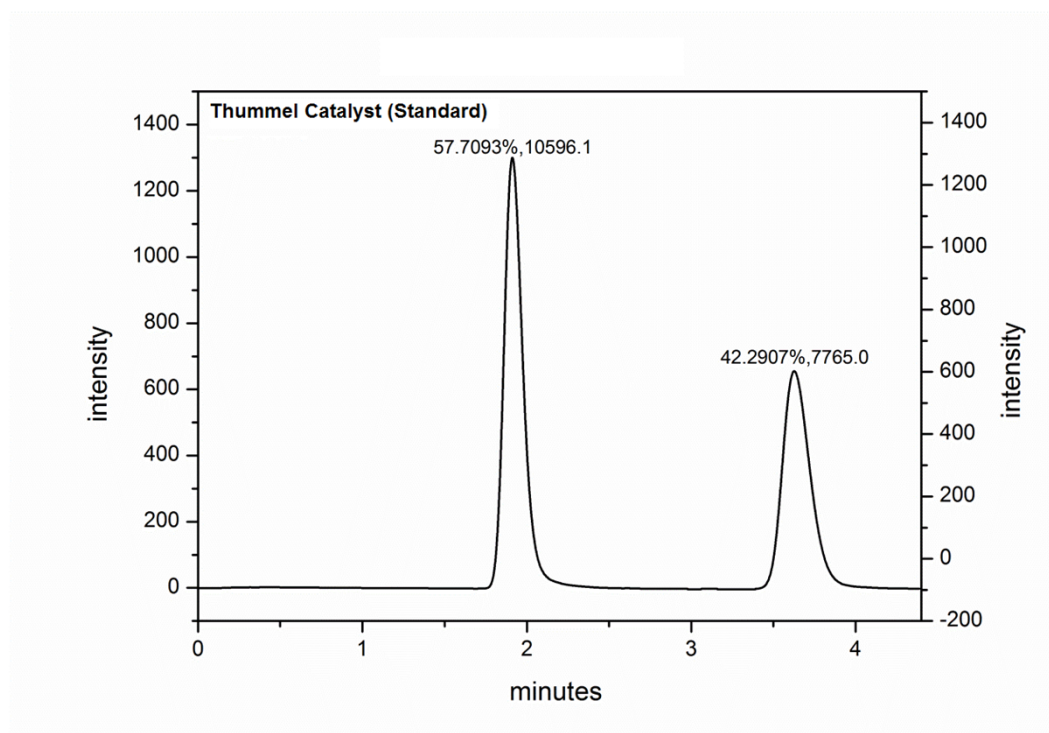


Figure S3: GC-TCD measured O₂ and N₂ peaks by using Thummel Catalyst as the catalytic water oxidation.

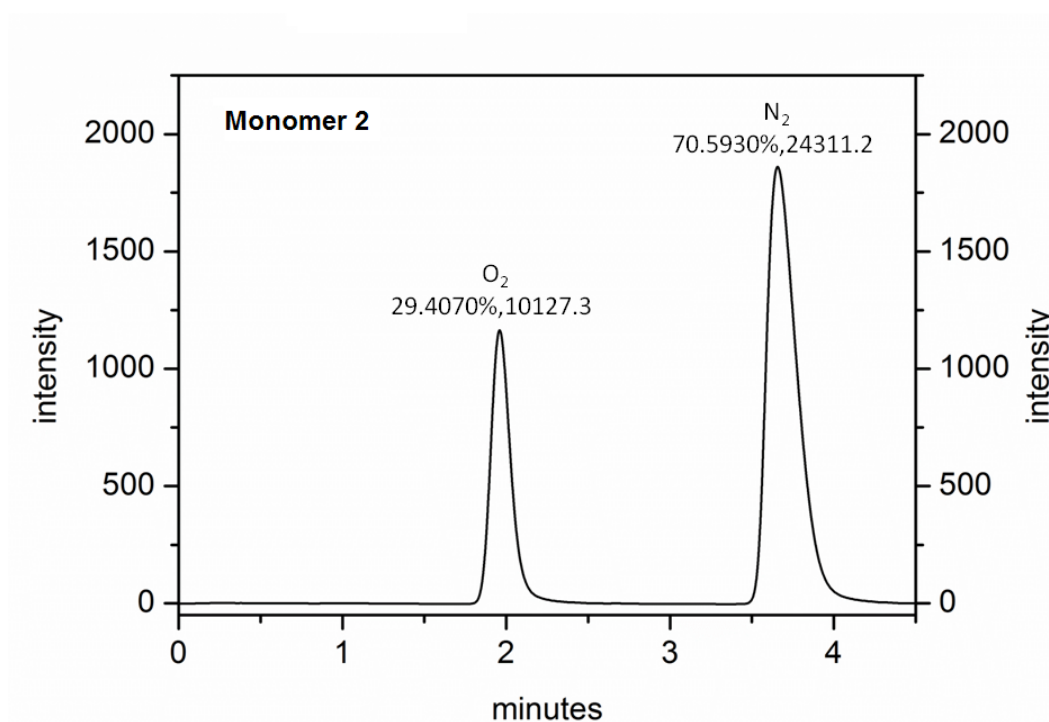


Figure S4: GC-TCD measured O₂ and N₂ peaks by using Monomer 2 as the catalytic water oxidation.

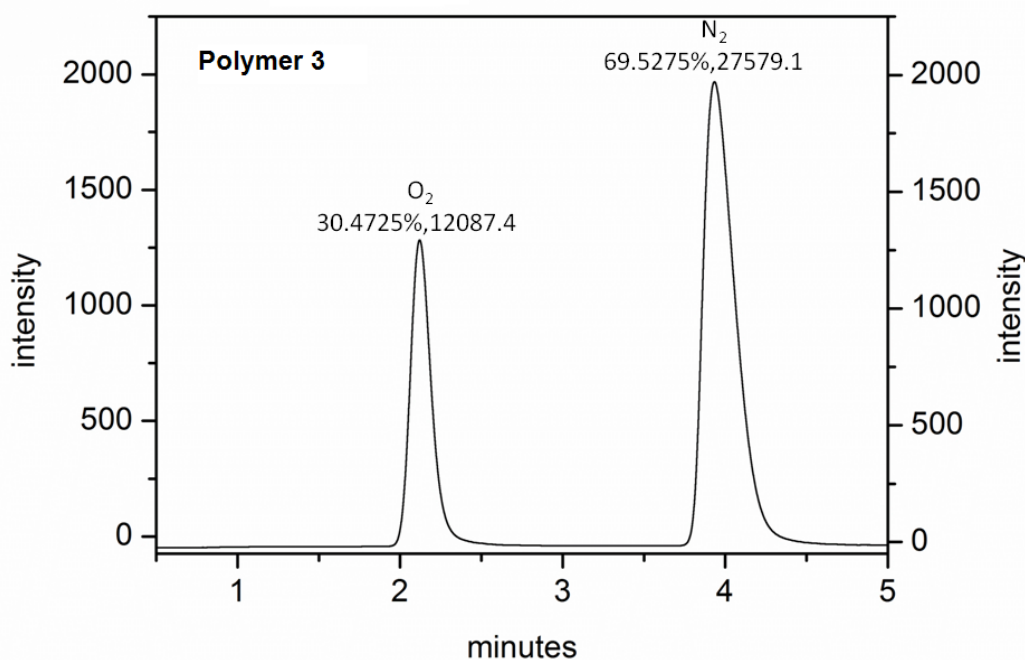


Figure S3: GC-TCD measured O₂ and N₂ peaks by using Polymer 3 as the catalytic water oxidation.

Synthesis and characterization of monomer 2 and the preparation of polymer 3.

The terpyridine ligand and TpyRuCl₃ 1 were synthesized according to literature procedures.^{S2}

Terpyridine Ligand:

¹H NMR (500 MHz, 298 K, CDCl₃, ppm) δ = 8.75 (d, 2H), 8.72 (s, 2H), 8.68 (d, 2H), 7.89 (m, 4H), 7.37 (t, 2H), 7.04 (d, 2H), 3.89 (s, 3H).

Monomer 2:

TpyRuCl₃ (142 mg, 0.026 mmol) and pyrazine (103 mg, 1 mmol) was added to a 50 mL flask, then 5 ml ethylene glycol was added as solvent. The suspension was stirred at 120 °C for 24 hours. After cooled to ambient temperature, the solution was slowly dropped to the diethyl ether to generate a red precipitant. The precipitant was resolvable in MeOH and purified by Al₂O₃ gel chromatography to afford Monomer 3 (113 g, 65 %) as a dark red solid. ¹H NMR (500 MHz, 298 K, CD₃OD, ppm) δ = 9.23 (d, 2H), 8.88 (s, 2H), 8.74 (d, 2H), 8.27 (d, 4H), 8.22 (d, 4H), 8.18 (t, 2H), 8.09 (d, 2H), 8.84 (t, 2H), 7.19 (d, 2H), 3.92 (s, 3H). ¹³C NMR (500 MHz, CD₃OD, ppm) δ = 163.24, 161.35, 160.37, 154.05, 149.04, 148.39, 145.43, 139.59, 130.10, 130.02, 129.88, 125.93, 122.20, 116.00, 56.05. MS (EI): m/z = 636.00 (calcd for [M-Cl]⁺: 636.09). MP: >300°C.

Polymer 3:

The exact amount of AgPF₆ was partially added to monomer 2 (25 mg) in CH₃CN solution at ambient temperature, and then the solution was stirred for another half an hour. After filtered the precipitation, the solvent was removed; the collected solid was sonicated with MeOH for 30 mins. The red solid was collected (85%) by filtration and washed with D. I. Water and MeOH. MP: >300°C.

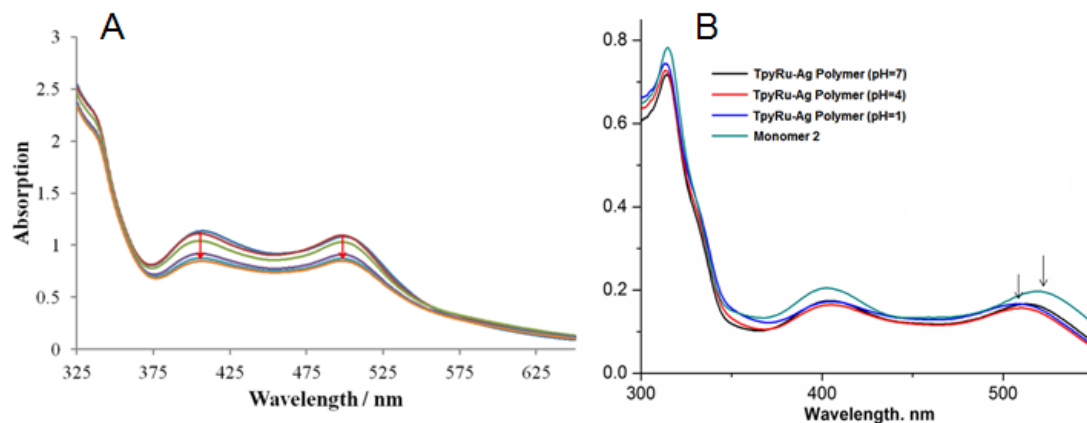
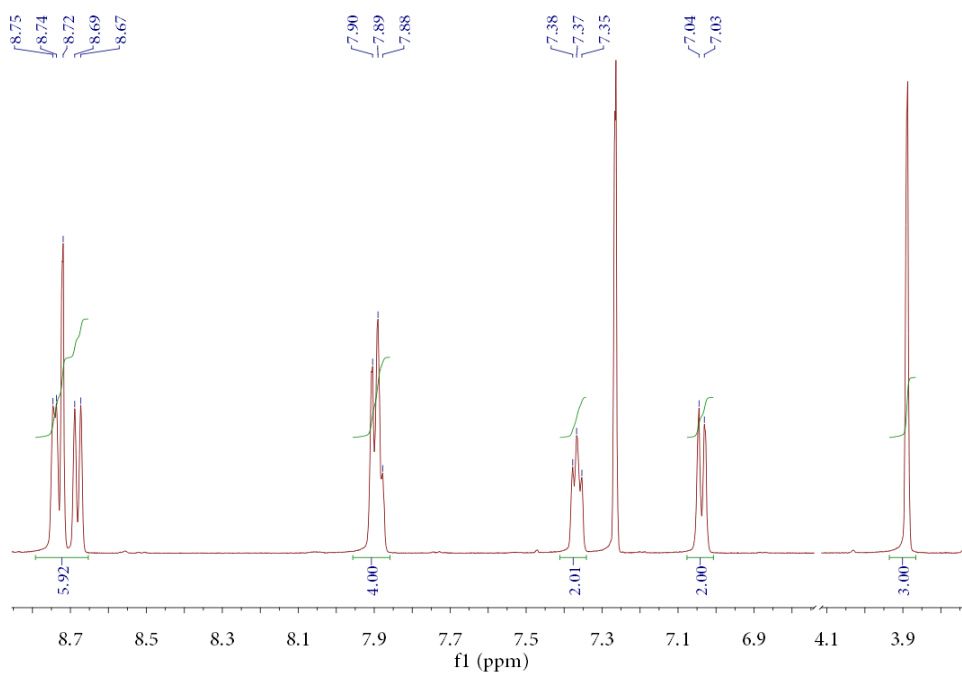
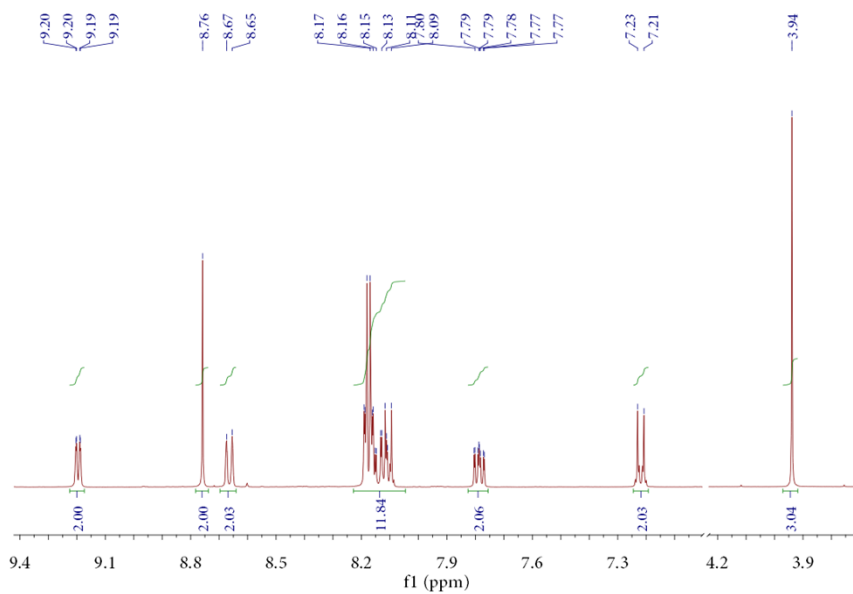


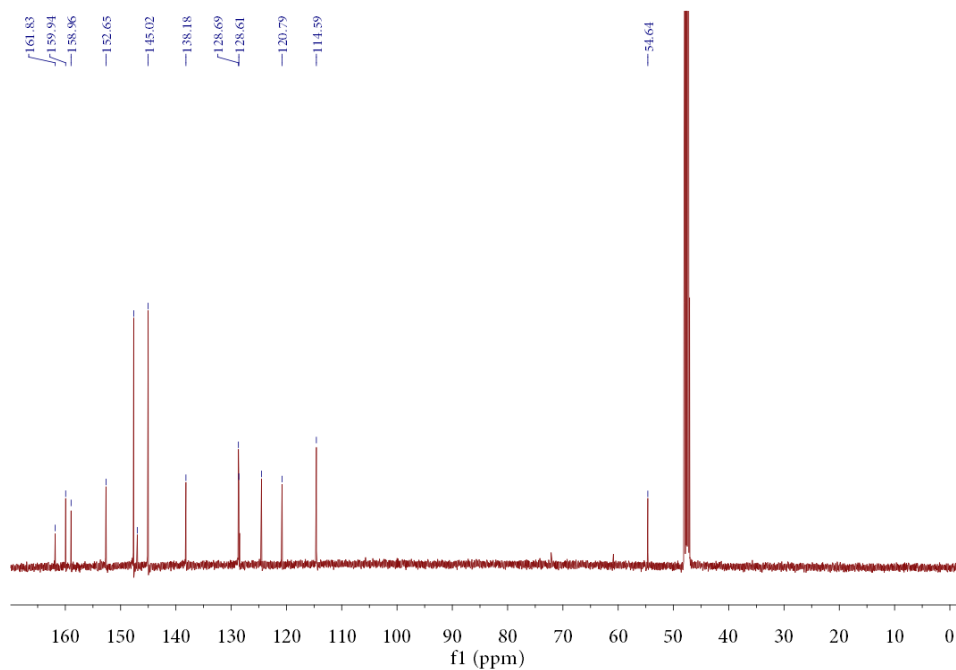
Figure S4. A: Time-dependent UV-Vis spectral shift of complex 2 in CH₃OH after adding with excess AgPF₆. B: UV-vis spectrum upon Monomer 2 (pH=7.0, 3.3 × 10⁻⁵M, green) and TpyRu-Ag polymer (black: pH=7; red: pH=4; blue: pH=1.0)



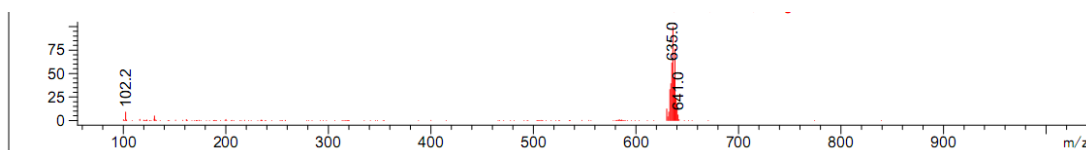
¹H NMR spectrum of terpyridine ligand in CDCl₃

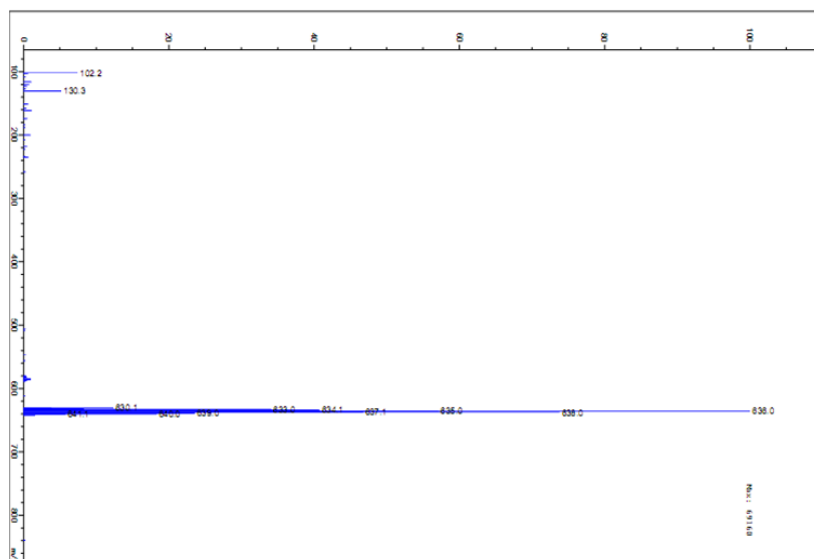


¹H NMR spectrum of Monomer 2 in CD₃CN.



¹³C NMR spectrum of Monomer 2 in CD₃OD





ESI-MS spectrum of monomer 2

References:

- S1. a) H.-W. Tseng, R. Zong, J. T. Muckerman and R. Thummel, *Inorg. Chem.*, 2008, **47**, 11763; b) D. J. Wasylenko, C. Ganesamoorthy, B. D. Koivisto, M. A. Henderson and C. P. Berlinguette, *Inorg. Chem.*, 2010, **49**, 2202.
- S2. U. S. Schubert, H. Hofmeier, G. R. Newkome, *Modern Terpyridine Chemistry*, Wiley-VCH, Verlag GmbH & Co. KGaA, Weinheim 2006.