

# CHEMISTRY

## A **European** Journal

### Supporting Information

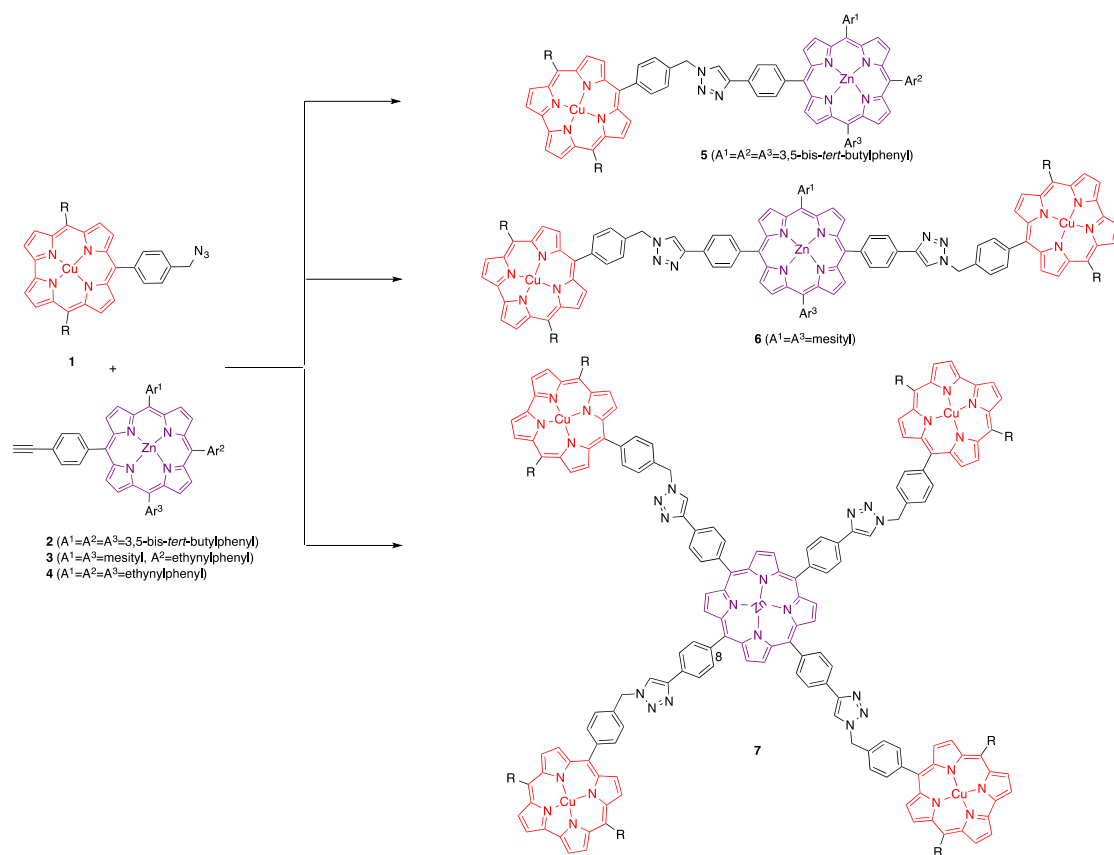
#### **Engaging Copper(III) Corrole as an Electron Acceptor: Photoinduced Charge Separation in Zinc Porphyrin–Copper Corrole Donor–Acceptor Conjugates**

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## Contents

Synthesis Scheme .....	S2
1.0 Synthetic details for triad <b>6</b> and pentad <b>7</b> .....	S3
2.0 Spectroscopic data for dyad <b>5</b> .....	S6
3.0 Spectroscopic data for triad <b>6</b> .....	S10
4.0 Spectroscopic data for pentad <b>7</b> .....	S14



**Scheme S1. Click synthesis of the conjugates 5, 6 and 7**

## 1.0 Synthetic methods for Triad 6 and Pentad 7

Method (a) described in the main manuscript was not investigated for the synthesis of compounds **6** and **7**.

### Triad 6

Method (b):  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (8 mg,  $3.2 \times 10^{-5}$  mol, 2.6 eq.) and ascorbic acid (6 mg,  $3.2 \times 10^{-5}$  mol, 2.6 eq.) were added to a solution of porphyrin **3** (10 mg,  $1.23 \times 10^{-5}$  mol, 1 eq.) and corrole **1** (23 mg,  $3.2 \times 10^{-5}$  mol, 2.6 eq.) in dry DMF (3mL) under an argon atmosphere. After stirring for 2 d at 50°C the reaction mixture was partitioned between dichloromethane (20 mL) and water (20 mL) and the layers were separated. The organic layer was washed with  $\text{H}_2\text{O}$  ( $3 \times 20$  mL), dried over  $\text{Na}_2\text{SO}_4$  and the solvent removed under reduced pressure. The crude product was purified by size exclusion chromatography (Biobeads SX-1, tetrahydrofuran) affording the corrole-porphyrin triconjugate **6** as a brown solid (24.9 mg, 89%).

Method (c):  $\text{CuI}$  (1 mg,  $5.25 \times 10^{-6}$  mol, 0.4 eq.), DIPEA (1 mg,  $7.74 \times 10^{-6}$  mol, 0.6 eq.) and acetic acid (1 mg,  $1.67 \times 10^{-5}$  mol, 1.4 eq.) were added to a solution of porphyrin **3** (10 mg,  $1.23 \times 10^{-5}$  mol, 1 eq.) and corrole **1** (18 mg,  $2.48 \times 10^{-5}$  mol, 2 eq.) in dry dichloromethane (3 mL). The reaction mixture was stirred for 1 d at r.t. The crude product was purified by size exclusion chromatography (Biobeads SX-1, tetrahydrofuran) affording the corrole-porphyrin triconjugate **6** as a brown solid (20,4 mg, 73%).

Method (d): A solution of azidocorrole **1** (36.2 mg,  $5.44 \times 10^{-5}$  mol), porphyrin **3** (20.2 mg,  $3.08 \times 10^{-5}$  mol) and  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (16 mg,  $4.29 \times 10^{-5}$  mol) in 4 mL DCM was stirred at 80 °C under  $\text{N}_2$  atmosphere. The reaction was monitored by t.l.c. After completion, water (20 mL) was added and the mixture was extracted with DCM ( $3 \times 20$  mL). The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$  and solvent evaporated under reduced pressure. After purification by size exclusion chromatography (Biobeads SX-1, chloroform) 55.4 mg (99%) of triad **6** was obtained as a brown solid.

#### **Pentad 7.**

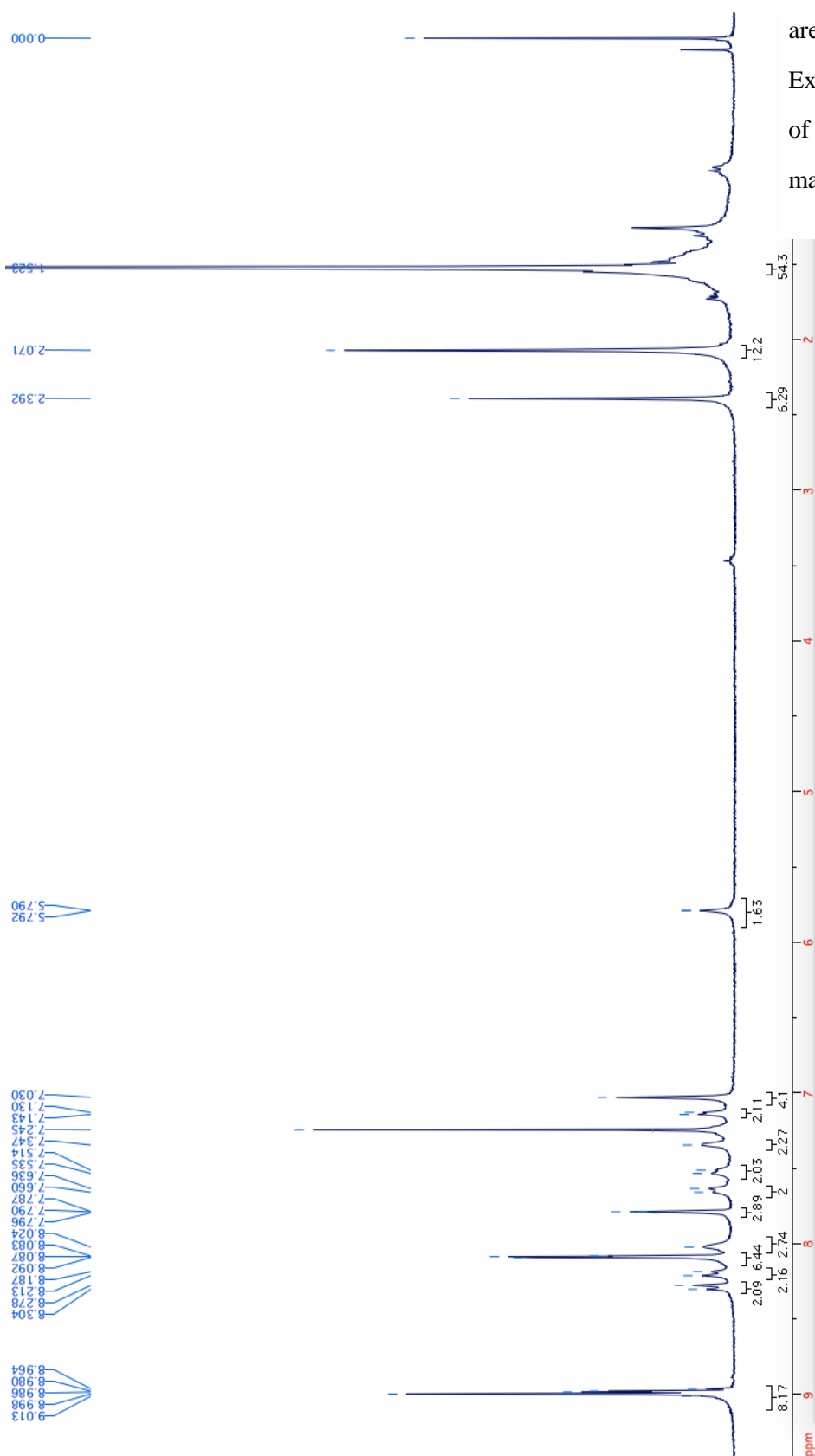
Method (b):  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (15 mg,  $5.92 \times 10^{-5}$  mol, 4.5 eq.) and ascorbic acid (11 mg,  $5.92 \times 10^{-5}$  mol, 4.5 eq.) were added to a solution of porphyrin **4** (10 mg,  $1.29 \times 10^{-5}$  mol, 1 eq.) and corrole **1** (43 mg,  $5.92 \times 10^{-5}$  mol, 4.5 eq.) in dry DMF (3 mL) under an argon atmosphere. After stirring for 2d at 50°C the reaction mixture was partitioned between dichloromethane (20 mL) and  $\text{H}_2\text{O}$  (20 mL) and the layers separated. The organic layer was washed with  $\text{H}_2\text{O}$  ( $3 \times 20$  mL), dried over  $\text{Na}_2\text{SO}_4$  and the solvent removed under reduced pressure. The crude product was purified by size exclusion chromatography (eluent, THF) affording the corrole-porphyrin pentaconjugate **7** as a brown solid (38 mg, 79%).

Method (c):  $\text{CuI}$  (1 mg,  $5.25 \times 10^{-6}$  mol, 0.4 eq.), DIPEA (1 mg,  $7.74 \times 10^{-6}$  mol, 0.6 eq.) and acetic acid (1 mg,  $1.67 \times 10^{-5}$  mol, 1.4 eq.) were added to a solution of porphyrin **4** (10 mg,  $1.29 \times 10^{-5}$  mol, 1 eq.) and corrole **1** (38 mg,  $5.23 \times 10^{-5}$  mol, 4 eq.) in dry DCM

(3 mL). The reaction mixture was stirred for 1d at r.t. The crude product was purified by size exclusion chromatography (Biobeads SX-1, THF) affording the corrole-porphyrin pentaconjugate **7** as a brown solid (33 mg, 63%).

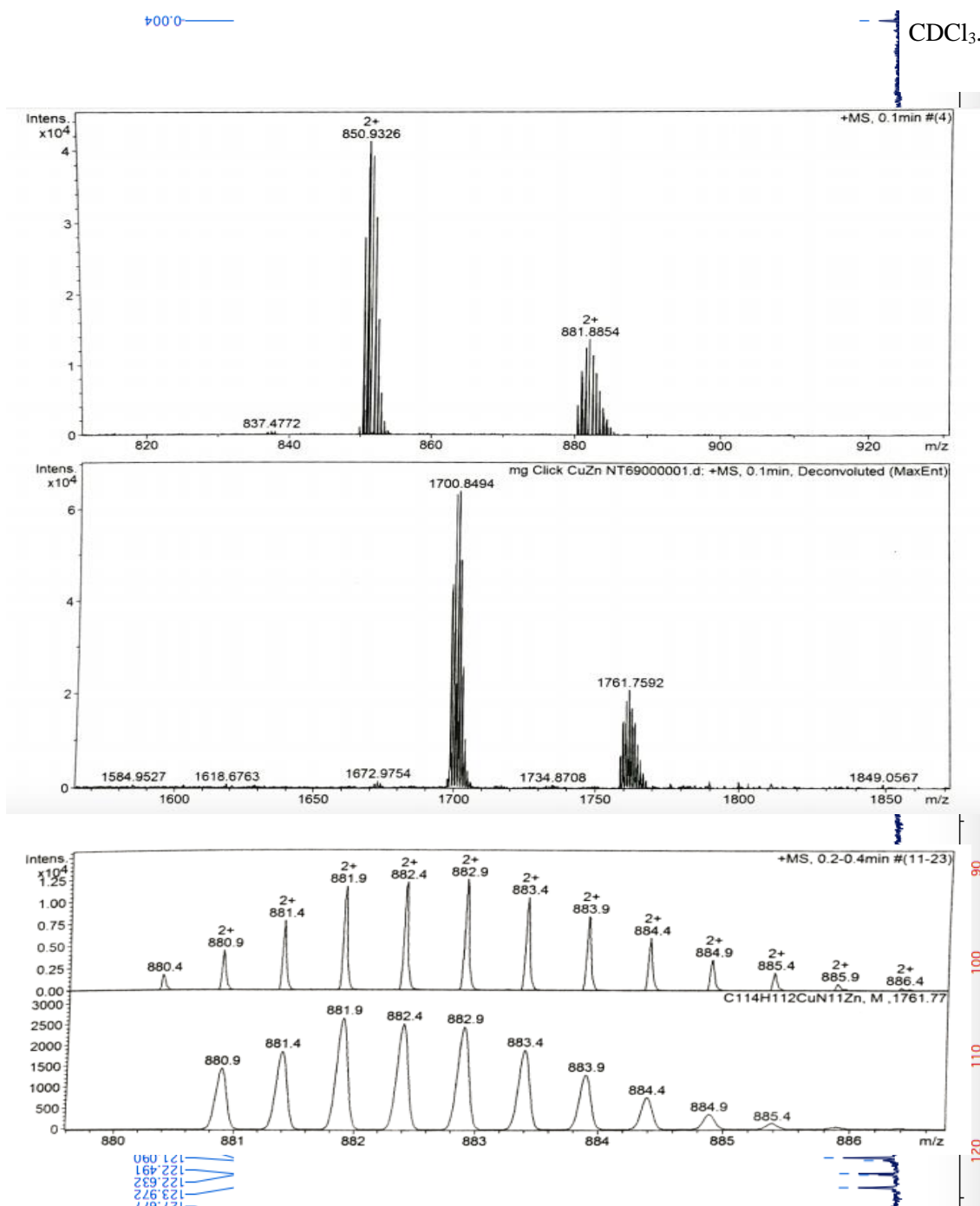
Method (d): A solution of azidocorrole **1** (6.45 mg,  $6.44 \times 10^{-5}$  mol), porphyrin **4** (10 mg,  $1.29 \times 10^{-5}$  mol) and  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (25 mg,  $6.70 \times 10^{-5}$  mol) in 5 mL DCM was stirred at 80 °C under  $\text{N}_2$  atmosphere. The reaction was monitored using t.l.c. After completion, water (20 mL) was added and the mixture was extracted with DCM ( $3 \times 20$  mL). The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$  and solvent evaporated under reduced pressure. After purification by size extrusion chromatography (polystyrene, biobeads, chloroform) 47 mg (98%) of pentad **7** was obtained as a brown solid.

## 2.0 Spectroscopic data for diad 5.



**Figure S1.** <sup>1</sup>H-NMR spectrum of diad **5** in CDCl<sub>3</sub>. Assignments are given in the Experimental section of the main manuscript.

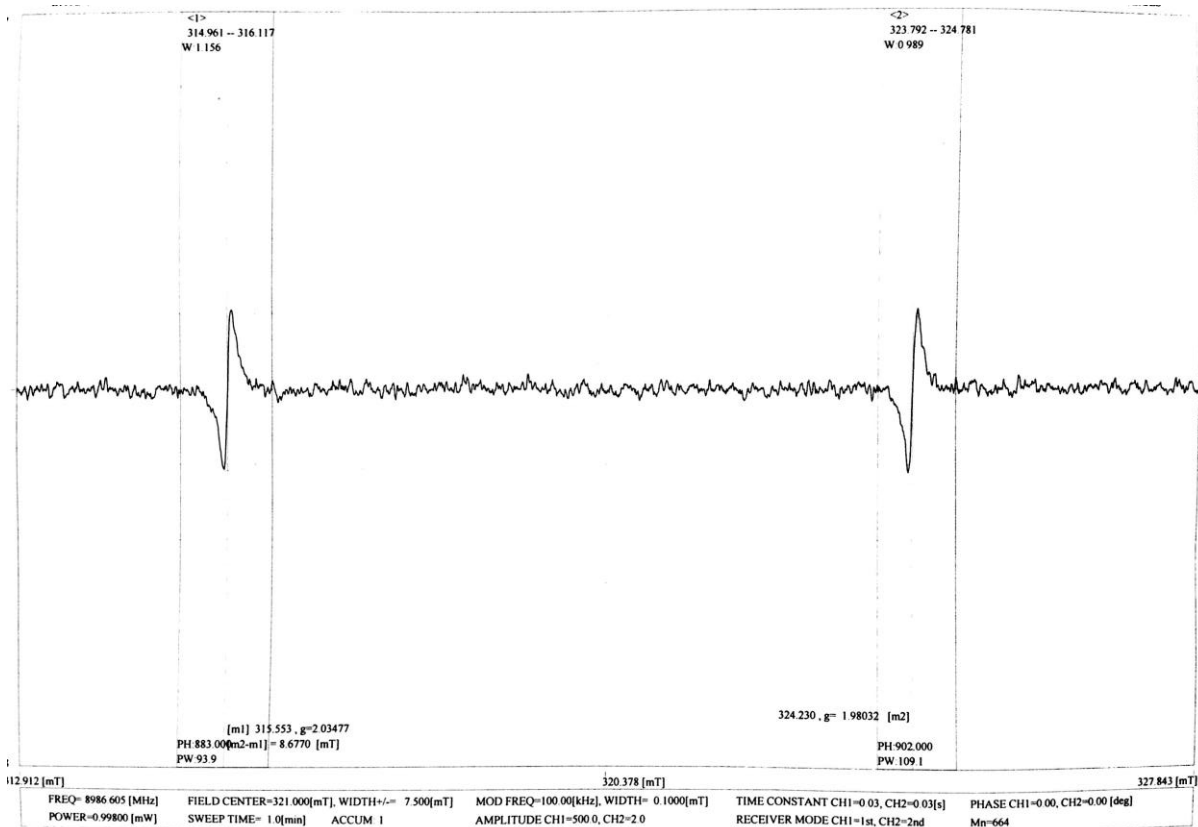
**Figure S2.**  $^{13}\text{C}$ -NMR spectrum of dyad **5** in  $\text{CDCl}_3$ .



**Figure S3.** ESI-mass spectrum of dyad **5**. Top panel: Peaks due to doubly charged **5**; middle panel: singly charged molecular ion; lower panels: isotope distribution pattern and model for the doubly charged ion.

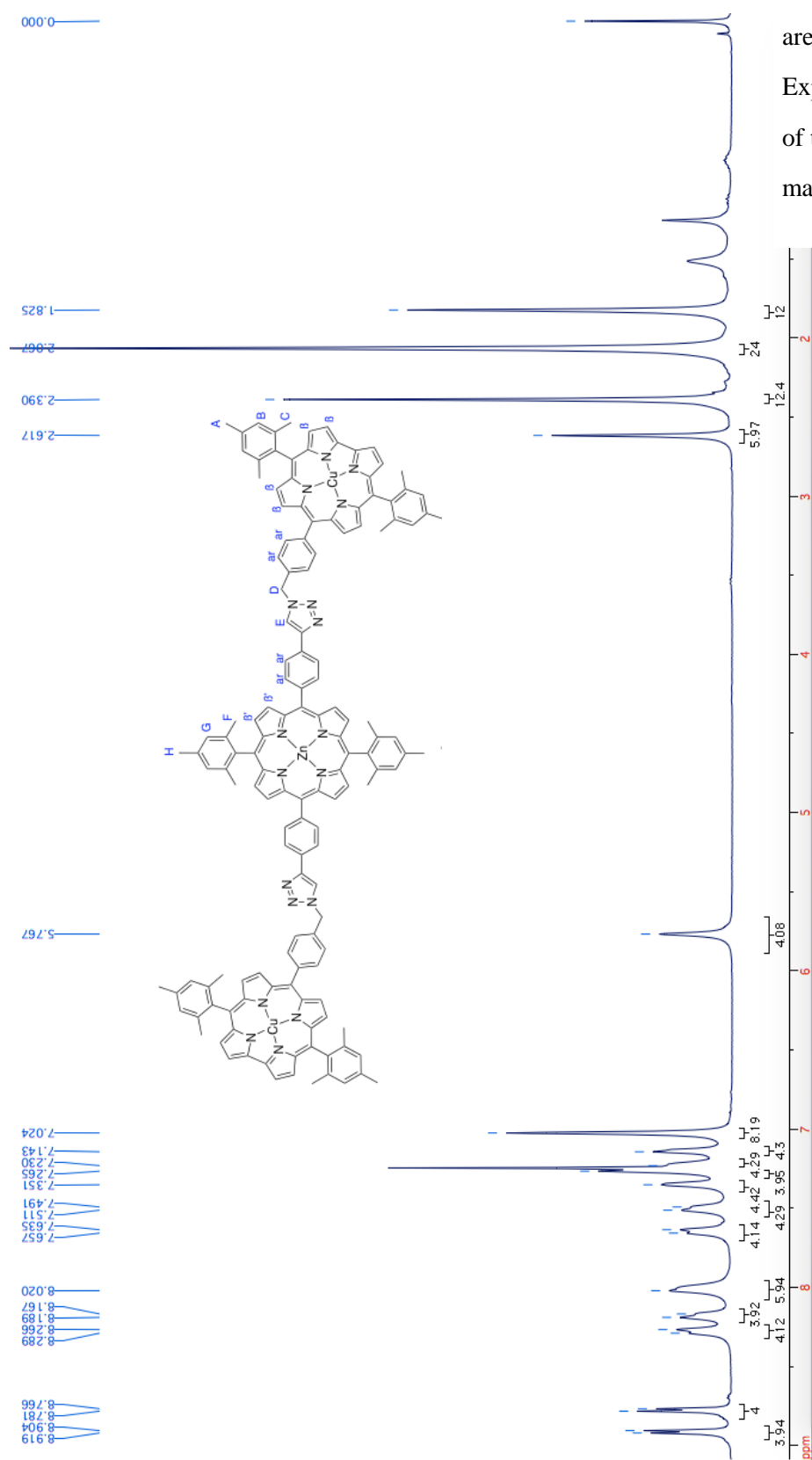






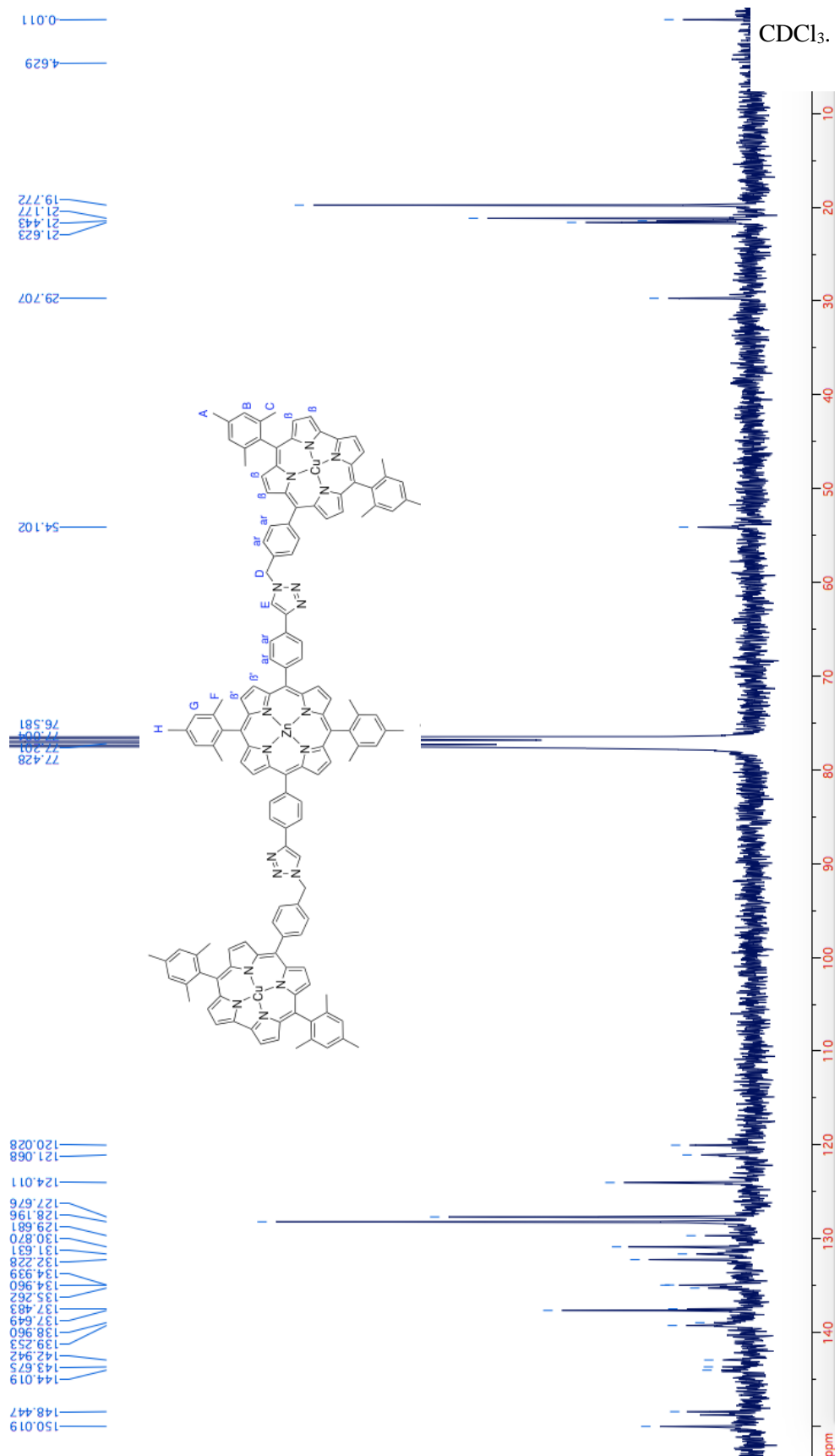
diamagnetic state. Two resonances present are due to the external standard.

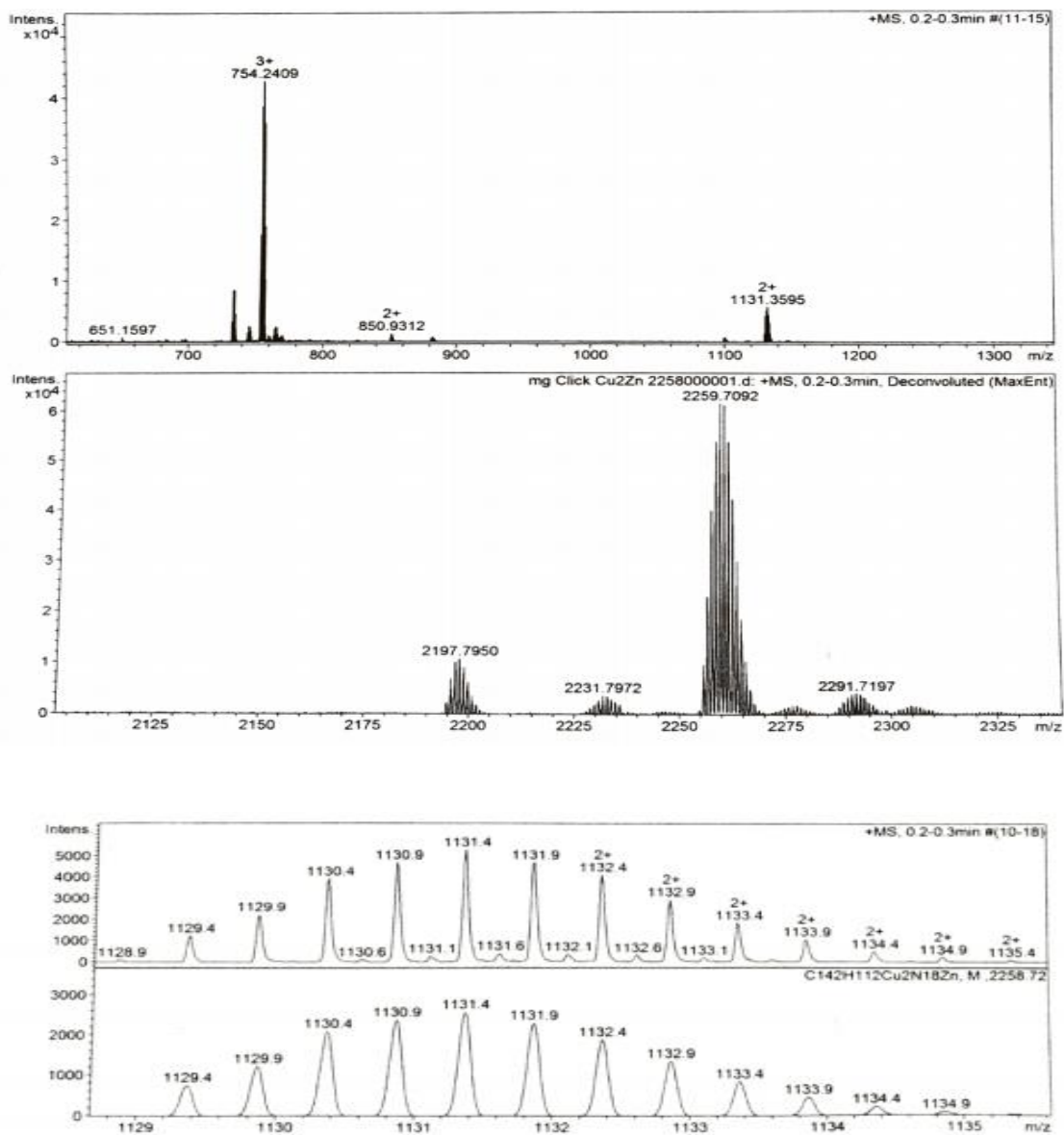
### 3.0 Spectroscopic data for triad **6**.



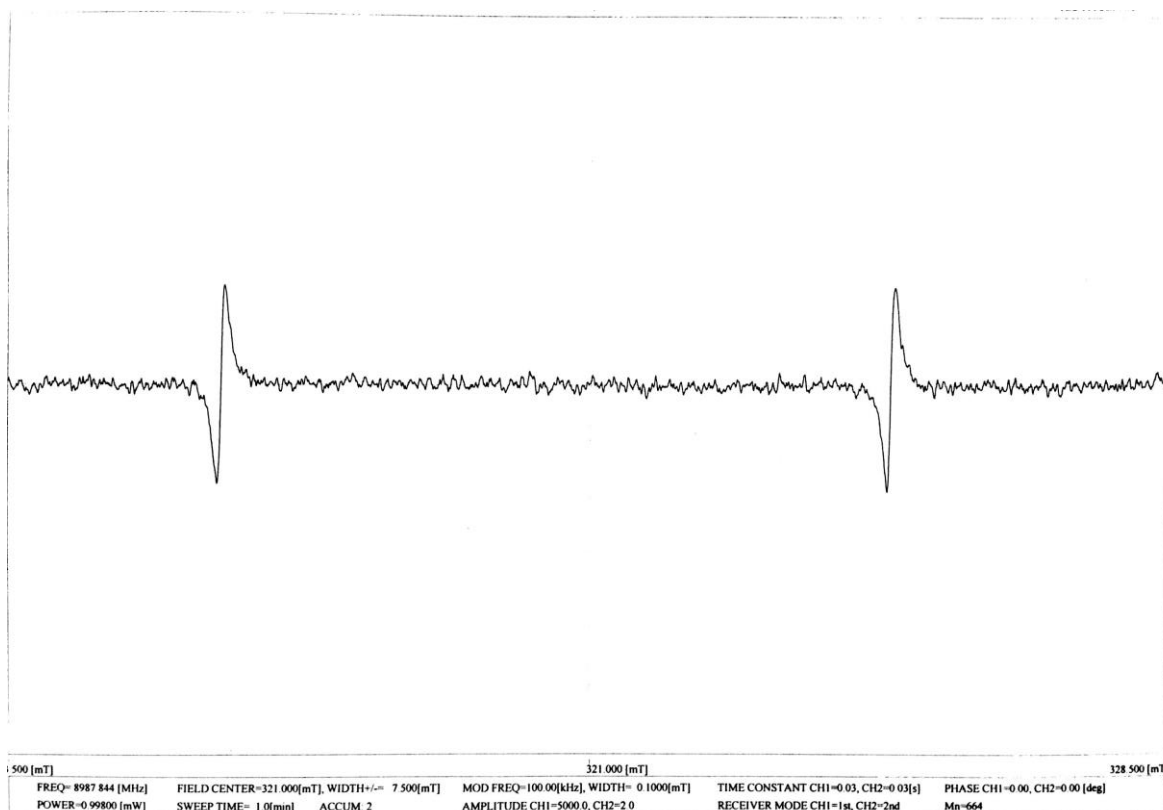
**Figure S5.** <sup>1</sup>H-NMR spectrum of triad **6** in CDCl<sub>3</sub>. Assignments are given in the Experimental section of the main manuscript.

**Figure S6.**  $^{13}\text{C}$ -NMR spectrum of triad **6** in  $\text{CDCl}_3$ .



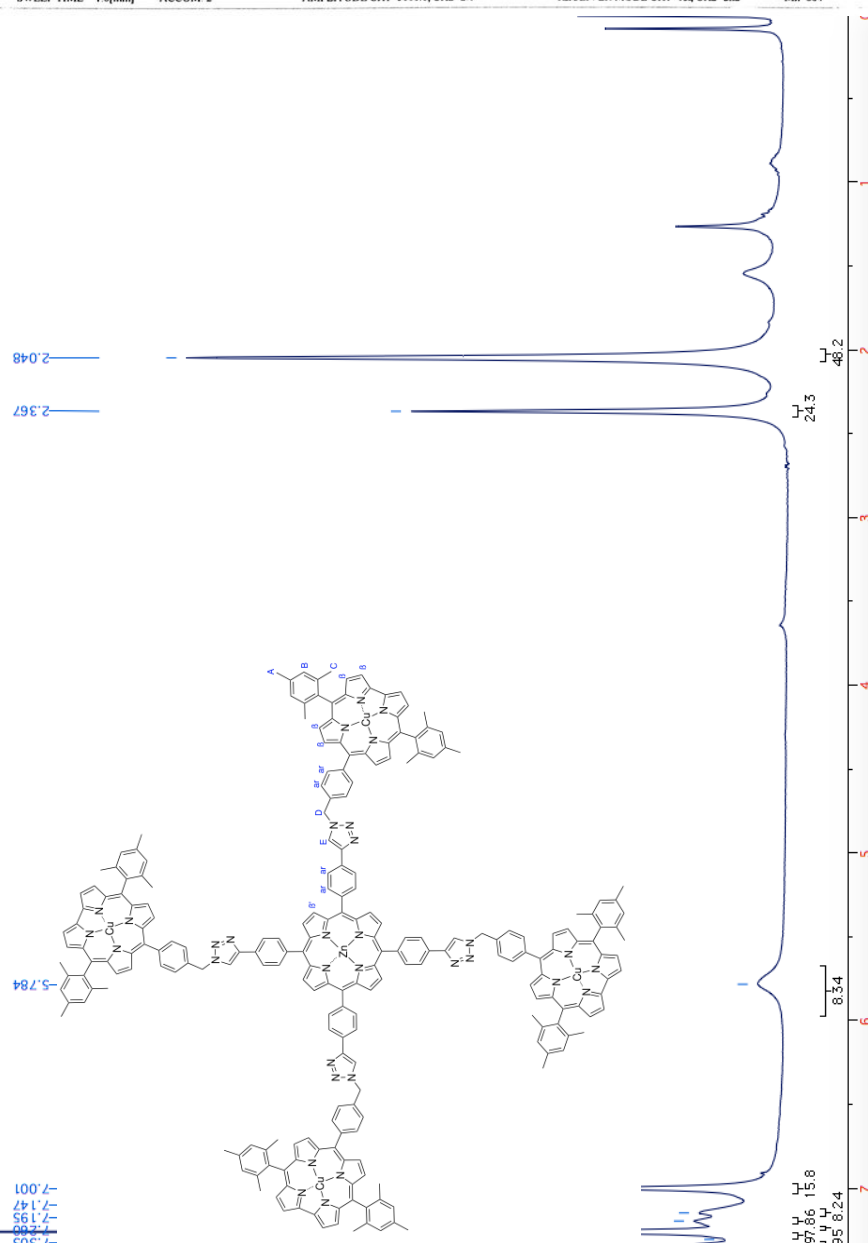


**Figure S7.** ESI-mass spectrum of triad **6**. Top panel: Peaks due to doubly charged **6**; middle panel: singly charged molecular ion; lower panels: isotope distribution pattern and model for the doubly charged ion.



diamagneti

#### 4.0 Spectro

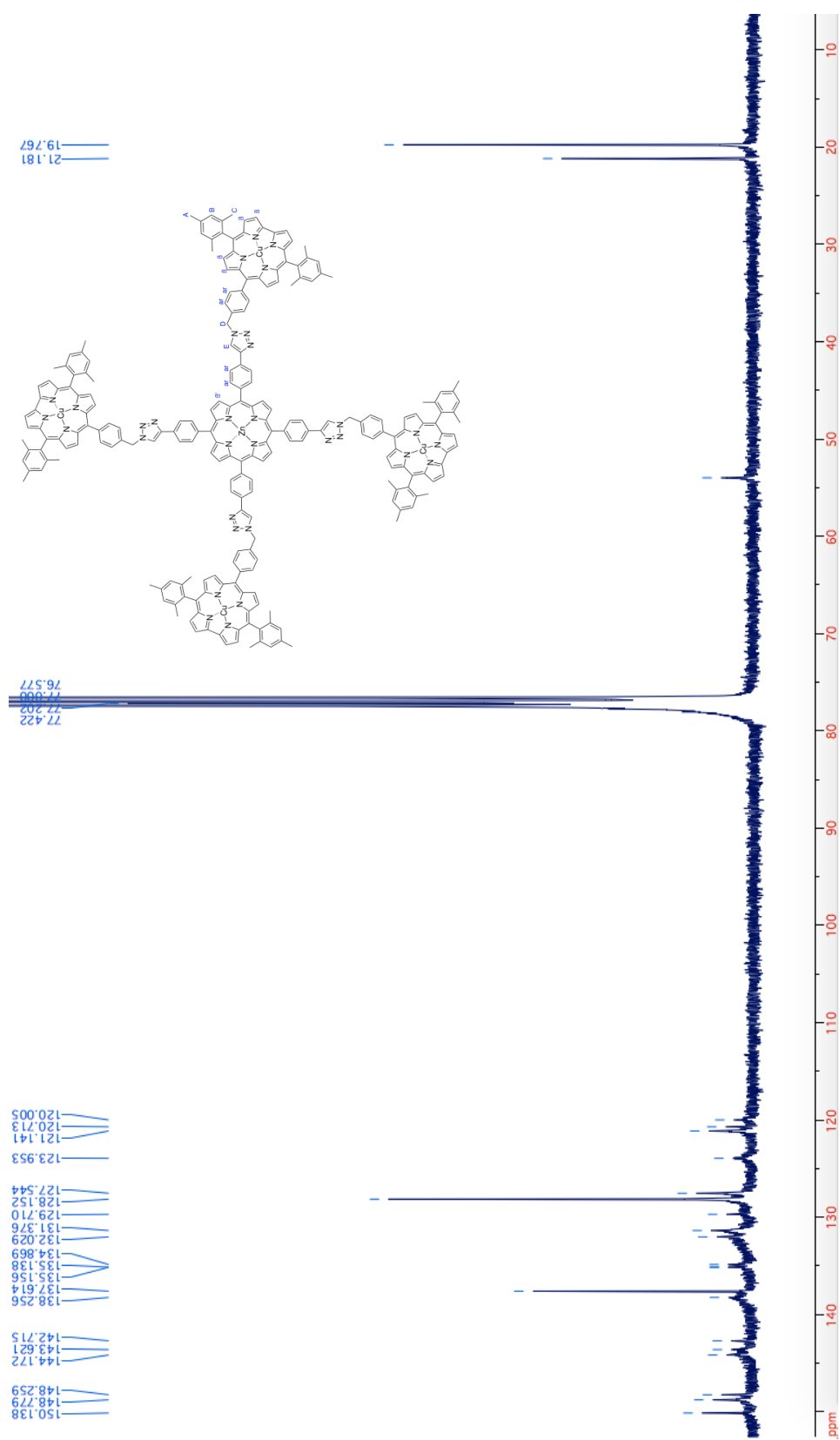


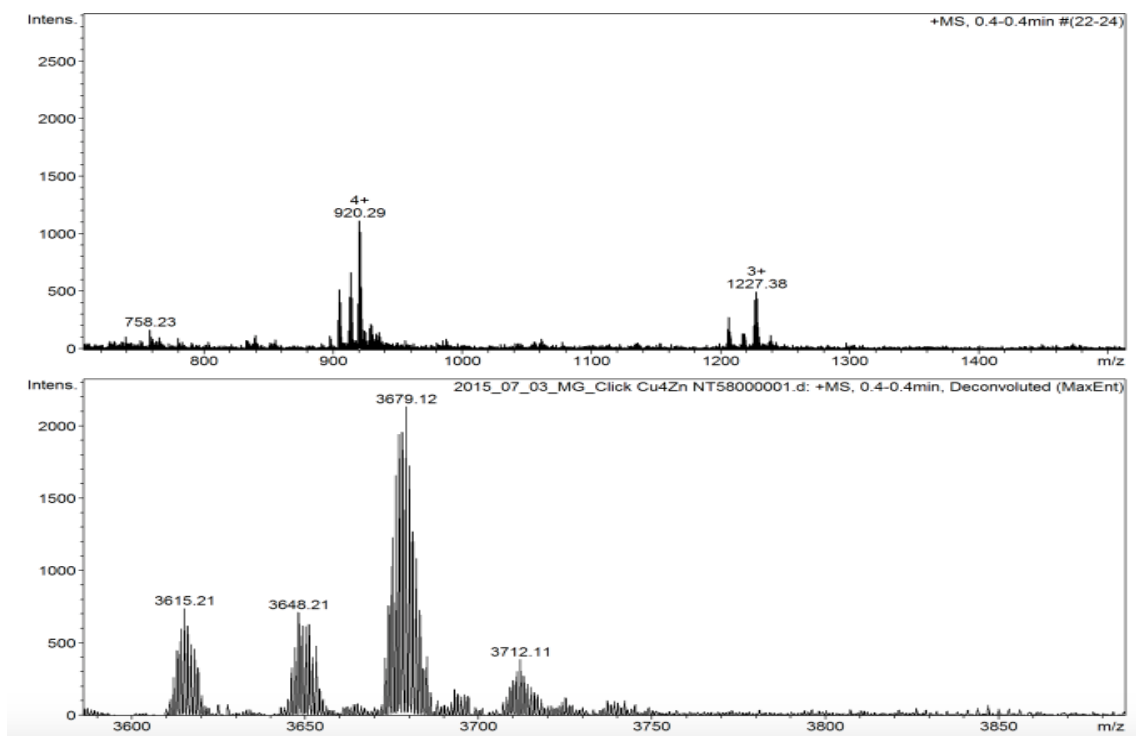
**Figure S9.**  $^1\text{H-NMR}$  spectrum of pentad **7** in  $\text{CDCl}_3$ . Assignments are given in the Experimental section of the main manuscript.

Figure S10.  $^{13}\text{C}$ -NMR

spectrum of pentad 7

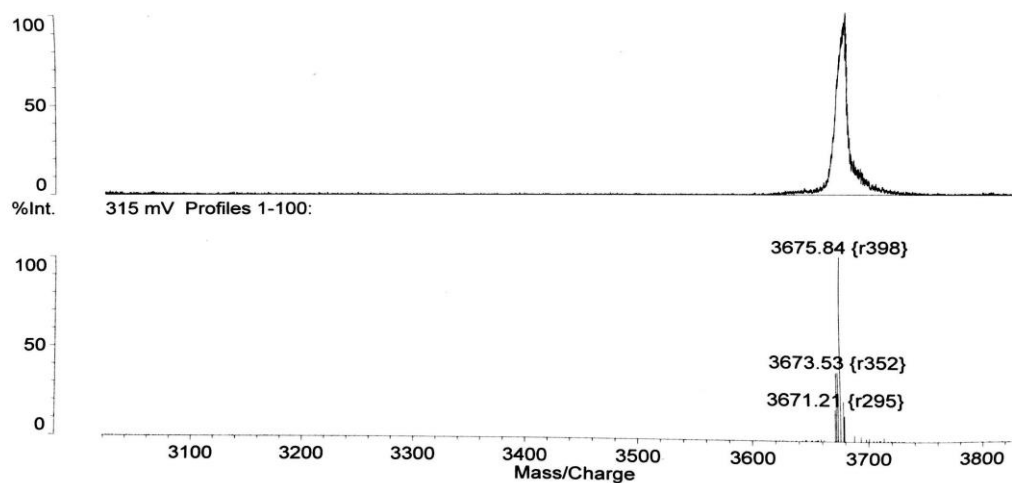
— in  $\text{CDCl}_3$ .



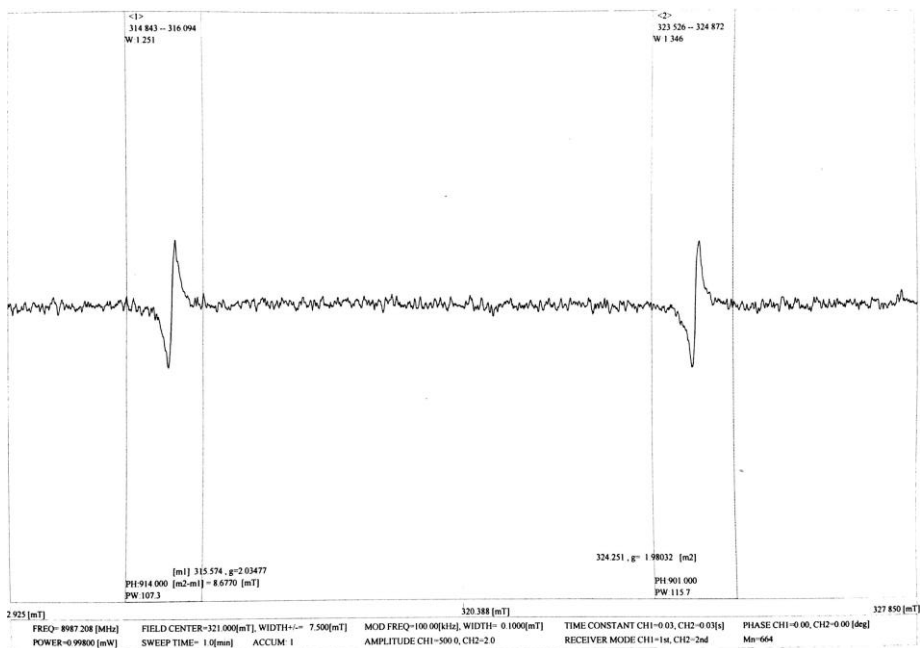


0deg\_300min

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 %Int. 13 mV[sum= 1266 mV] Profiles 1-100: Averaged

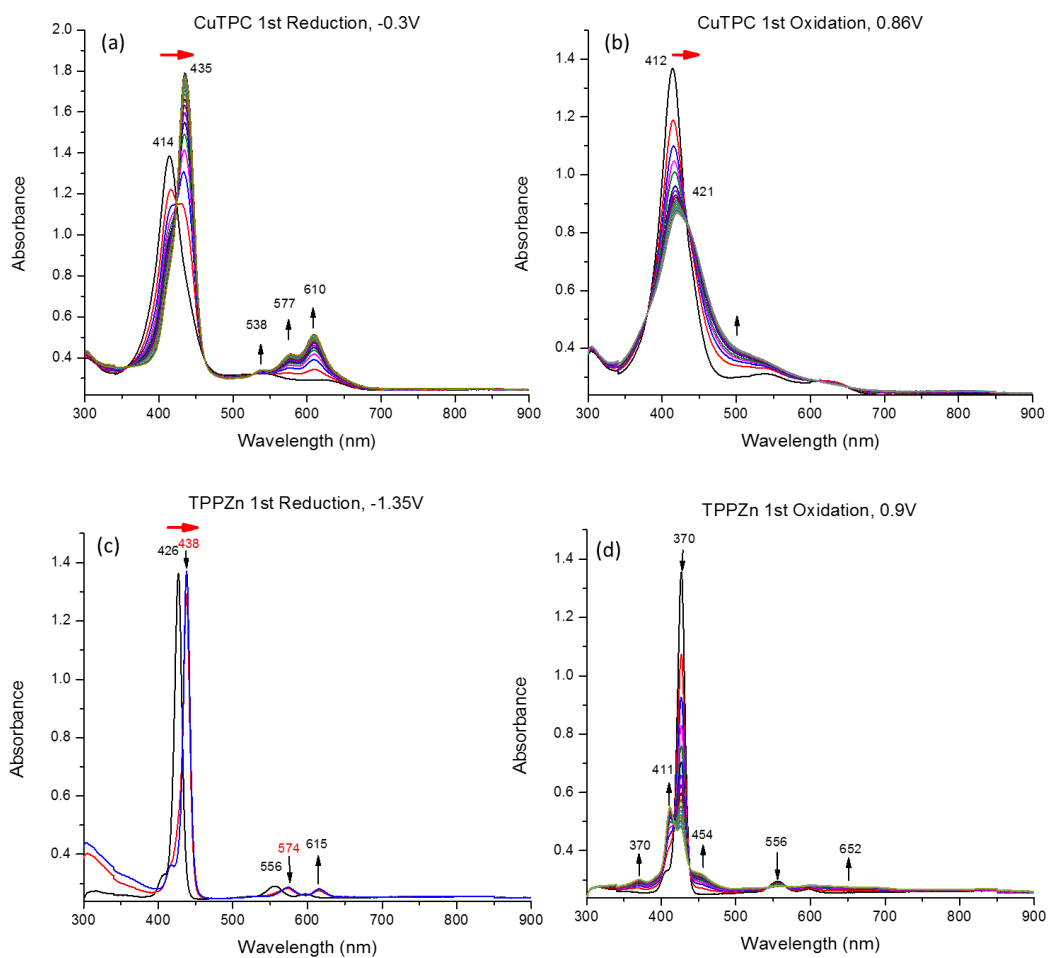


**Figure S11.** Mass spectrometric data for pentad **7**. Top panel: ESI-MS of triply and singly-charged **7**. Lower panel: MALDI-TOF-MS spectrum of **7**.



**Figure S12.** ESR spectrum of pentad 7 indicating its diamagnetic state. Two resonances present are due to the external standard.





**Figure S13.** Spectral changes observed during (a) first reduction of CuC, (b) first oxidation of CuC, (c) first reduction of ZnP, and (d) first oxidation of ZnP in benzonitrile containing 0.1 M (TBA)ClO<sub>4</sub>.