

Achieving ultra-low Ag loadings for CO₂ electroreduction via tailored molecular electrocatalysts

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Table of contents

Homogeneous Electrochemistry	2
Electrochemical Characterization	5
Homogeneous Electrochemical Characterization of 4- <i>n</i> -Hexyloxy-BIAN	5
Homogeneous Electrochemical Characterization of the [Ag(4- <i>n</i> -methyl-BIAN) ₂]BF ₄ (Ag-OMe) complex	9
[Ag(4- <i>n</i> -hexyloxy-BIAN) ₂]BF ₄ (Ag-OC ₆).....	14
Homogeneous Electrochemical Characterization of the [Ag(4- <i>n</i> -hexadecyloxy-BIAN) ₂]BF ₄ (Ag-OC ₁₆) complex	21
Electrochemical Characterization in zero-gap electrolyzers	27
Electrode Characterization & Post-mortem Characterization of the tested GDES	32
Comparison of the Ag-BIAN GDEs against the state-of-the-art	51
Scaling-up experiments and cost scenarios	54
Spectral Data	56
Spectral Data of 4-Methoxy-BIAN	56
Spectral Data of 4- <i>n</i> -Hexyloxy-BIAN	60
Spectral Data of 4- <i>n</i> -Hexadecyloxy-BIAN	64
Spectral Data of [Ag(4-OMe-BIAN) ₂]BF ₄ (Ag-OMe).....	68
Spectral Data of [Ag(4- <i>n</i> -hexyloxy-BIAN) ₂]BF ₄ (Ag-OC ₆).....	72
Spectral Data of [Ag(4- <i>n</i> -hexadecyloxy-BIAN) ₂]BF ₄ (Ag-OC ₁₆).....	76
References	80
References	80

Homogeneous Electrochemistry

Tetrabutylammonium hexafluorophosphate (TBAPF₆) for electrochemical studies was purchased from Sigma-Aldrich and recrystallized twice from absolute ethanol (Acros Organics), dried under high vacuum and stored under argon prior to use. Anhydrous ACN and THF were obtained from a molar sieve MB-SPS-7 (M. Braun Inertgas-Systeme GmbH) under argon atmosphere. Aqueous solutions for electrochemical experiments were prepared using high purity water (18 MΩ). Homogeneous electrochemical measurements were conducted in a low volume cell from Pine using a three-electrode setup at 25 °C under argon or CO₂, respectively, utilizing a Pine WaveDriver 20 DC Bipotentiostat. The investigated solutions were prepared from dry, degassed solvents and contained 0.1M supporting electrolyte

(TBAPF₆) and 1mM of the respective complexes or ligands, except for 4-*n*-hexyloxy-BIAN where 0.5mM solutions were examined in ACN due to its limited solubility. Electrochemical measurements of the homoleptic Ag(I) 4-*n*-hexadecyloxy-BIAN complex **Ag-OC₁₆** had to be performed in THF at diminished concentrations of 0.3mM due to its particularly non-polar substituents. For all electrochemical measurements a glassy carbon (Pine, 65 mm long, 6.4 mm OD PCTFE shroud, 3 mm OD disk, 0.28 cm² approximate surface area) as working, platinum wire (Pine, 65 mm long, 7 mm OD epoxy tube shroud, 0.58 cm² approximate surface area) as counter and a non-aqueous Ag/AgCl quasi-reference electrode were used. Prior to each measurement, the glassy carbon WE was polished with a 0.05 μm alumina suspension (deagglomerated, Allied High Tech Products) on a MicroCloth polishing pad (Buehler). Subsequently, the electrode was cleaned in an ultrasonic bath in pure water for 2 min and finally rinsed with pure water as well as the respective employed solvent to remove any residual alumina particles. Ensuing each experiment, ferrocene was added as internal standard and the Fc/Fc⁺ half wave potential determined. The converted potentials against Fc/Fc⁺ were transformed to V vs NHE with the conversion of +0.630 V vs NHE in ACN and +0.720 V vs NHE in THF according to literature.⁵⁻⁷ If not stated otherwise, CVs were recorded at a scan rate of 100 mV s⁻¹ applying cathodic potentials first.

Preparation of Non-Aqueous Ag/AgCl Quasi-Reference Electrode

For the preparation of the non-aqueous Ag/AgCl quasi-reference electrode, a PTFE capped silver wire from Pine (53 mm long, 3.5 mm OD) was first sanded using 600 grit sandpaper before being subjected to electrochemical treatment in aqueous 0.1M HCl solution. In this process, the polished silver wire was implemented as working electrode, a Pt wire as counter electrode and an aqueous Ag/AgCl/3M KCl electrode as RE. Initially, CVs in a range from -0.4 to 0.4 V vs the utilized RE were scanned for 20 cycles with a scan rate of 20 mV s⁻¹ in order to roughen the Ag surface. Subsequently, CPE was applied first for 2 min at 0.3 V, followed by CPE at 0.7 V vs Ag/AgCl/3M KCl for 15 min. The thus fabricated AgCl coated Ag wire QRE was finally rinsed with high purity water and stored in the dark.

DFT Calculations

All calculations in this work were performed using the Gaussian 09 D01 package. The M06 functional was used in DFT calculations, and the def2 general basis sets were used (Ag: def2-TZVPPD; H, C, N and O: def2-TZVP).

To understand of the electronic structure and properties of the investigated Ag-BIAN complexes, a series of DFT calculations have been conducted. First, screening of various DFT methods and basis sets were performed to find the best agreement, for both the Ag–N bond lengths and the dihedral angles between the two chelated rings, among the optimized and solid-state structures (Table SXY, ESI). Some of the frontier orbitals for the structure of Ag-OCH₃ are illustrated in Fig. SXY. As anticipated, the HOMO appears to consist predominantly of a d

orbital from the Ag(I) center, with spin density distributed over the iminoaryl parts of ligand, and almost no contribution from the acenaphthene fragment. In contrast, the LUMO (Fig. SXY) and LUMO+1 (Fig. SXY) are mainly comprised of orbital components from the acenaphthene fragments. In fact, inter-ligand lobes connecting both the imino moieties of the ligands can be observed in the LUMO, alluding to ligand-to-ligand charge transfer characteristics in Ag-OMe.

Ag(4-OMe-BIAN)₂]BF₄ (Ag-OMe)

For Ag-OCH₃, residual electron density was found in a solvent-accessible void of 892 Å³ with an electron count of 208. It was not possible to determine and/or refine the solvent molecule. The electron density was therefore squeezed using PLATON. Disorders in the BF₄⁻ anion were not refined. Due to measurement at ambient temperature, the ellipsoids are comparably larger. CCDC 2167847 contains the supplementary crystallographic data for compound Ag-OCH₃. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk.

Electrochemical Characterization

Homogeneous Electrochemical Characterization of 4-*n*-Hexyloxy-BIAN

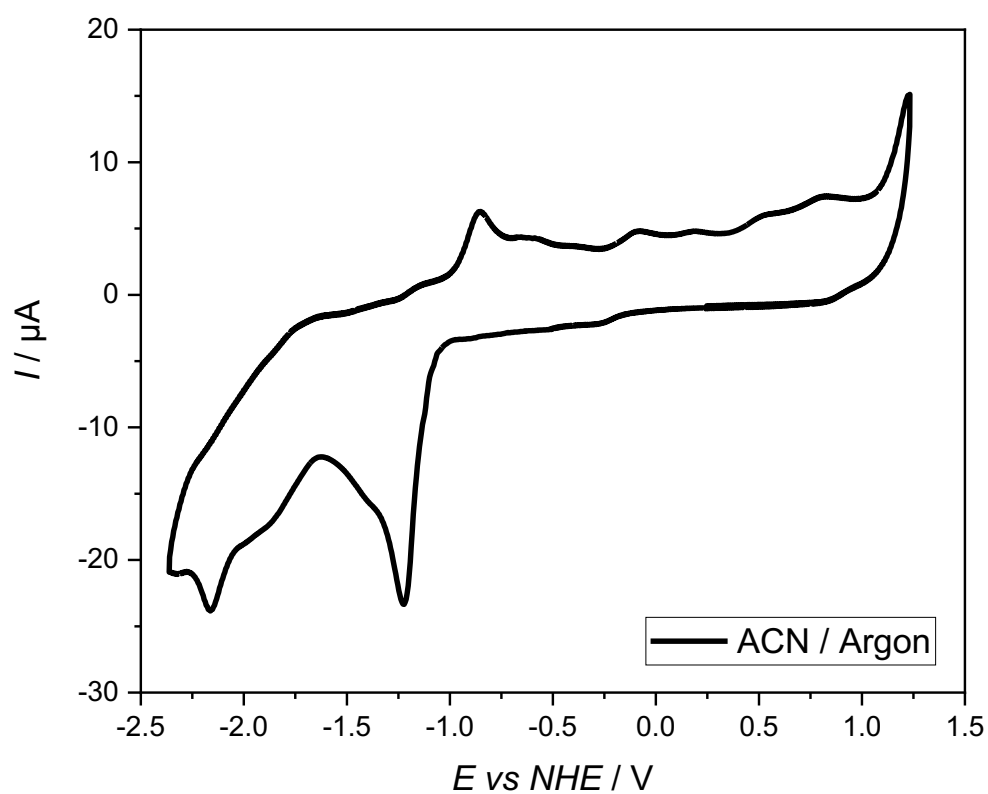


Figure S1: Cyclic voltammogram of 0.5mM 4-*n*-hexyloxy-BIAN in acetonitrile under argon.

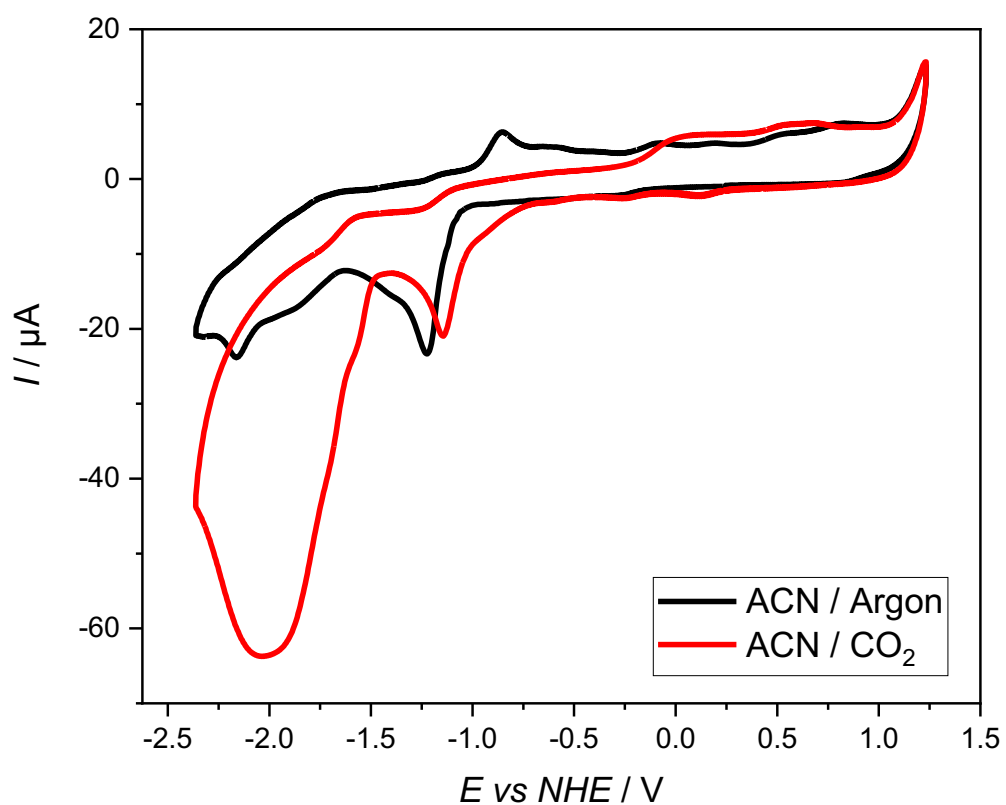


Figure S2: Comparison of cyclic voltammograms of 0.5mM 4-n-hexyloxy-BIAN in acetonitrile under argon and CO_2 .

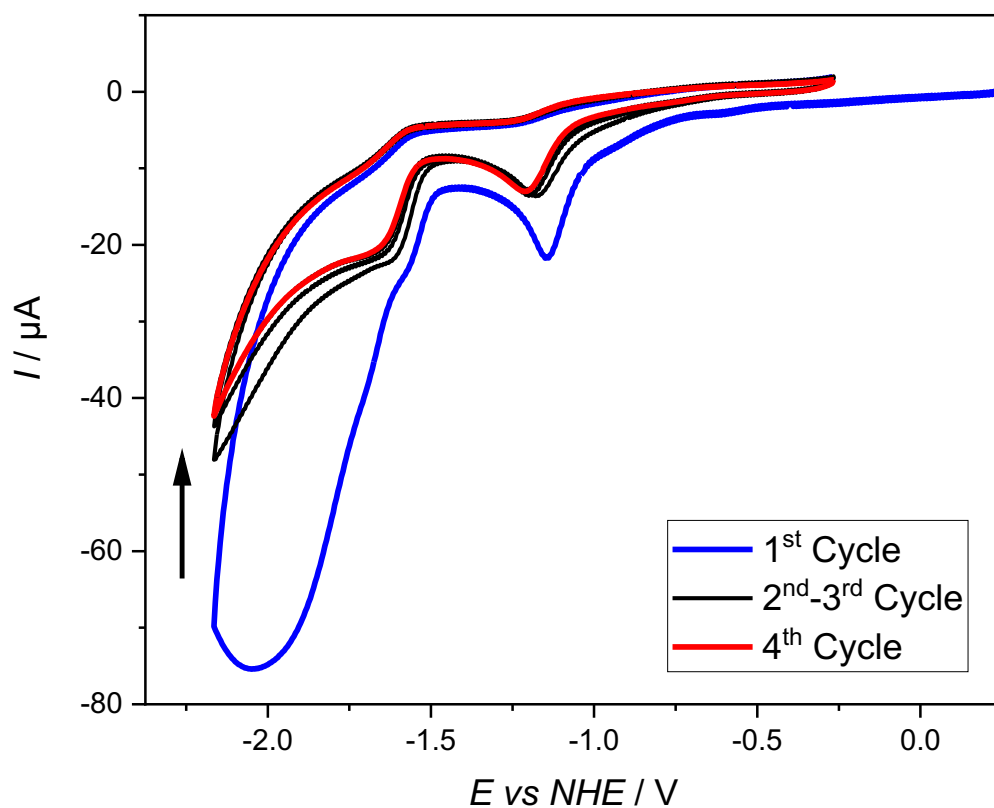


Figure S3: Stability test cyclic voltammogram of the reductive part 0.5mM 4-n-hexyloxy-BIAN in acetonitrile under CO_2 .

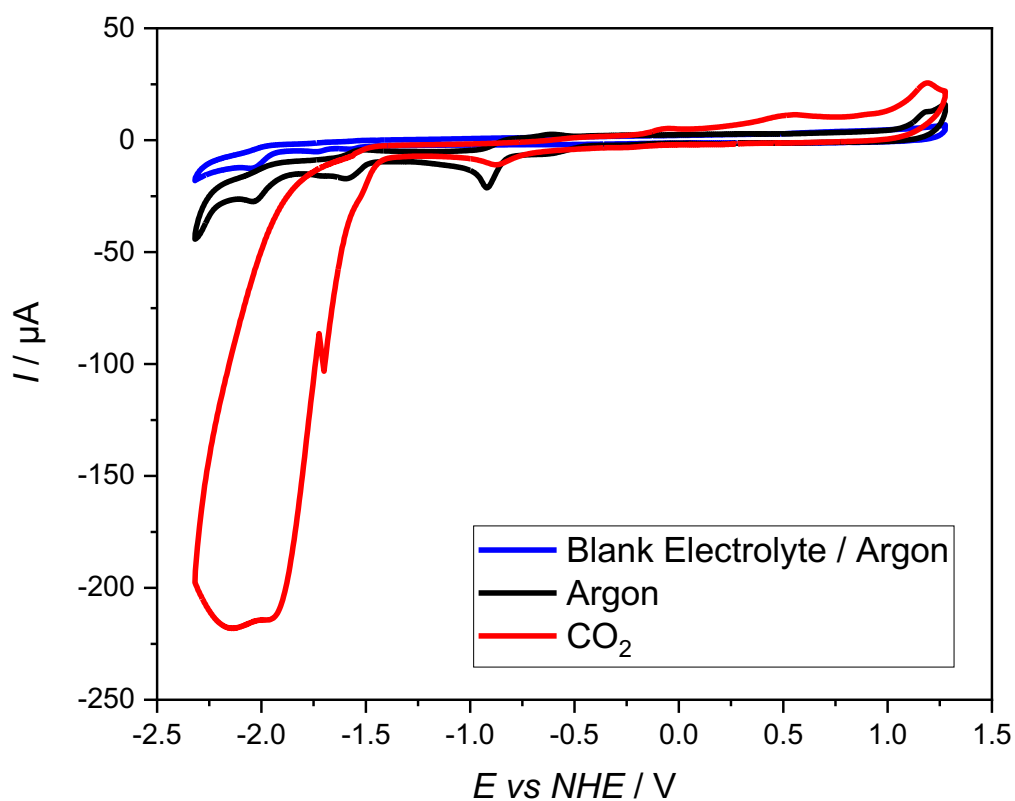


Figure S4: Comparison of cyclic voltammograms of 0.5mM 4-n-hexyloxy-BIAN in acetonitrile with 2% H_2O under argon and CO_2 and the blank electrolyte.

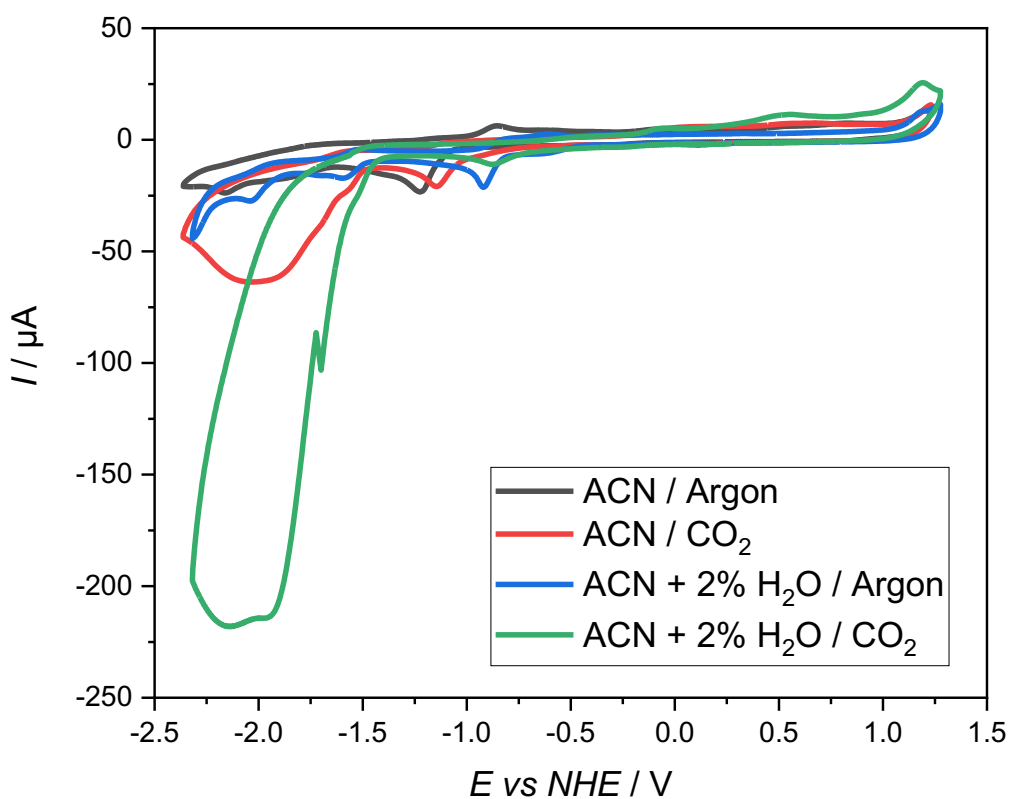


Figure S5: Comparison of cyclic voltammograms of 0.5mM 4-n-hexyloxy-BIAN in acetonitrile and acetonitrile with 2% H_2O under argon and CO_2 .

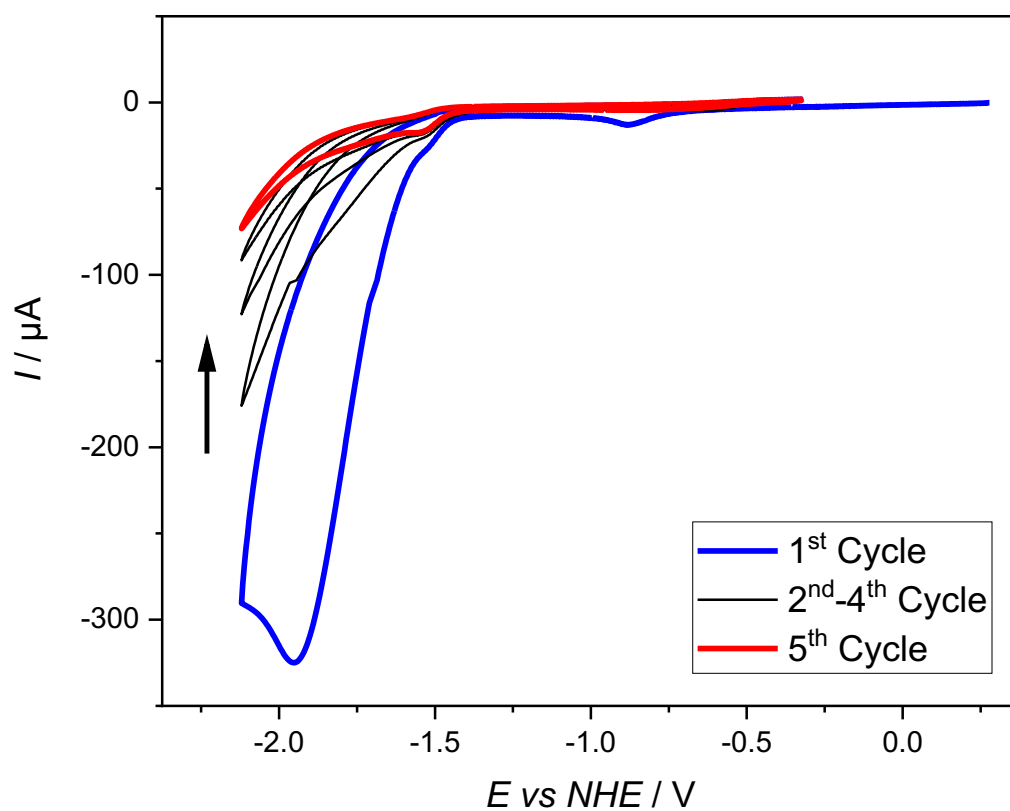


Figure S6: Stability test cyclic voltammogram of the reductive part of 0.5mM 4-n-hexyloxy-BIAN in acetonitrile with 2% H₂O under CO₂.

Homogeneous Electrochemical Characterization of the [Ag(4-*n*-methyl-BIAN)₂]₂BF₄ (Ag-OMe) complex

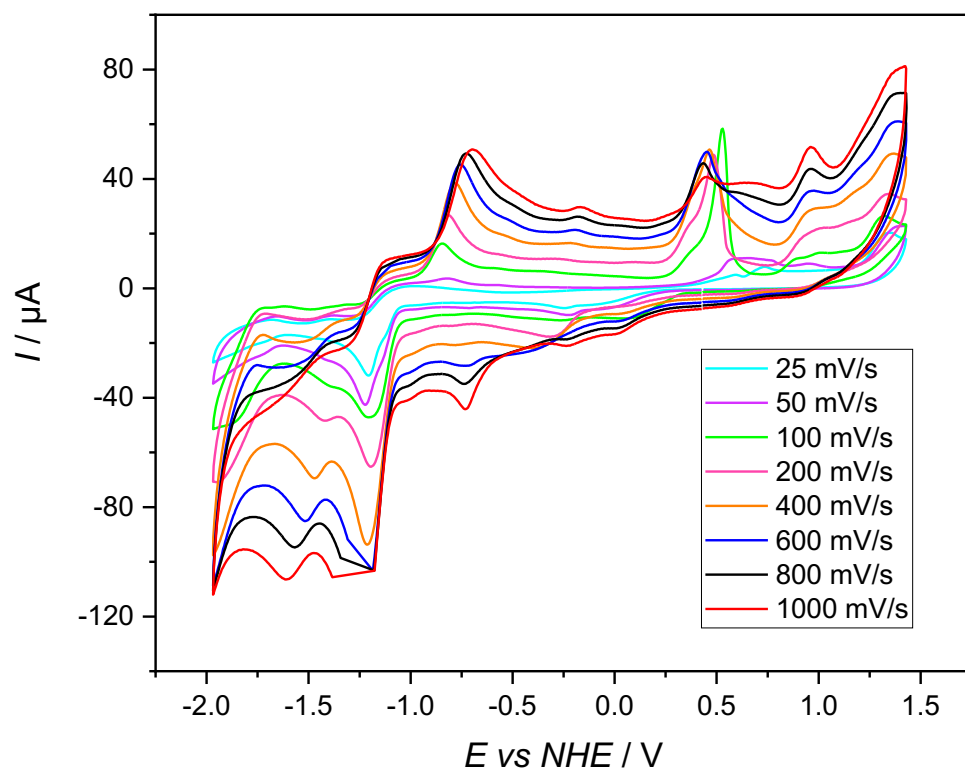


Figure S7: Scan rate dependency of [Ag(4-OMe-BIAN)₂]₂BF₄ Ag-OMe in acetonitrile under argon. Cut off peaks at high scan rates are caused by limitations of the employed potentiostat.

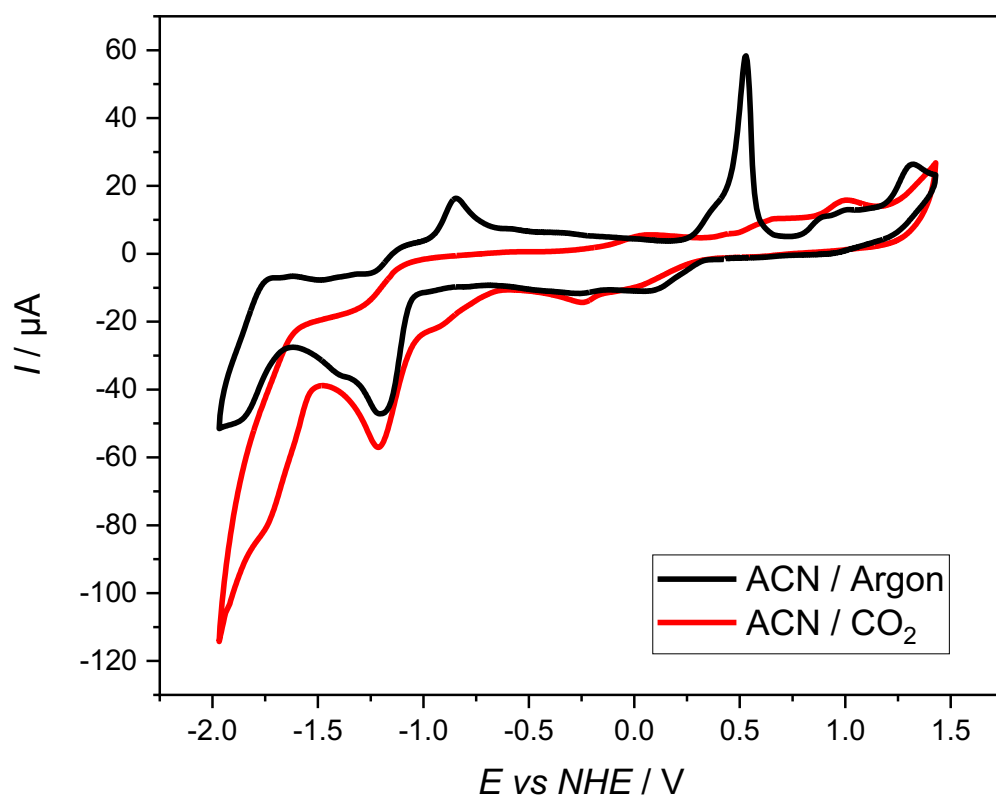


Figure S8: Comparison of cyclic voltammograms of [Ag(4-OMe-BIAN)₂]BF₄ Ag-OMe in acetonitrile under argon and CO₂.

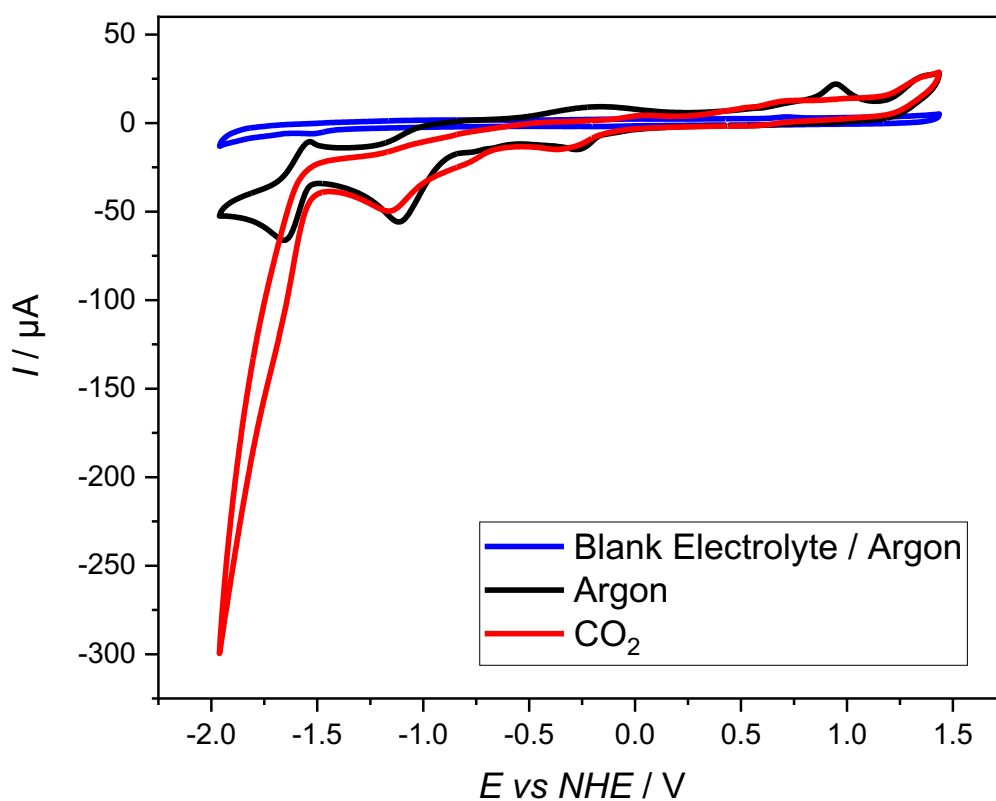


Figure S9: Comparison of cyclic voltammograms of [Ag(4-OMe-BIAN)₂]BF₄ Ag-OMe in acetonitrile with 2% H₂O under argon and CO₂ and the blank electrolyte.

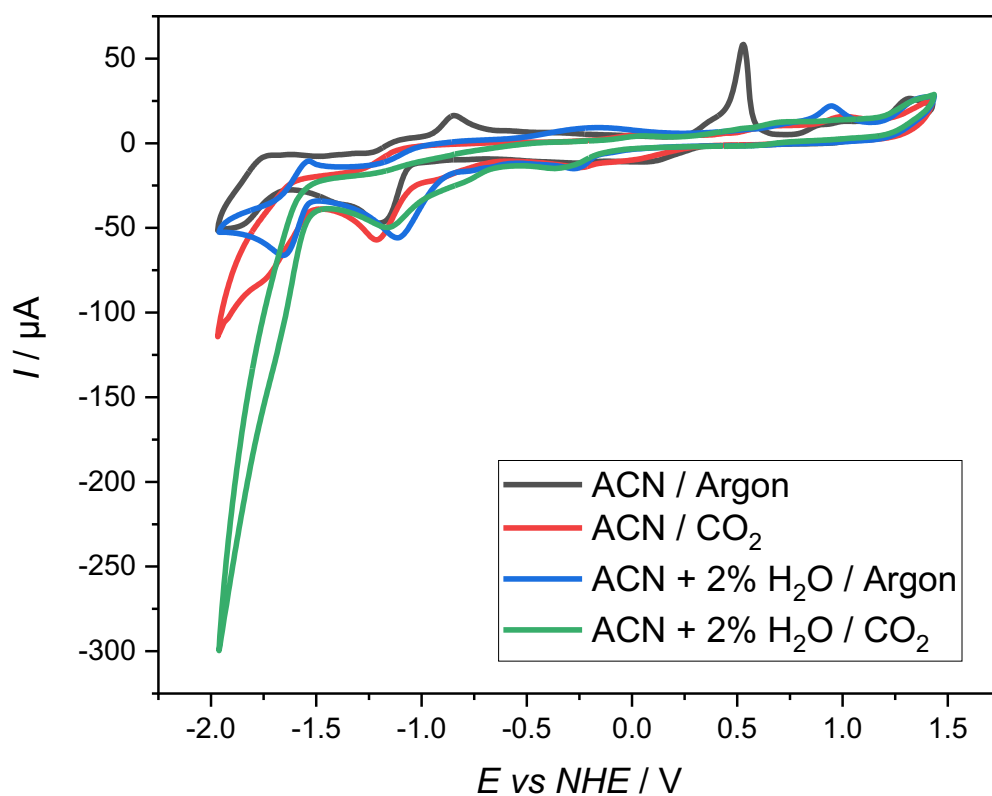


Figure S10: Comparison of cyclic voltammograms of $[\text{Ag}(\text{4-OMe-BIAN})_2]\text{BF}_4$ Ag-OMe in acetonitrile and acetonitrile with 2% H_2O under argon and CO_2 .

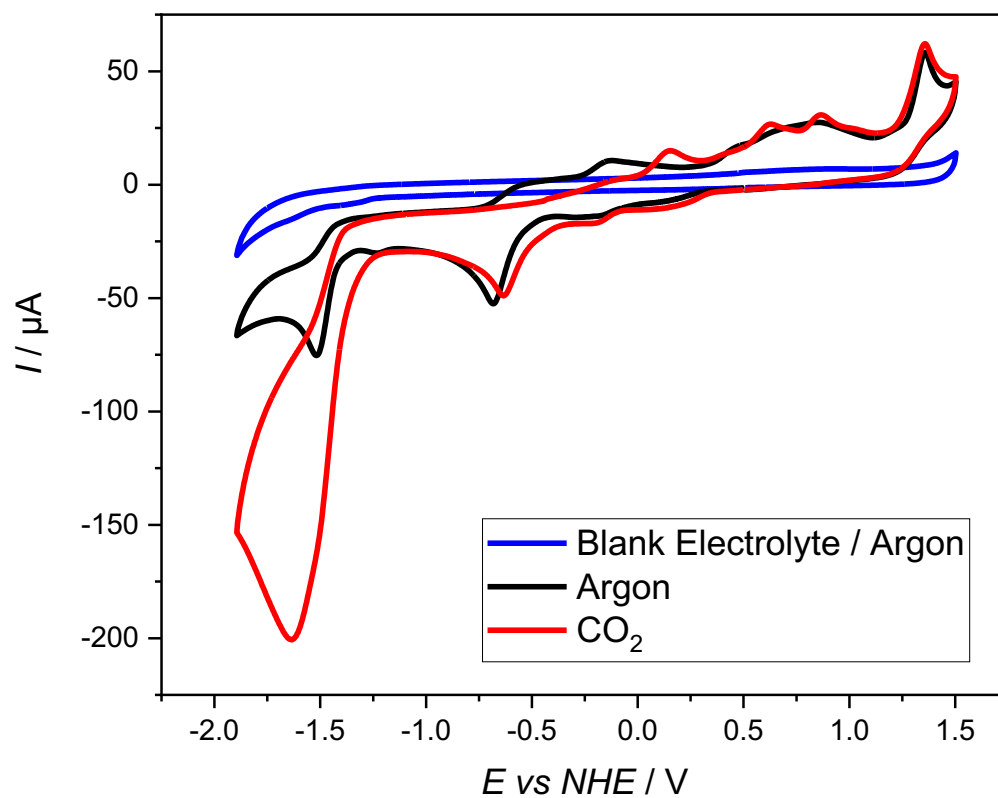


Figure S11: Comparison of cyclic voltammograms of $[\text{Ag}(\text{4-OMe-BIAN})_2]\text{BF}_4$ Ag-OMe in acetonitrile with 20% H_2O under argon and CO_2 and the blank electrolyte.

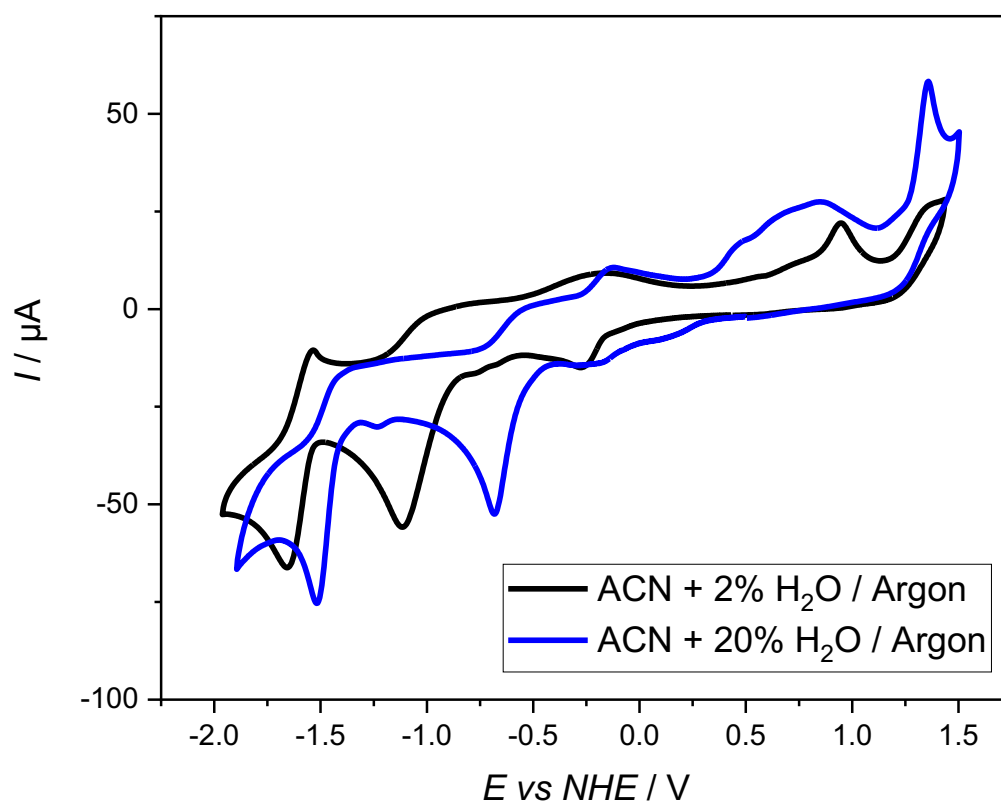


Figure S12: Comparison of cyclic voltammograms of $[\text{Ag}(\text{4-OMe-BIAN})_2]\text{BF}_4 \text{ Ag-OMe}$ in acetonitrile with 2% and 20% H_2O under argon.

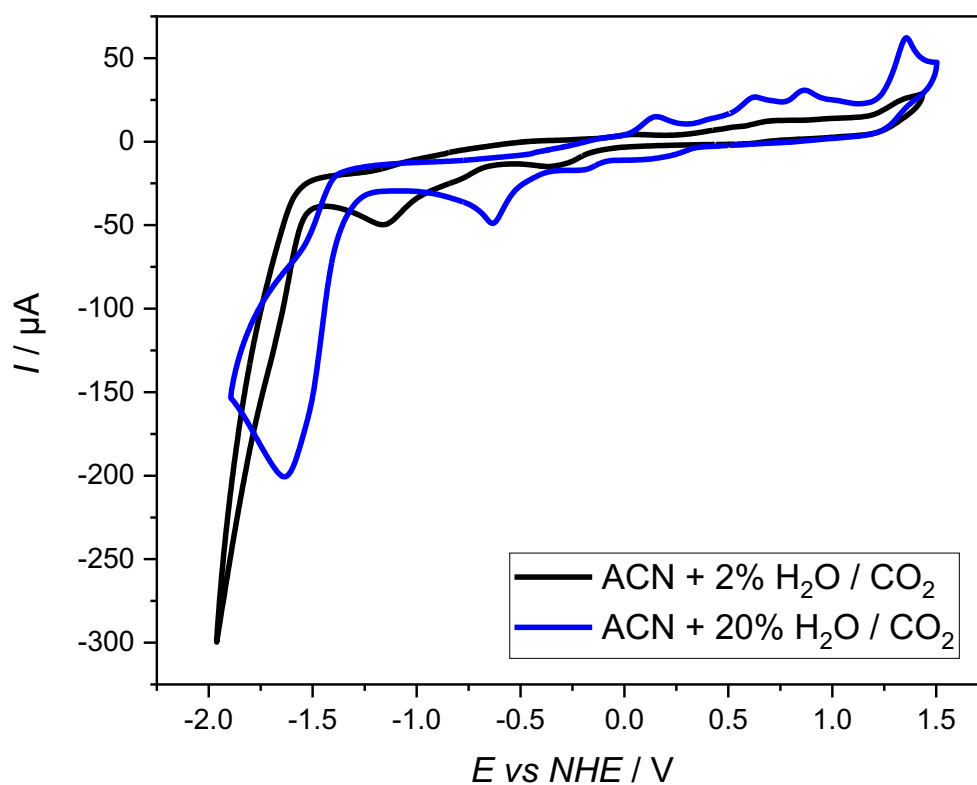


Figure S13: Comparison of cyclic voltammograms of $[\text{Ag}(\text{4-OMe-BIAN})_2]\text{BF}_4 \text{ Ag-OMe}$ in acetonitrile with 2% and 20% H_2O under CO_2 .

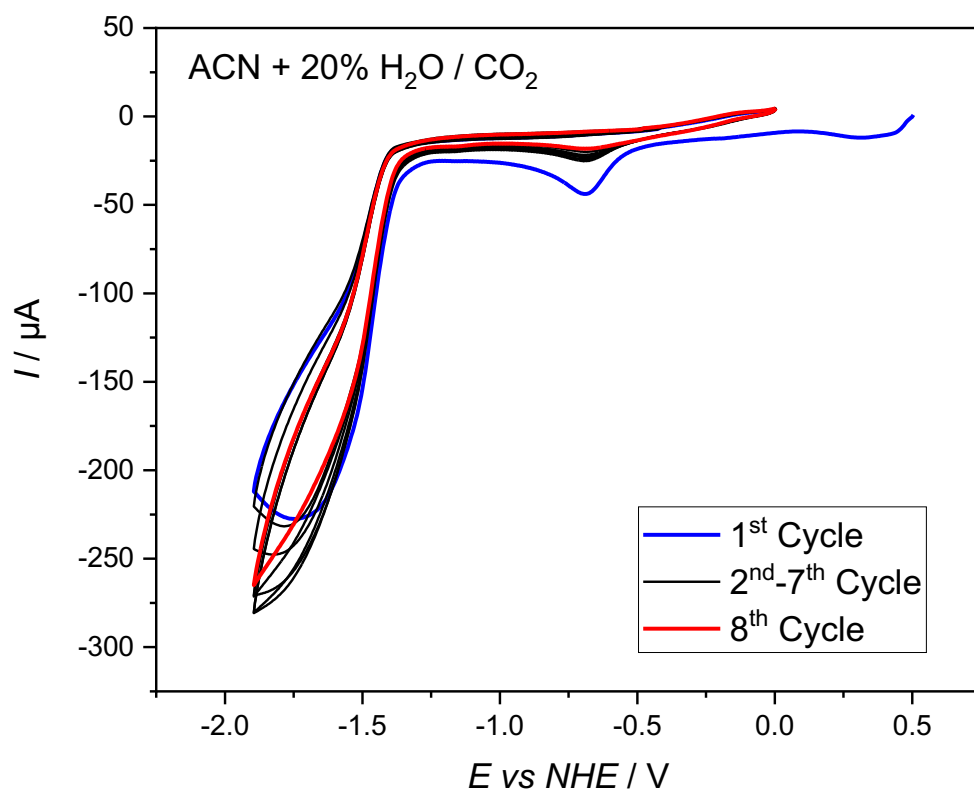


Figure S14: Catalytic stability test of the reductive section of $[\text{Ag}(\text{4-OMe-BIAN})_2]\text{BF}_4$ Ag-OMe in acetonitrile with 20% H₂O under CO₂.

[Ag(4-*n*-hexyloxy-BIAN)₂]BF₄ (Ag-OC₆)

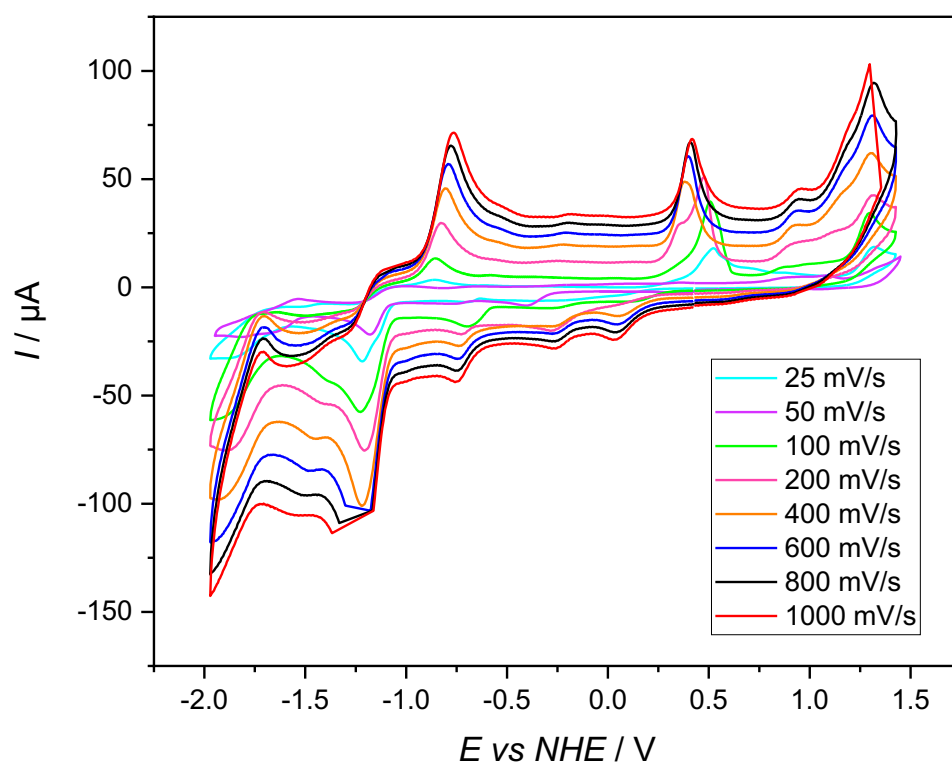


Figure S15: Scan rate dependency of [Ag(4-*n*-hexyloxy-BIAN)₂]BF₄ Ag-OC₆ in acetonitrile under argon. Cut off peaks at high scan rates are caused by limitations of the employed potentiostat.

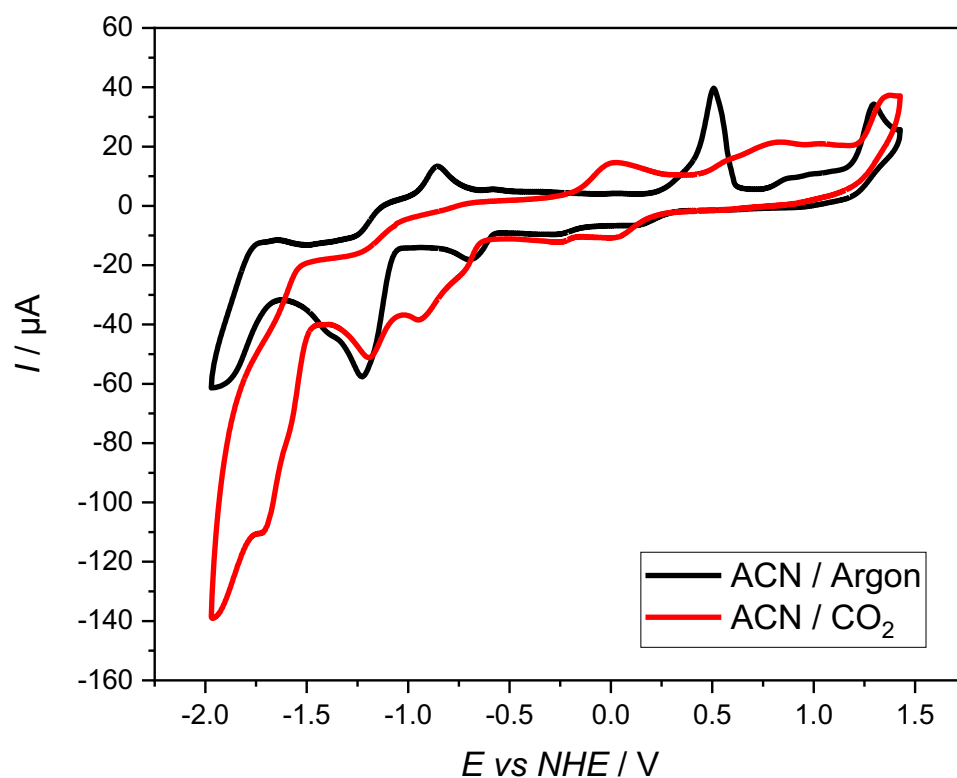


Figure S16: Comparison of cyclic voltammograms of [Ag(4-*n*-hexyloxy-BIAN)₂]BF₄ Ag-OC₆ in acetonitrile under argon and CO₂.

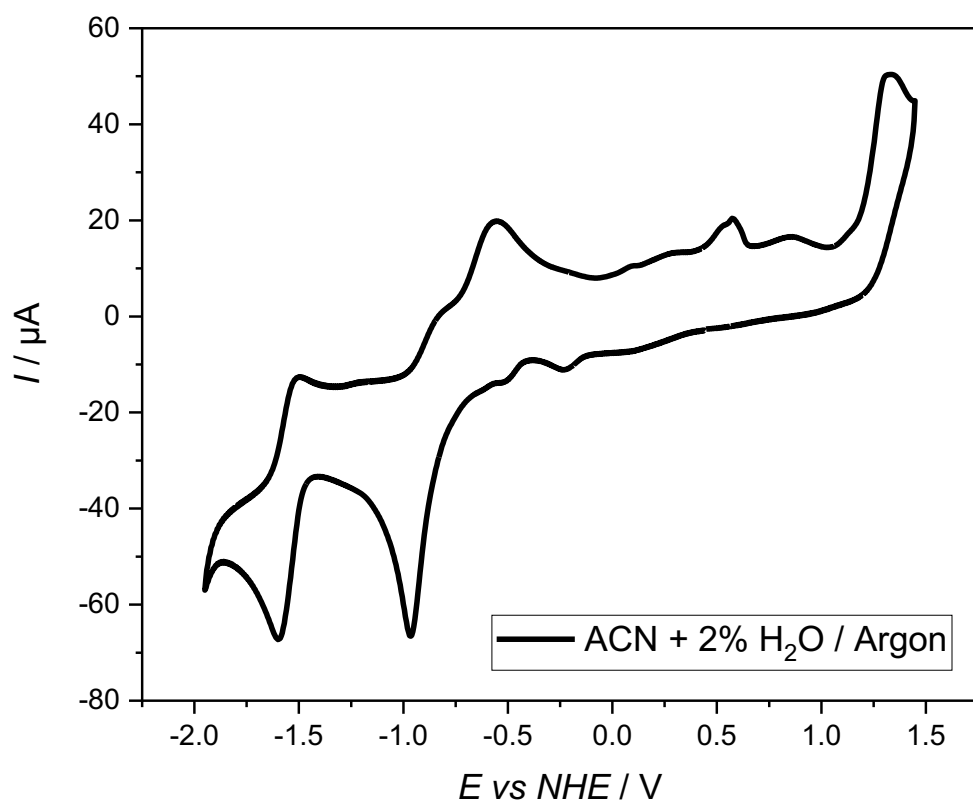


Figure S17: Cyclic voltammogram of $[\text{Ag}(4\text{-n-hexyloxy-BIAN})_2]\text{BF}_4$ **Ag-OC₆** in acetonitrile with 2% H_2O under argon.

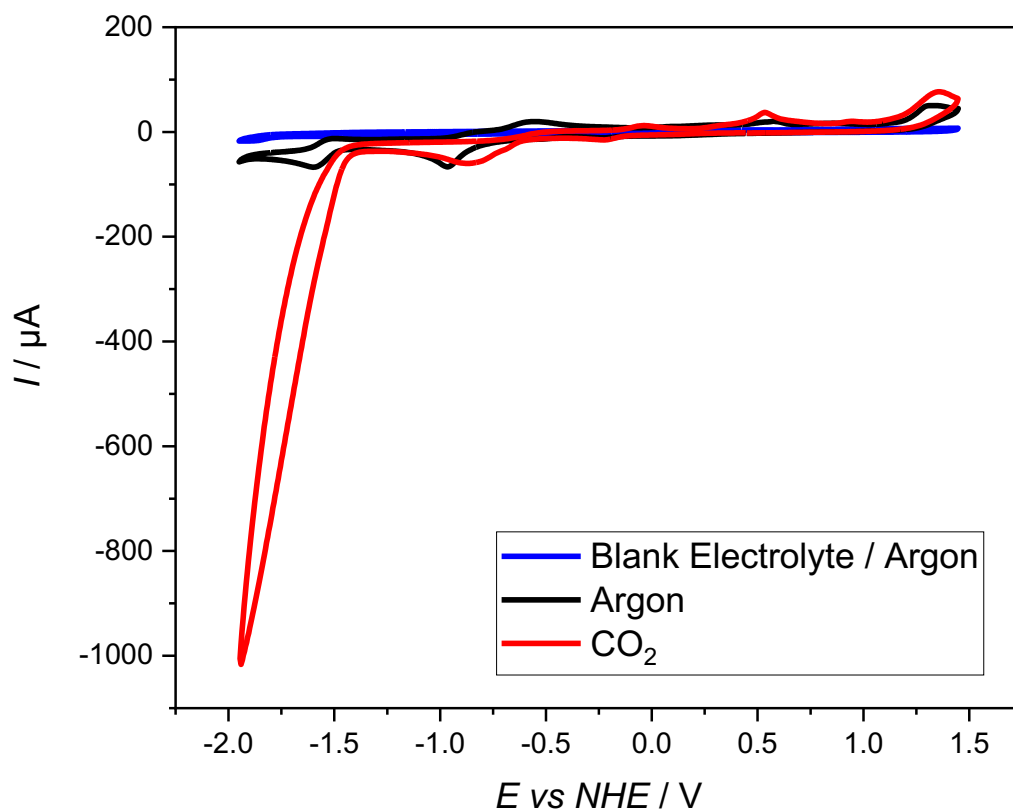


Figure S18: Comparison of cyclic voltammograms of $[\text{Ag}(4\text{-n-hexyloxy-BIAN})_2]\text{BF}_4$ **Ag-OC₆** in acetonitrile with 2% H_2O under argon and CO_2 and the blank electrolyte.

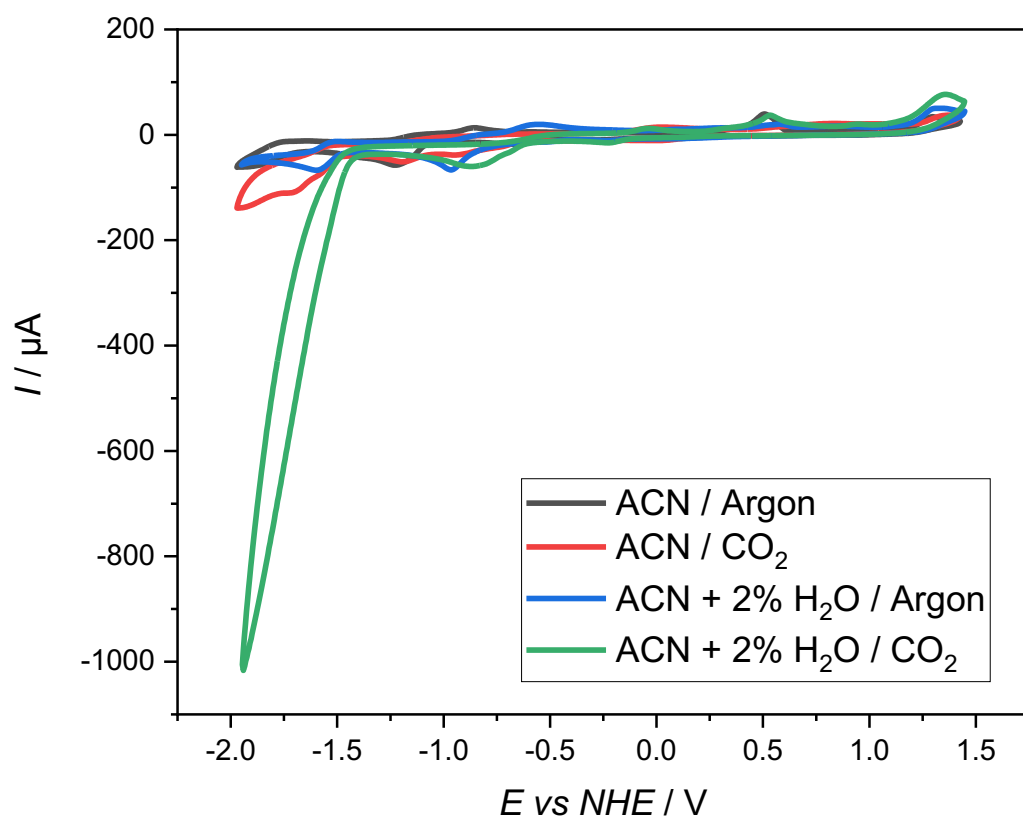


Figure S19: Comparison of cyclic voltammograms of $[\text{Ag}(4\text{-n-hexyloxy-BIAN})_2]\text{BF}_4$ Ag-OC₆ in acetonitrile and acetonitrile with 2% H_2O under argon and CO_2 .

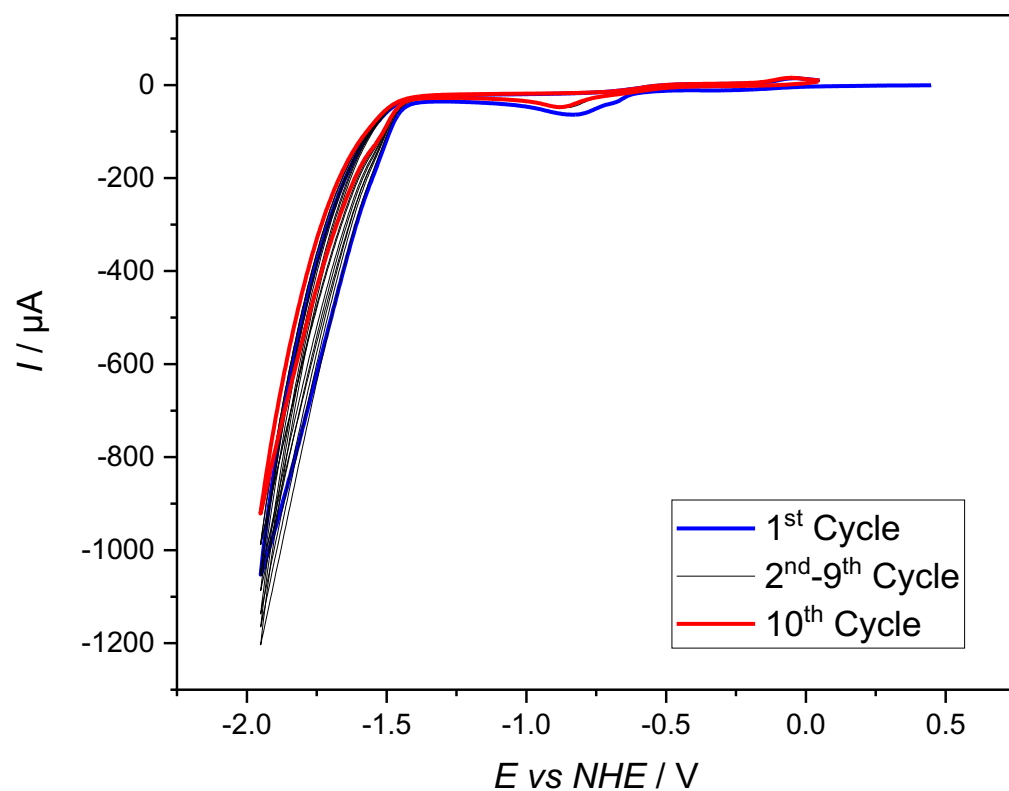


Figure S20: Stability test of $[\text{Ag}(4\text{-n-hexyloxy-BIAN})_2]\text{BF}_4$ Ag-OC₆ in acetonitrile with 2% H_2O under CO_2 .

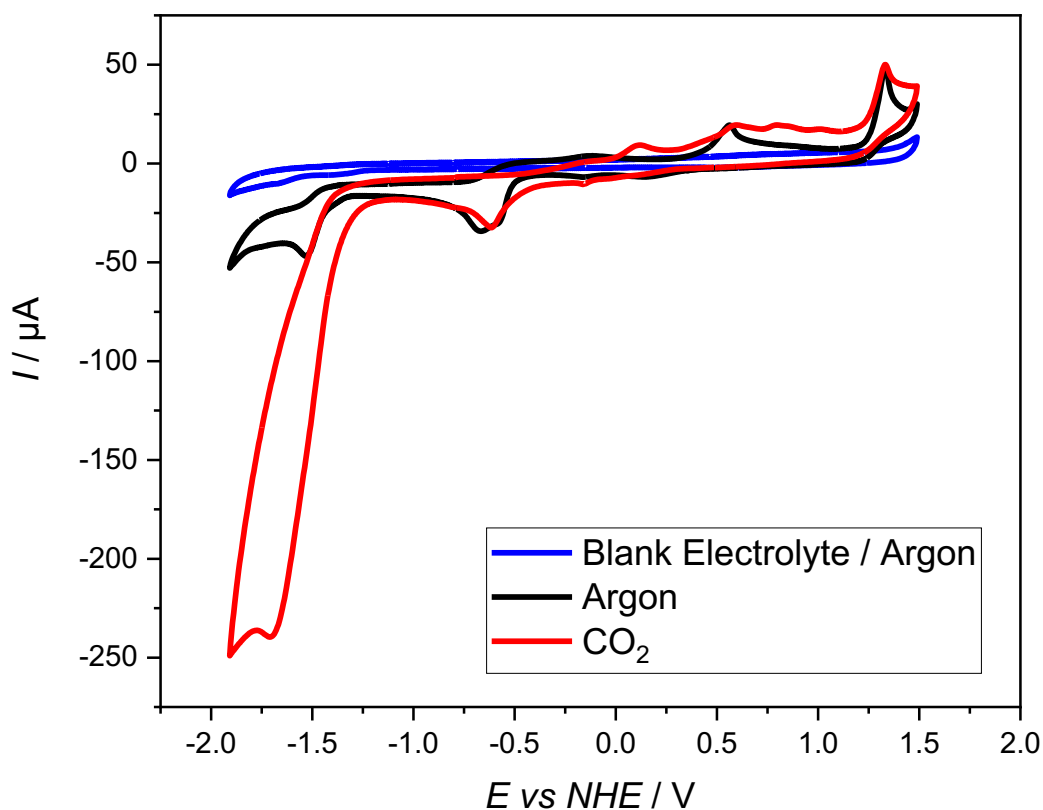


Figure S21: Comparison of cyclic voltammograms of 0.7mM $[\text{Ag}(4\text{-n-hexyloxy-BIAN})_2]\text{BF}_4$ Ag-OC₆ in acetonitrile with 15% H₂O under argon and CO₂ and the blank electrolyte.

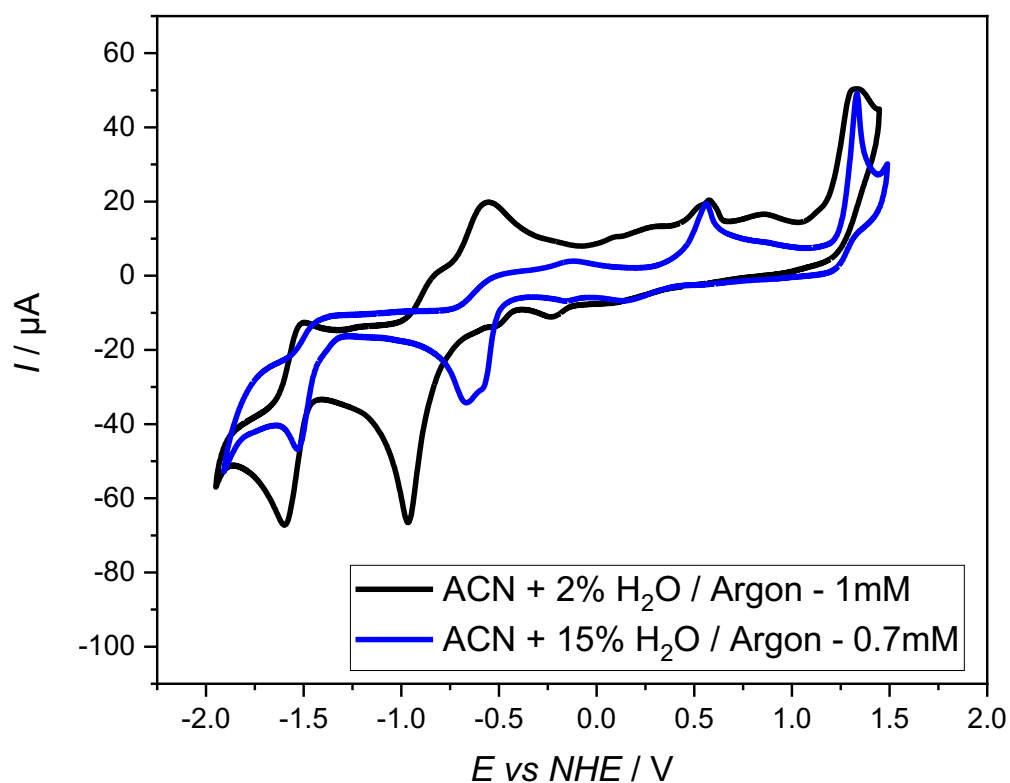


Figure S22: Comparison of cyclic voltammograms of $[\text{Ag}(4\text{-n-hexyloxy-BIAN})_2]\text{BF}_4$ Ag-OC₆ in acetonitrile with 2% H₂O (1mM) and 15% H₂O (0.7mM) under argon.

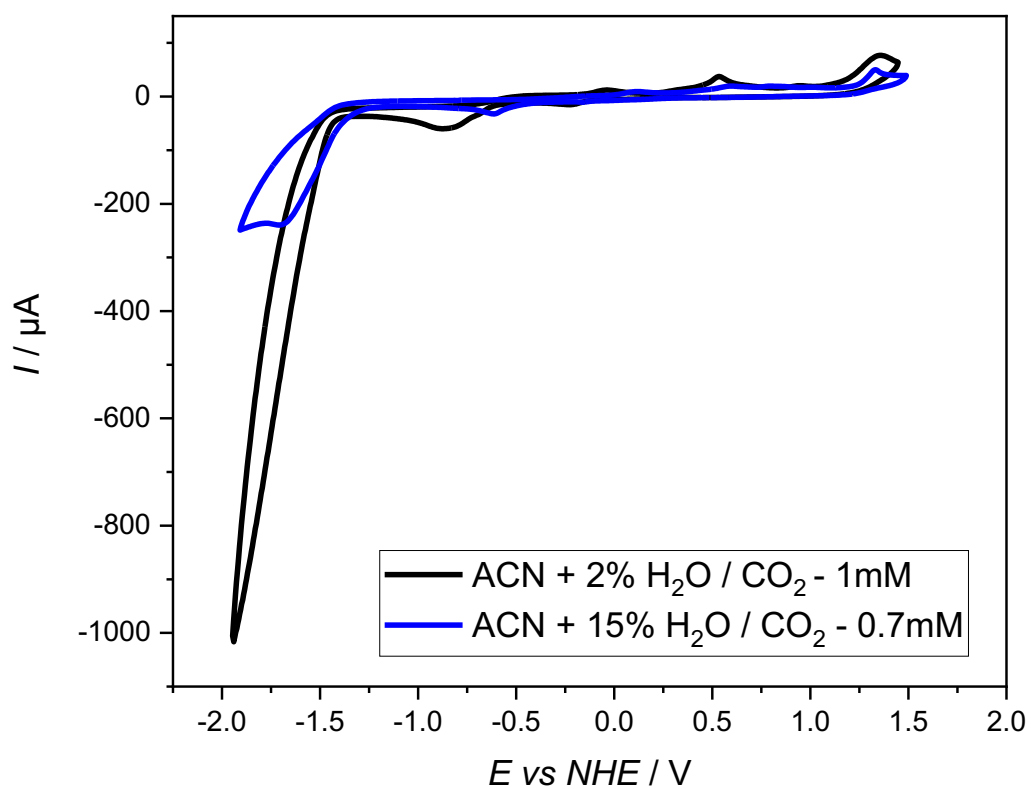


Figure S23: Comparison of cyclic voltammograms of $[\text{Ag}(\text{4-n-hexyloxy-BIAN})_2]\text{BF}_4$ Ag-OC₆ in acetonitrile with 2% H₂O (1mM) and 15% H₂O (0.7mM) under CO₂.

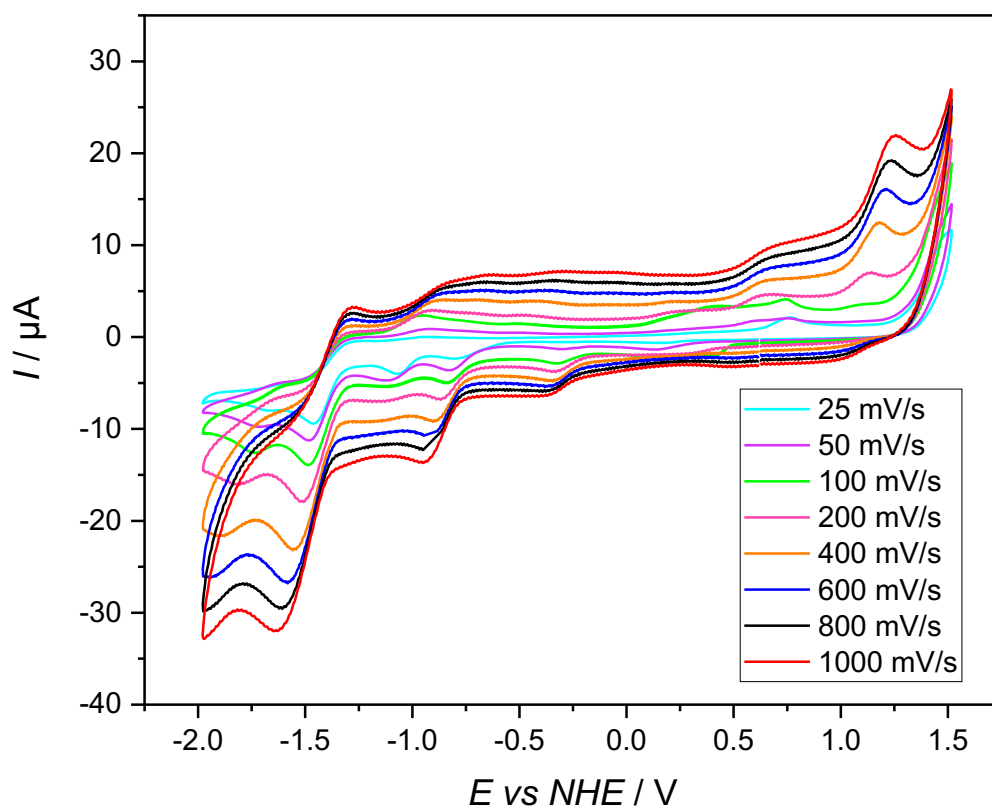


Figure S24: Scan rate dependency of 0.3mM $[\text{Ag}(\text{4-n-hexyloxy-BIAN})_2]\text{BF}_4$ Ag-OC₆ in THF under argon.

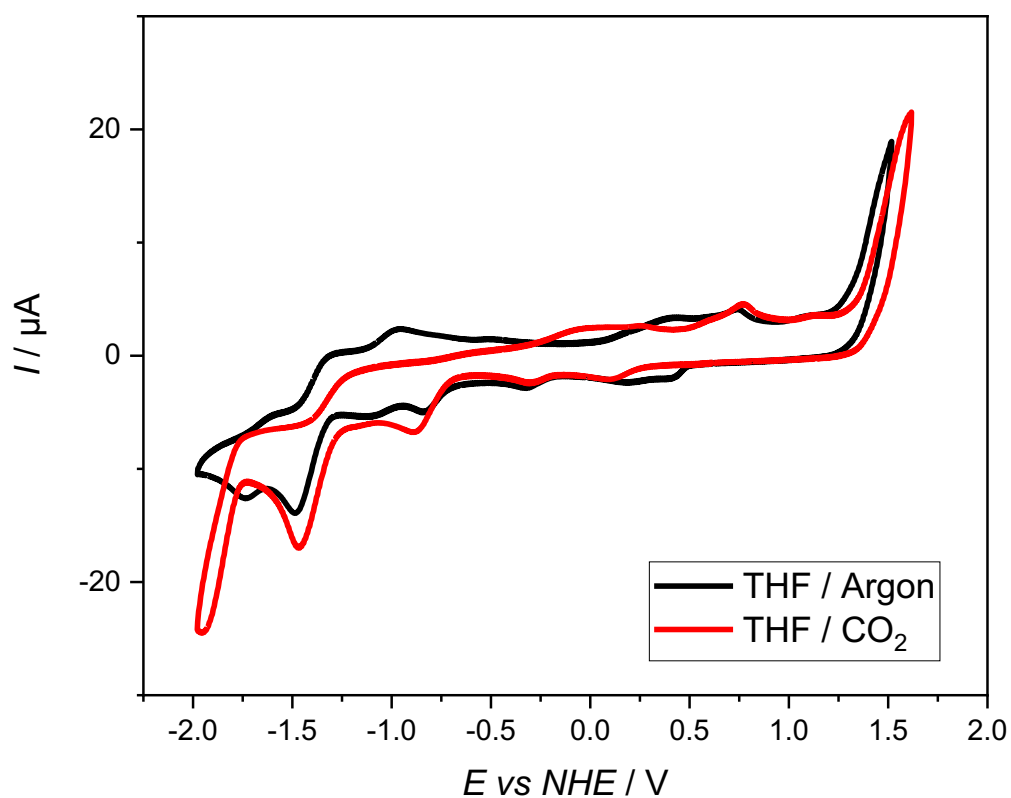


Figure S25: Comparison of cyclic voltammograms of 0.3mM [Ag(4-n-hexyloxy-BIAN)₂]BF₄ Ag-OC₆ in THF under argon and CO₂.

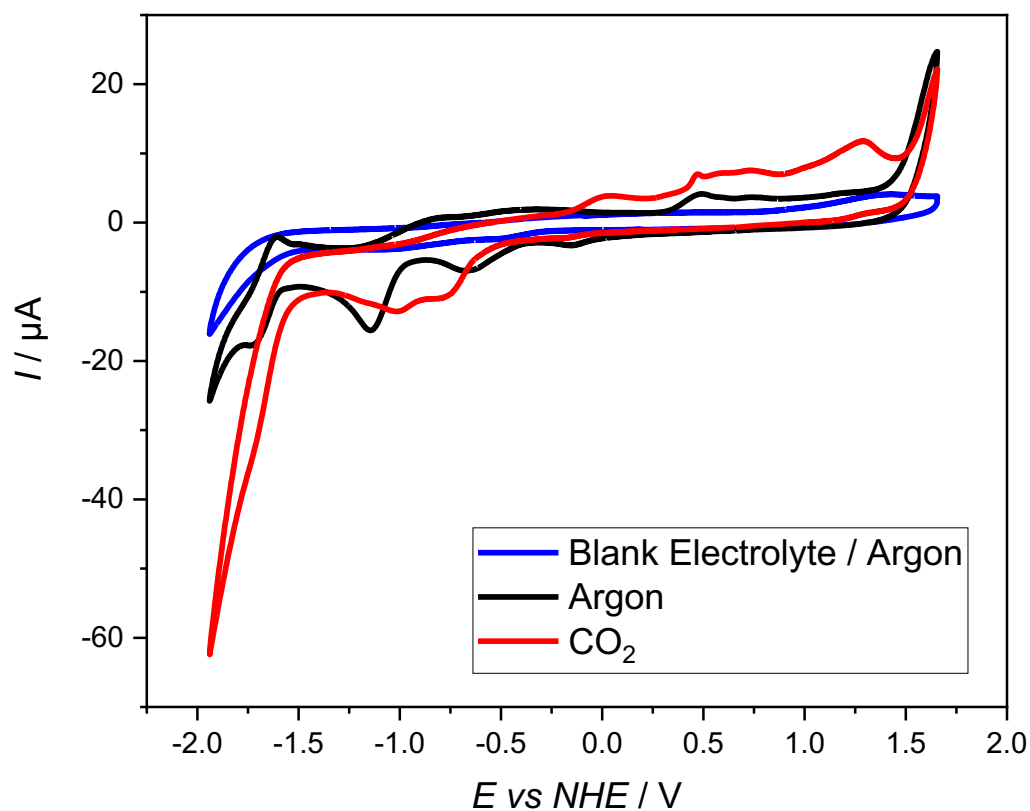


Figure S26: Comparison of cyclic voltammograms 0.3mM [Ag(4-n-hexyloxy-BIAN)₂]BF₄ Ag-OC₆ in THF with 2% H₂O under argon and CO₂ and the blank electrolyte.

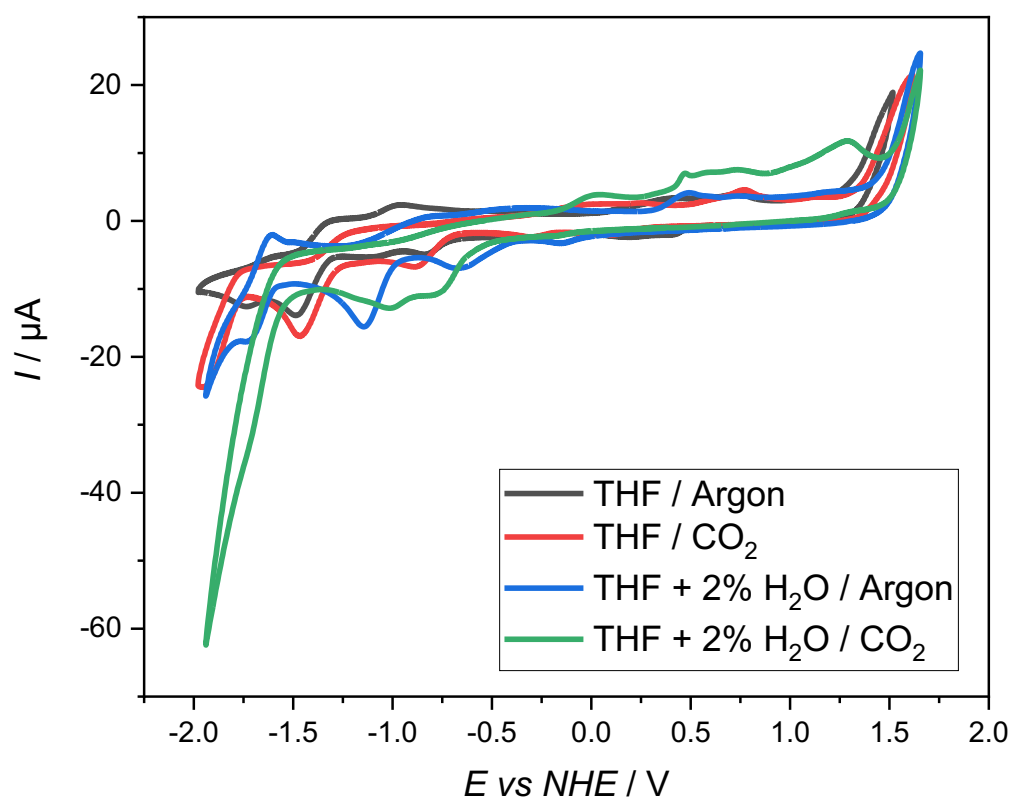


Figure S27: Comparison of cyclic voltammograms of 0.3mM $[\text{Ag}(\text{4-n-hexyloxy-BIAN})_2]\text{BF}_4 \cdot \text{Ag-OC}_6$ in THF and THF with 2% H_2O under argon and CO_2 .

Homogeneous Electrochemical Characterization of the $[\text{Ag}(4\text{-}n\text{-hexadecyloxy-BIAN})_2]\text{BF}_4$ (**Ag-OC₁₆**) complex

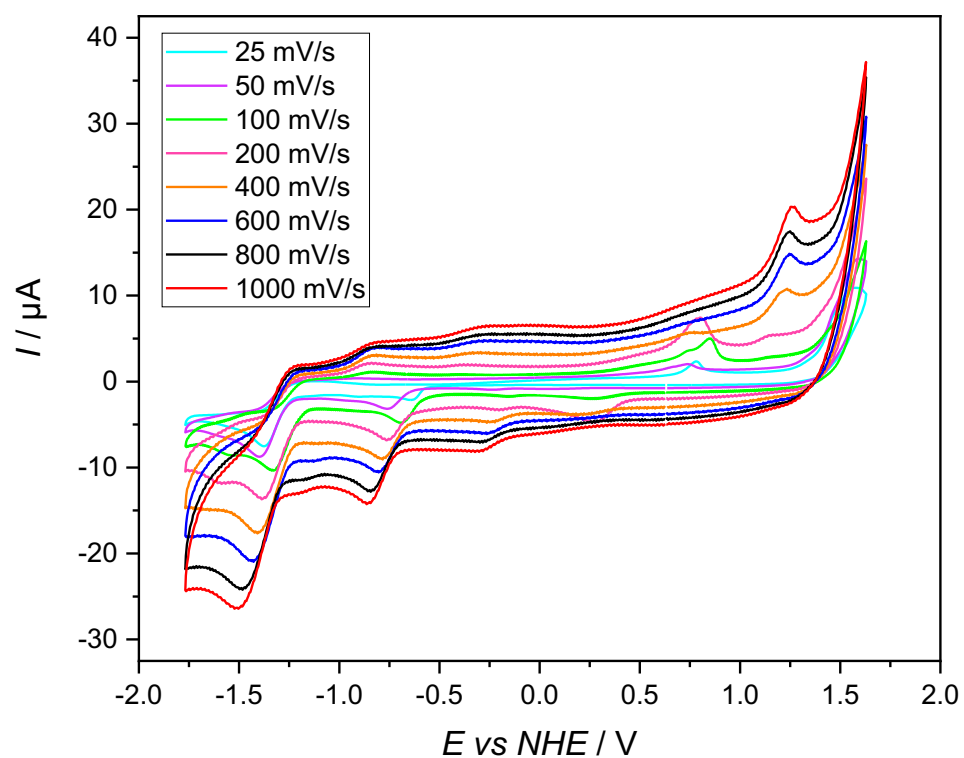


Figure S28: Scan rate dependency of 0.3mM $[\text{Ag}(4\text{-}n\text{-hexadecyloxy-BIAN})_2]\text{BF}_4$ **Ag-OC₁₆** in THF under argon.

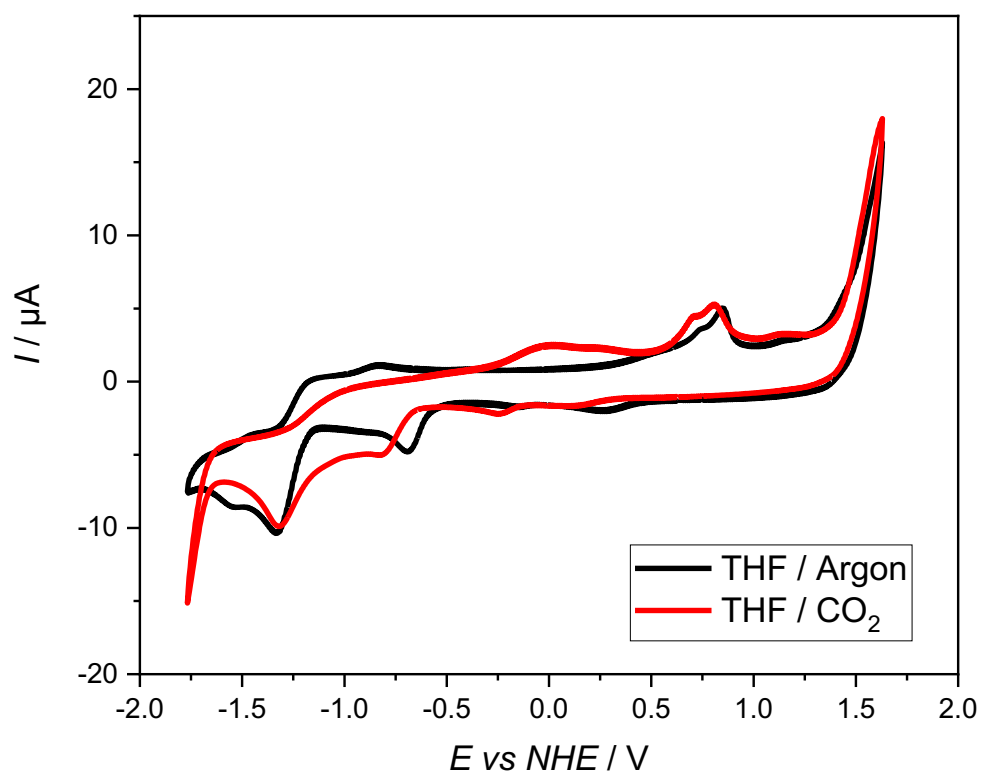


Figure S29: Comparison of cyclic voltammograms of 0.3mM [Ag(4-n-hexadecyloxy-BIAN)₂]BF₄ Ag-OC₁₆ in THF under argon and CO₂.

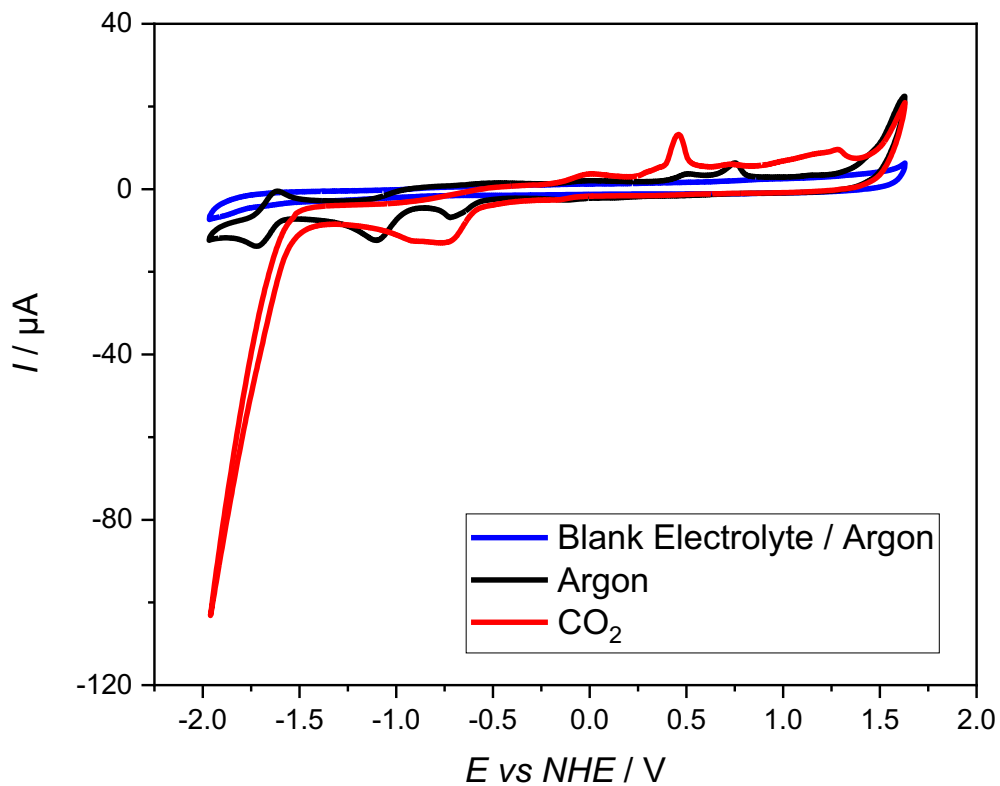


Figure S30: Comparison of cyclic voltammograms of 0.3mM [Ag(4-n-hexadecyloxy-BIAN)₂]BF₄ Ag-OC₁₆ in THF with 2% H₂O under argon and CO₂ and the blank electrolyte.

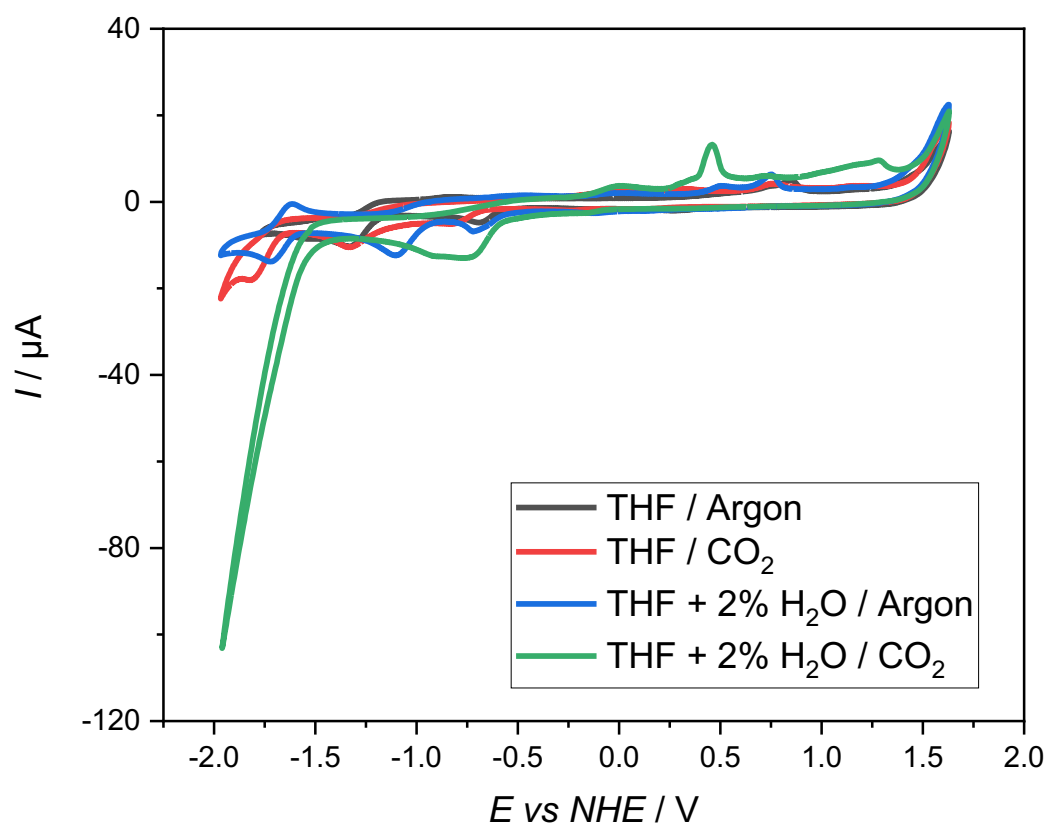


Figure S31: Comparison of cyclic voltammograms of 0.3mM $[Ag(4\text{-}n\text{-hexadecyloxy-BIAN})_2]BF_4 \text{ Ag-OC}_{16}$ in THF and THF with 2% H_2O under argon and CO_2 .

Figure S32: Stability test of 0.3mM $[\text{Ag}(\text{4-n-hexadecyloxy-BIAN})_2]\text{BF}_4$ Ag-OC₁₆ in THF with 2% H₂O under CO₂.

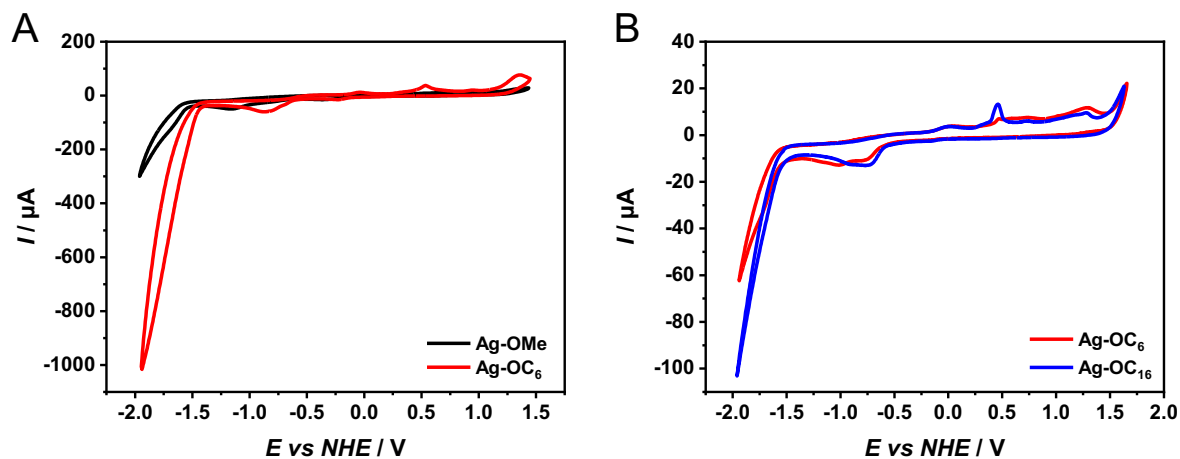


Figure S33: A) Comparison of cyclic voltammograms of 1mM Ag-OMe and Ag-OC₆ in ACN + 2% H₂O under CO₂. B) Comparison of cyclic voltammograms of 0.3mM Ag-OC₆ and Ag-OC₁₆ in THF + 2% H₂O under CO₂.

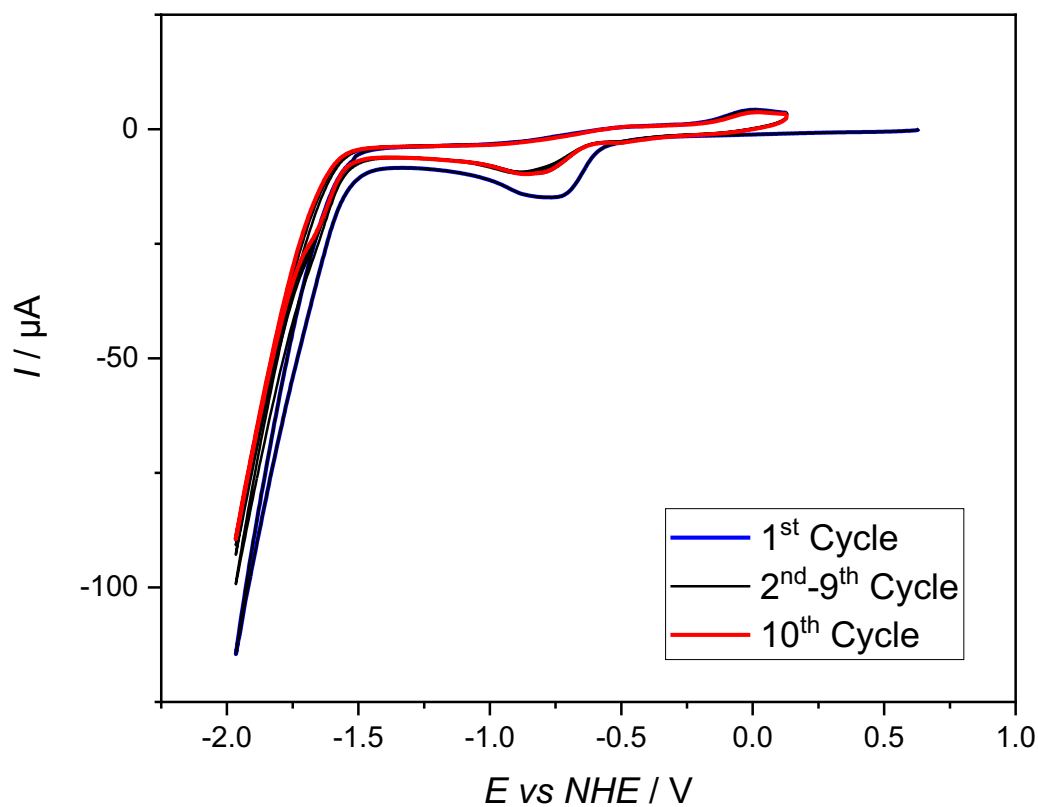


Table S1: Full range CV current densities (0.28 cm² glassy carbon WE) of 1mM or 0.3mM Ag(I) BIAN complexes **Ag-OMe**, **Ag-OC₆** and **Ag-OC₁₆** under argon or CO₂ in 2% aqueous acetonitrile or THF solutions at a potential of -1.90 V vs NHE and cathodic scan rate of 100 mV s⁻¹.

Compound	1 mM ACN + 2% H ₂ O		0.3 mM THF + 2% H ₂ O	
	$j_{Ar} / \mu\text{A cm}^{-2}$	$j_{CO_2} / \mu\text{A cm}^{-2}$	$j_{Ar} / \mu\text{A cm}^{-2}$	$j_{CO_2} / \mu\text{A cm}^{-2}$
Ag-OMe	-187	-895	-	-
Ag-OC₆	-184	-3349	-80	-198
Ag-OC₁₆	-	-	-42	-306

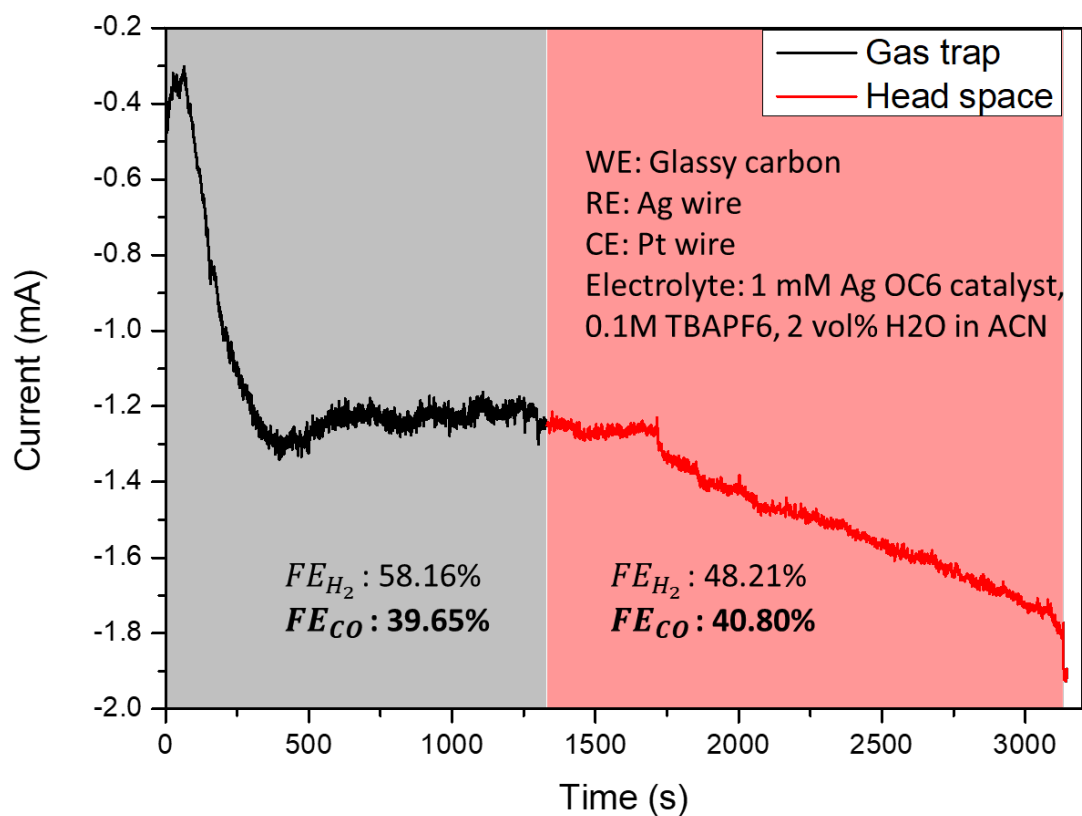


Figure S34: Chronoamperometric measurement of a homogeneous electrocatalytic CO₂ reduction at -2.0 V vs. NHE, with the respected FE-values for the obtained gaseous products.

Electrochemical Characterization in zero-gap electrolyzers

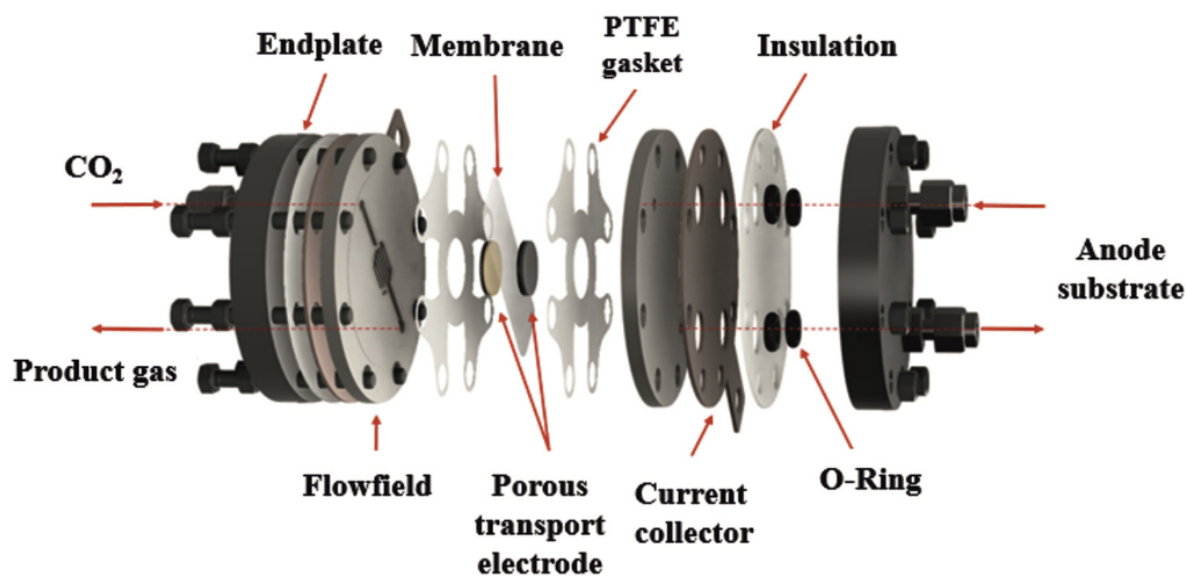


Figure S35 Schematic representation of the zero-gap electrolyzer employed in this work, developed in our previous investigation reported by Hoof *et al.*⁸

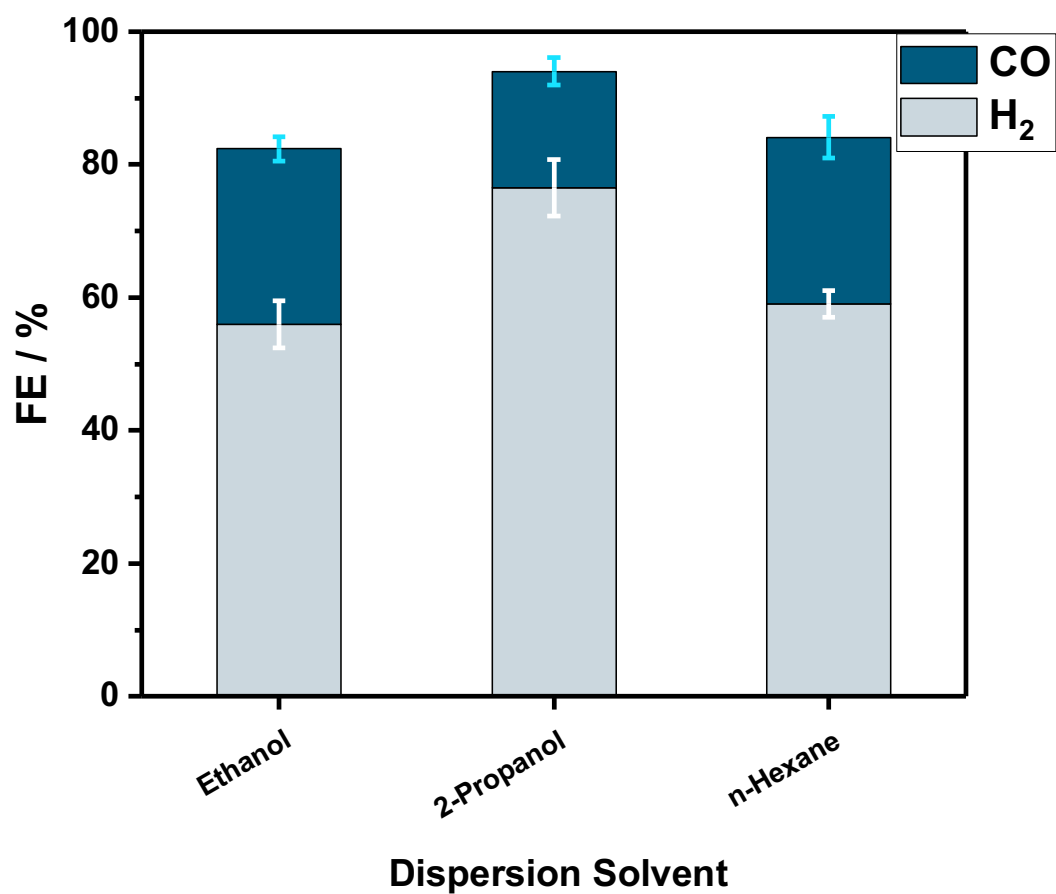


Figure S36 Comparison of the effect of employed dispersion solvent for the generation for the generation of the catalytic ink on the performance of Ag-OC₁₆ for the CO₂ reduction in a zero-gap electrolyzer at 100 mA cm⁻² at 25°C after 1 h of electrolysis. All investigated GDEs possessed a catalytic loading of 0.5 mg cm⁻² of active material.

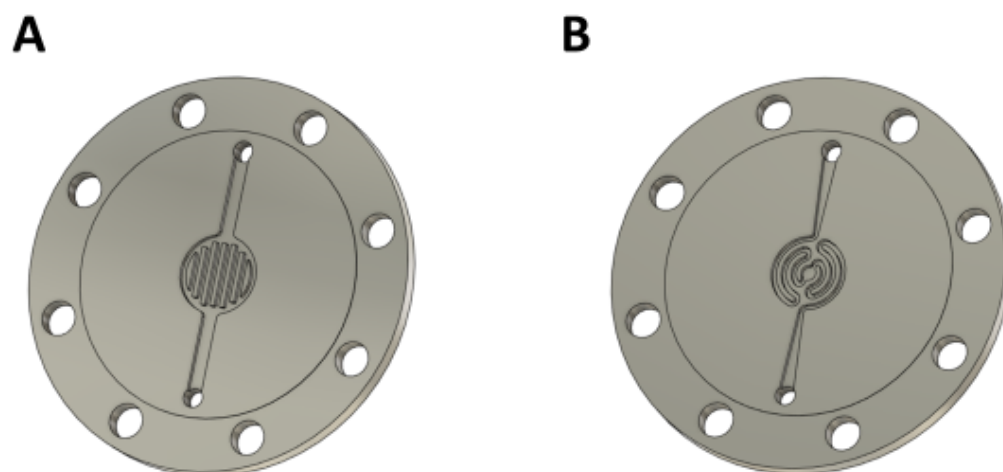


Figure S37 Schematics of the flow-fields parallel (A) and serpentine (B) used in this work.

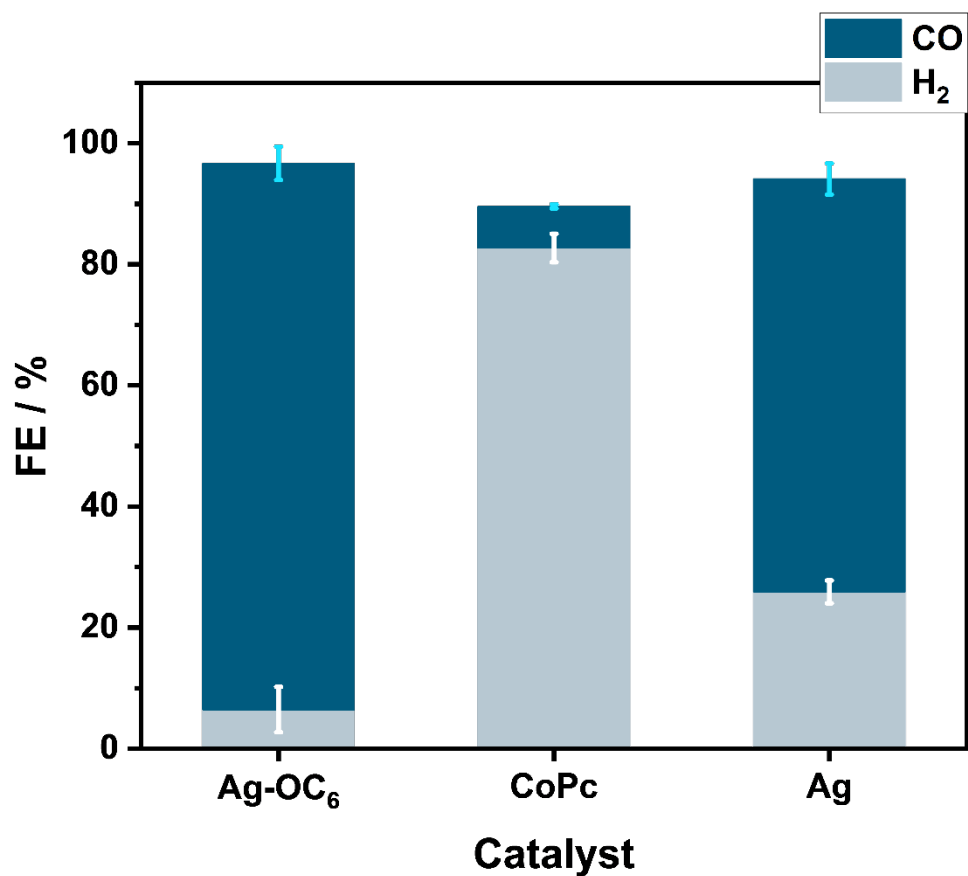


Figure S38: Comparison of the performance of Ag-OC₆, Co(II) phthalocyanine (CoPC) and Ag-NPS for the CO₂ reduction in a zero-gap electrolyzer at 300 mA cm⁻² at 60°C after 1 h of electrolysis. All investigated GDEs possessed a catalytic loading of 0.5 mg cm⁻² of active material.

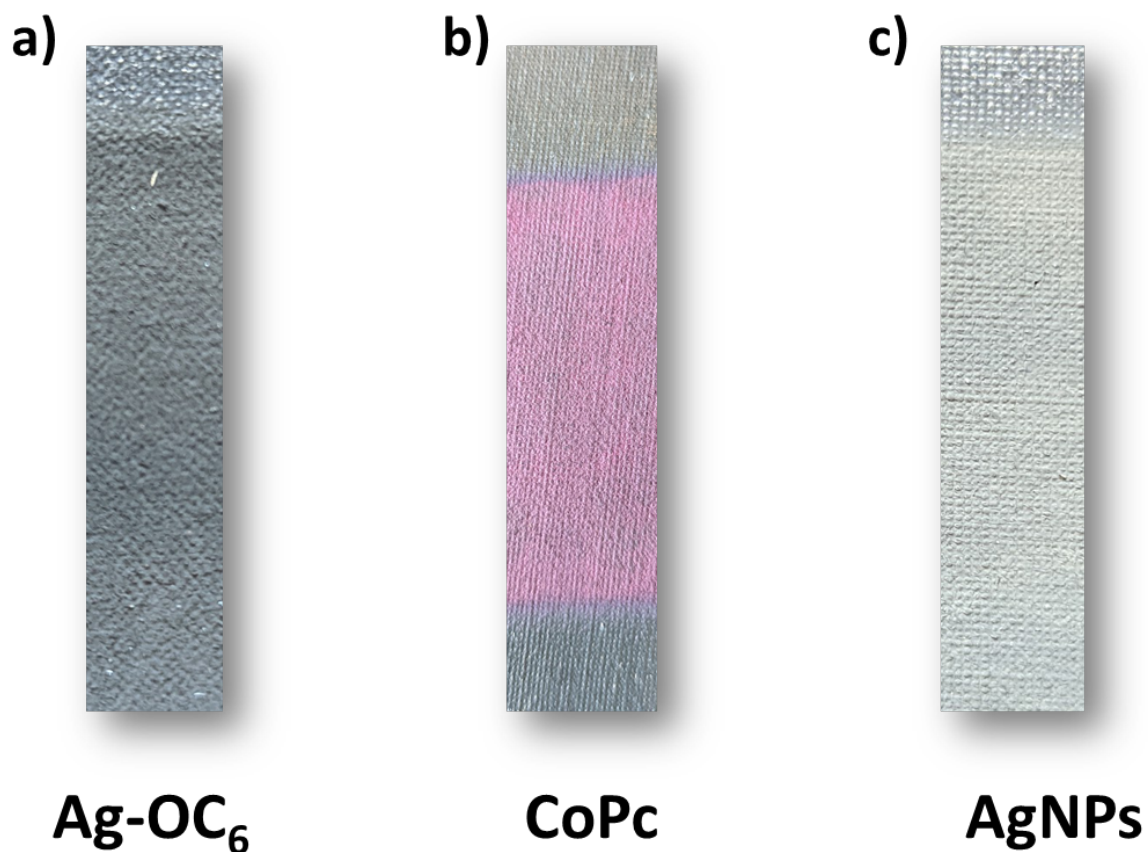


Figure S39 Photograph of the generated GDEs: Ag-OC₆ (a), CoPc (b), AgNPs (c). Evidently, the Ag-OC₆ catalysts is finely dispersed within the carbon matrix, while CoPc and AgNPs show significant agglomeration under similar electrode preparation.

Electrode Characterization & Post-mortem Characterization of the tested GDES

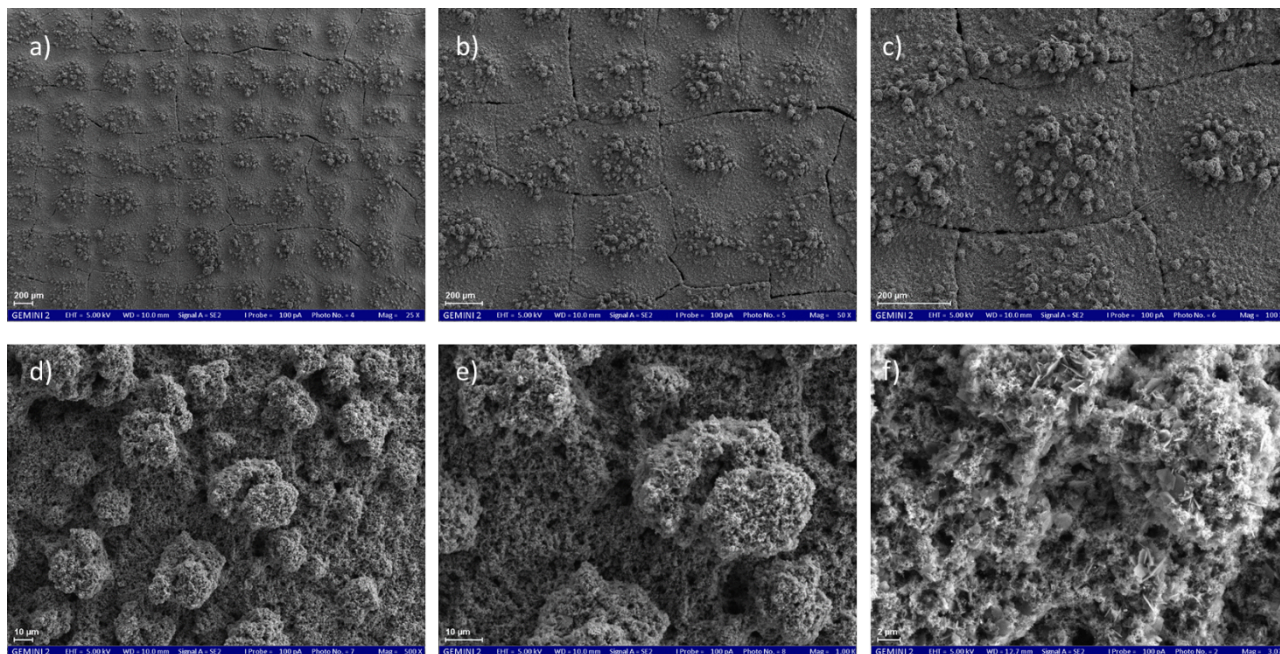


Figure S40 SEM Analysis of a Ag-OC₆ GDE (0.5 mg cm⁻² loading) at a magnification of x25 (a), x50 (b), x100 (c), x500 (d), x1000(e), x3000(f).

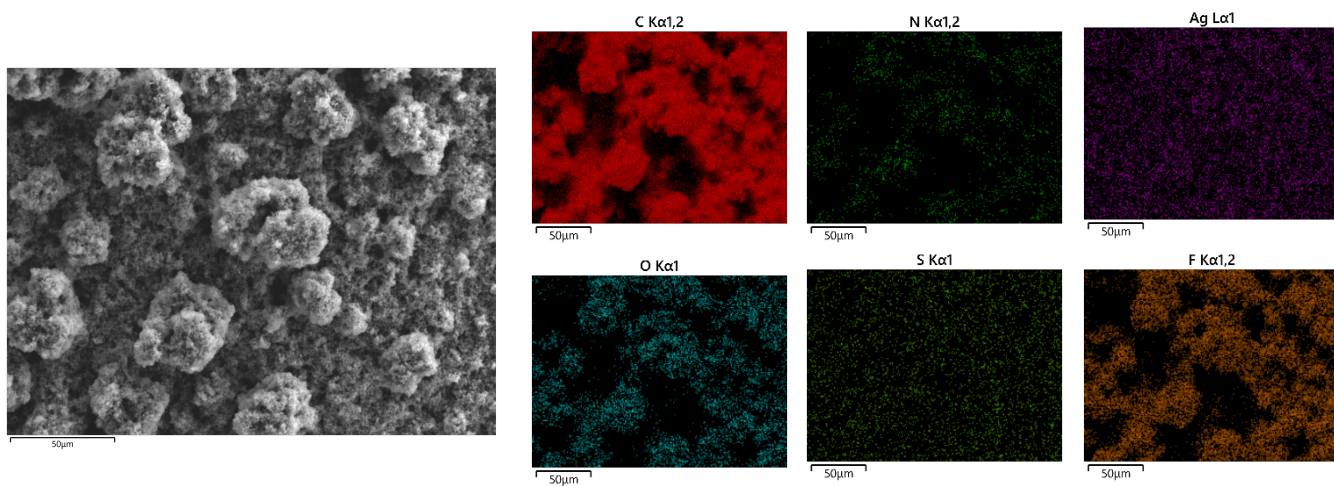


Figure S41 EDX Analysis of a Ag-OC₆ GDE (0.5 mg cm⁻² loading) prior to electrolysis.

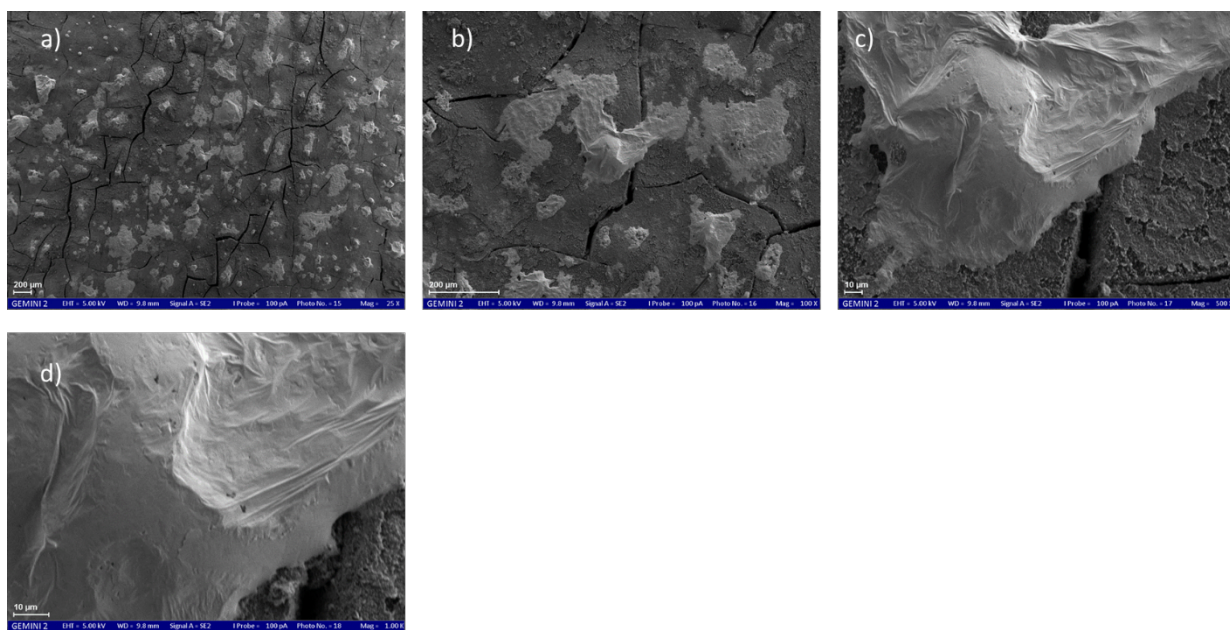


Figure S42 SEM Analysis of a Ag-OC₆ GDE (0.5 mg cm⁻² loading) after 1 h of electrolysis at 300 mA cm⁻² at a magnification of x25 (a), x100 (b), x500 (c), x1000 (d).

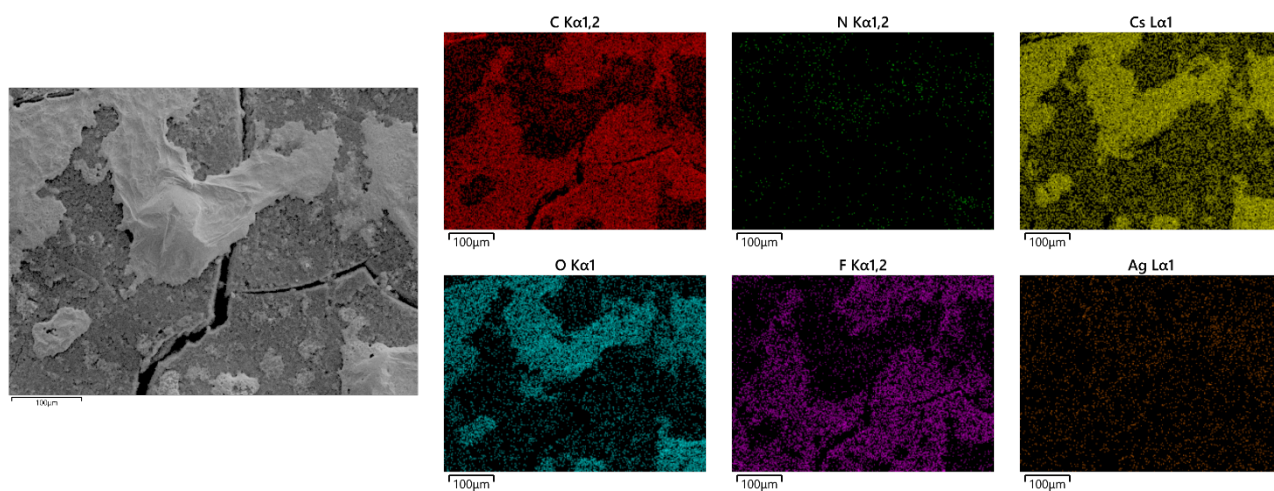


Figure S43 EDX Analysis of a Ag-OC₆ GDE (0.5 mg cm⁻²) after 1 h of electrolysis at 300 mA cm⁻² at 60°C.

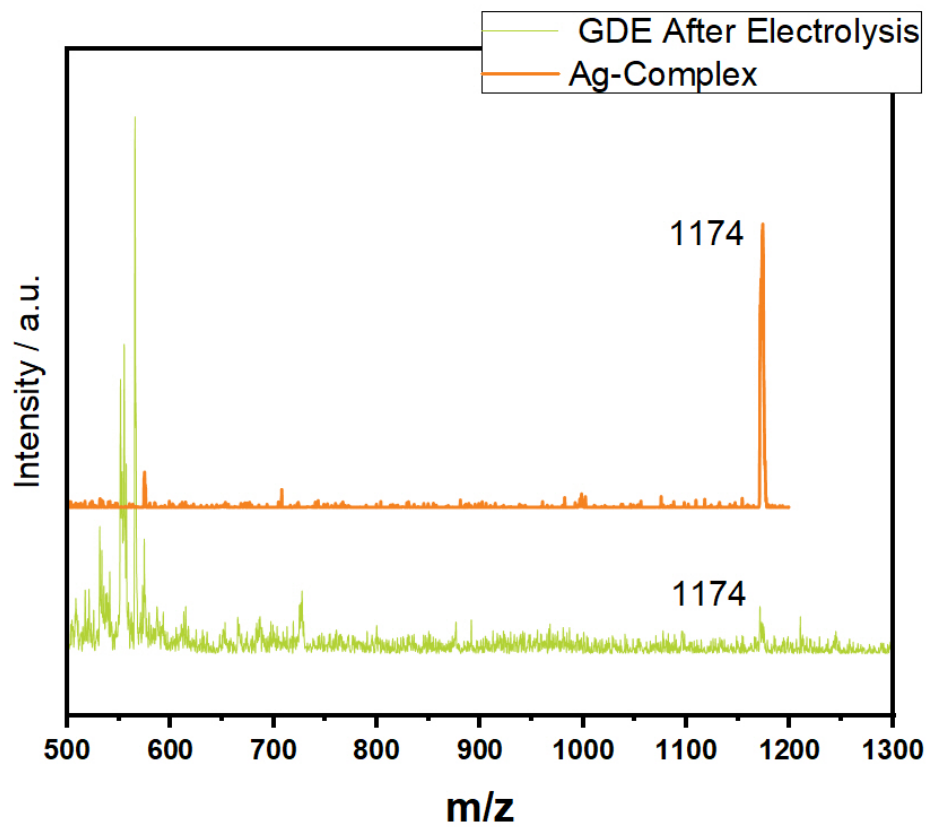


Figure S44 ESI-Analysis of the Ag-OC₆ complex and respective GDE after electrolysis at 300 mA cm⁻² for 1 h at 60°C.

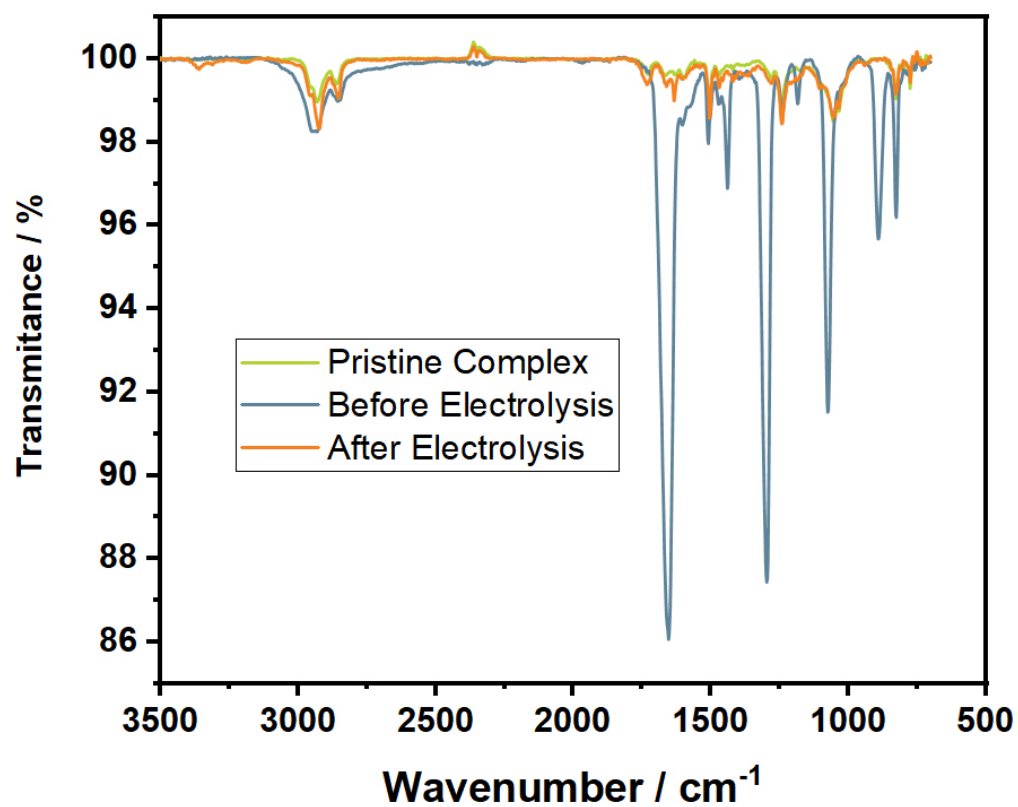


Figure S45 IR-Analysis of the Ag-OC₆ molecular electrocatalyst as well as of the the investigated GDE before and after electrolysis. The emerging additional peaks could be assigned to the ionomer involved in the zero-gap set-up (Nafion Binder and Piperion Membrane) and the built-up carbonate.

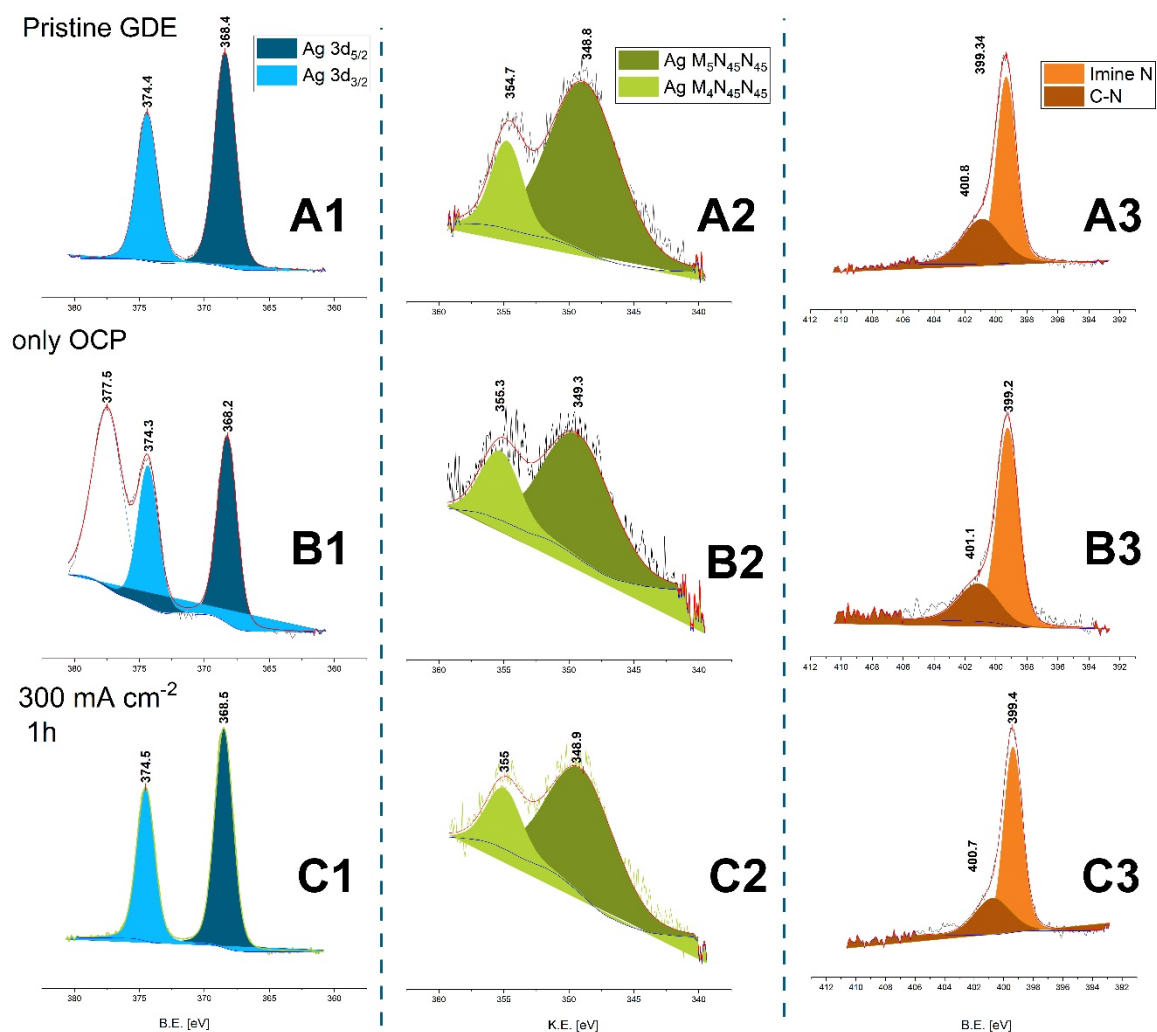


Figure S46 XPS Analysis of the Ag 3d (A1) Ag MNN (A2) and N 1S (A3) regions of the pristine Ag-OC₆ GDE prior to electrolysis. XPS Analysis of the Ag 3d (B1) Ag MNN (B2) and N 1S (B3) regions of the pristine Ag-OC₆ GDE after 1 h of electrochemical testing under OCP. XPS Analysis of the Ag 3d (C1) Ag MNN (C2) and N 1S (C3) regions of the Ag-OC₆ after 1 h of electrolysis at 300 mA cm⁻² at 60°C.

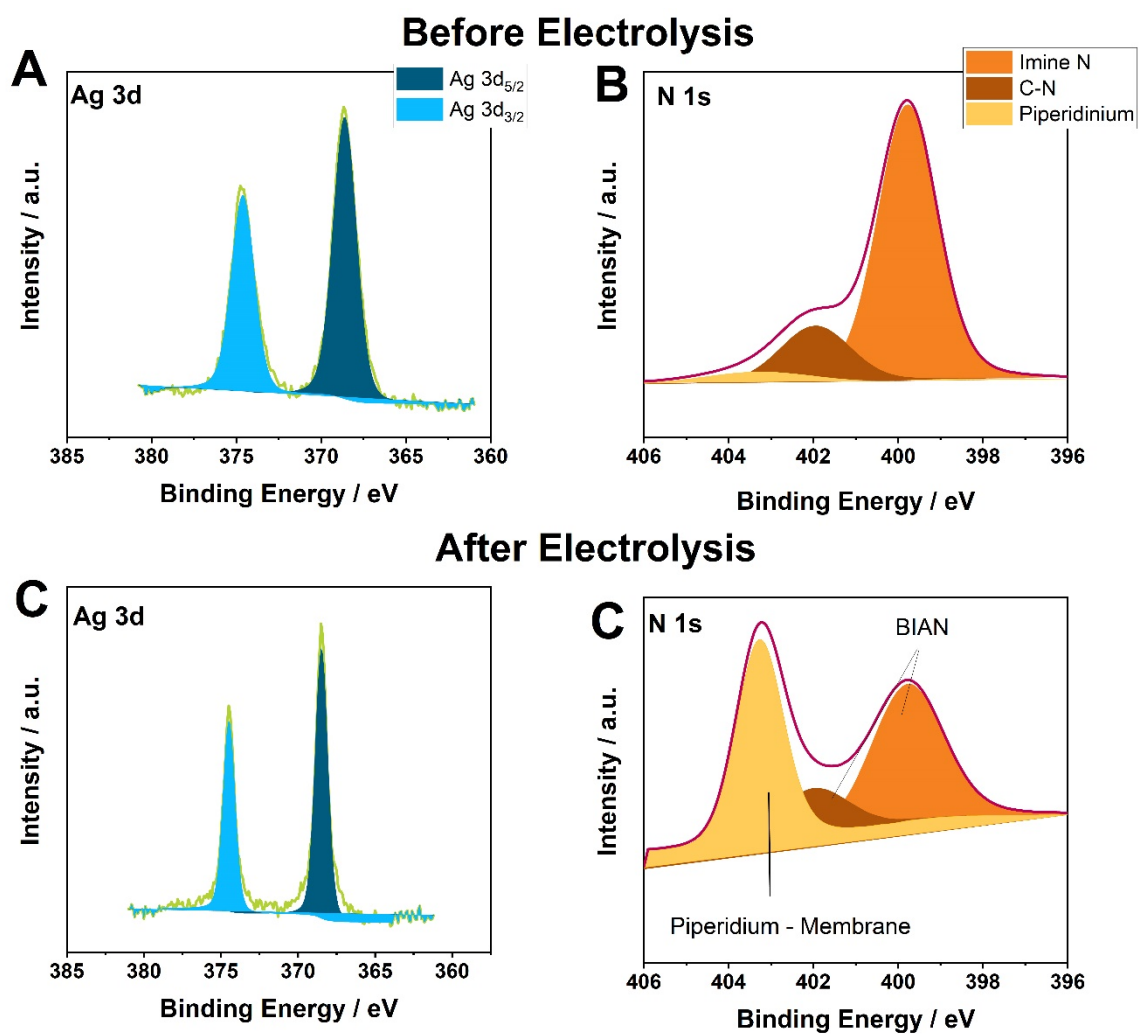


Figure S47 XPS Analysis of the Ag-OC₆ GDE prior and after 20 h of electrolysis at 300 mA cm⁻² at 60°C.

Table S2 Post-mortem eleelectrolysis characterization of the Ag-OC₆ complex after 20 h of electrolysis.

	Ag- 3d_{5/2} value /eV	Auger Parameter
Ag-GDE	368.8	725.8
Ag-OC₆ GDE		
Pristine GDE	368.4	723.1
Prior to electrolysis	368.5	723.3
After 1 h of electrolysis	368.6	725.6
After 20 h of electrolysis	368.8	725.8

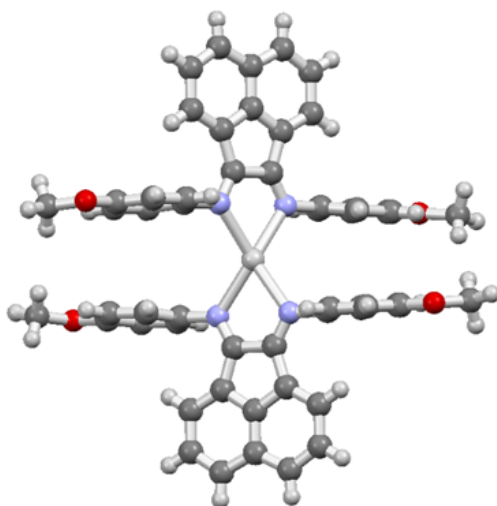


Figure S48 Crystal Data, data collection and structure refinement details for Ag-OMe.

Compound	Ag4
Empirical formula	C ₈₂ H ₄₀ Ag ₁ N ₄ O ₄ B ₁ F ₄
Formula weight [g/mol]	979.56
Color	dark red
Crystal size [mm]	0.59 × 0.36 × 0.36
Crystal system	Orthorhombic
Space group	Ccca
<i>a</i> [Å]	12.749(2)
<i>b</i> [Å]	22.706(5)
<i>c</i> [Å]	17.737(3)
α [°]	90
β [°]	90
γ [°]	90
<i>V</i> [Å ³]	5134.5(16)
<i>Z</i>	4
<i>D</i> _{calc} [g/cm ³]	1.267
μ [mm ⁻¹]	0.45
<i>T</i> [K]	296

θ range [°]	2.9-24.4
No. of reflections measured	41788
No. of independent reflections	2361
Obs. Reflections with $I > 2\sigma(I)$	1825
No. of Parameters refined/restraints	153/0
Absorption correction	multi-scan
<i>T</i> _{min} , <i>T</i> _{max}	0.80, 0.86
$\Delta\rho_{\min}/\Delta\rho_{\max}$ [e Å ⁻³]	-0.31/0.40
<i>F</i> (000)	2000
<i>R</i> _{int}	0.041
<i>R</i> ₁ ($R[F^2 \geq 2\sigma(F^2)]$)	0.040
<i>wR</i> ₂ (<i>wR</i> (<i>F</i> ²))	0.121
GooF	1.10
CCDC no.	2167847

Figure S49 Data collection details for the crystal structure Ag-OMe

Table S3: Structure refinement XYZ coordinates of Ag(4-OMe-BIAN)₂]BF₄ (Ag-OCH₃)

Ag	6.374500	5.676500	4.434250
C	6.755695	8.637589	5.096195
O	10.068395	7.451655	10.317081
N	7.120317	7.543614	5.606311
C	7.529559	12.102298	6.546727
H	7.922433	12.540251	7.265661
C	7.529559	10.698159	6.537858
H	7.916721	10.218517	7.233521
C	6.946930	10.050130	5.478959
C	6.374500	10.810327	4.434250
C	6.374500	12.233993	4.434250
C	6.977528	12.852731	5.548134
H	7.000017	13.780839	5.602515
C	7.845735	7.528401	6.846482
C	9.221352	7.560644	6.843289
H	9.681527	7.596928	6.036238
C	9.911073	7.539981	8.017124
H	10.839455	7.580512	8.000008
C	9.268523	7.461192	9.217032
C	7.896731	7.363102	9.229980
H	7.440112	7.277614	10.035807
C	7.198085	7.392392	8.028830
H	6.270621	7.317803	8.036706
C	9.440635	7.331767	11.589178
H	8.974799	8.147299	11.793633
H	10.105979	7.167558	12.260772
H	8.816023	6.603654	11.571033
C	5.993305	8.637589	3.772305
O	2.680605	7.451655	-1.448581
N	5.628684	7.543614	3.262189
C	5.219441	12.102298	2.321773
H	4.826567	12.540251	1.602839
C	5.219441	10.698159	2.330642
H	4.832279	10.218517	1.634979
C	5.802070	10.050130	3.389541
C	5.771472	12.852731	3.320366
H	5.748983	13.780839	3.265985
C	4.903265	7.528401	2.022018
C	3.527648	7.560644	2.025211
H	3.067473	7.596928	2.832262
C	2.837927	7.539981	0.851376
H	1.909545	7.580512	0.868492
C	3.480477	7.461192	-0.348532
C	4.852269	7.363102	-0.361480

H	5.308888	7.277614	-1.167307
C	5.550915	7.392392	0.839670
H	6.478379	7.317803	0.831794
C	3.308365	7.331767	-2.720678
H	3.774201	8.147299	-2.925133
H	2.643021	7.167558	-3.392272
H	3.932977	6.603654	-2.702533
C	5.993305	2.715411	5.096195
O	2.680605	3.901345	10.317081
N	5.628684	3.809386	5.606311
C	5.219441	-0.749298	6.546727
H	4.826567	-1.187251	7.265661
C	5.219441	0.654841	6.537858
H	4.832279	1.134483	7.233521
C	5.802070	1.302870	5.478959
C	6.374500	0.542673	4.434250
C	6.374500	-0.880993	4.434250
C	5.771472	-1.499731	5.548134
H	5.748983	-2.427839	5.602515
C	4.903265	3.824599	6.846482
C	3.527648	3.792356	6.843289
H	3.067473	3.756072	6.036238
C	2.837927	3.813019	8.017124
H	1.909545	3.772488	8.000008
C	3.480477	3.891808	9.217032
C	4.852269	3.989898	9.229980
H	5.308888	4.075386	10.035807
C	5.550915	3.960608	8.028830
H	6.478379	4.035197	8.036706
C	3.308366	4.021233	11.589178
H	3.774201	3.205701	11.793633
H	2.643021	4.185442	12.260772
H	3.932977	4.749346	11.571033
C	6.755695	2.715411	3.772305
O	10.068395	3.901345	-1.448581
N	7.120317	3.809386	3.262189
C	7.529559	-0.749298	2.321773
H	7.922433	-1.187251	1.602839
C	7.529559	0.654841	2.330642
H	7.916721	1.134483	1.634979
C	6.946930	1.302870	3.389541
C	6.977528	-1.499731	3.320366
H	7.000017	-2.427839	3.265985
C	7.845735	3.824599	2.022018
C	9.221352	3.792356	2.025211
H	9.681527	3.756072	2.832262
C	9.911073	3.813019	0.851376
H	10.839455	3.772488	0.868492
C	9.268523	3.891808	-0.348532
C	7.896731	3.989898	-0.361480
H	7.440112	4.075386	-1.167307
C	7.198085	3.960608	0.839670

H	6.270621	4.035197	0.831794
C	9.440635	4.021233	-2.720678
H	8.974799	3.205701	-2.925133
H	10.105979	4.185442	-3.392272
H	8.816023	4.749346	-2.702533
F	5.612110	6.484607	12.545380
B	6.374500	5.676500	13.302750
F	7.136890	6.484607	14.060120
F	7.136890	4.868393	12.545380
F	5.612110	4.868393	14.060120

Table S4: Geometry-optimized XYZ coordinates of Ag(4-OMe-BIAN)₂]BF₄ (Ag-OCH₃)

Ag	0.000000	0.000000	0.000100
C	-0.451400	3.058000	-0.619700
O	-4.203300	1.661400	-5.579100
N	-0.836300	1.954500	-1.131200
C	-1.429800	6.533000	-1.964300
H	-1.994000	7.035300	-2.737400
C	-1.416200	5.116100	-1.949800
H	-1.962900	4.570700	-2.702300
C	-0.696600	4.470600	-0.962500
C	0.000000	5.245600	-0.000000
C	-0.000000	6.653300	-0.000000
C	-0.748300	7.287100	-1.027600
H	-0.783900	8.367600	-1.074000
C	-1.673000	1.915700	-2.287200
C	-3.063100	1.825800	-2.143900
H	-3.501200	1.830400	-1.155200
C	-3.877400	1.743900	-3.262800
H	-4.952000	1.685500	-3.165100
C	-3.319200	1.736500	-4.549100
C	-1.930500	1.803000	-4.693400
H	-1.471300	1.791800	-5.669800
C	-1.114500	1.885700	-3.562300
H	-0.040300	1.929300	-3.678500
C	-3.702800	1.634600	-6.911300
H	-3.138300	2.542200	-7.142800
H	-4.575700	1.581100	-7.556000
H	-3.072100	0.756700	-7.079000
C	0.451300	3.058000	0.619700
O	4.203400	1.661500	5.579100
N	0.836300	1.954500	1.131200
C	1.429800	6.533000	1.964200
H	1.994000	7.035400	2.737300
C	1.416100	5.116200	1.949700
H	1.962900	4.570800	2.702300
C	0.696600	4.470600	0.962500
C	0.748300	7.287200	1.027500

H	0.783900	8.367600	1.073900
C	1.673000	1.915800	2.287200
C	3.063100	1.825800	2.143900
H	3.501200	1.830500	1.155200
C	3.877400	1.744000	3.262900
H	4.952000	1.685600	3.165100
C	3.319200	1.736600	4.549100
C	1.930500	1.803100	4.693400
H	1.471300	1.791900	5.669900
C	1.114500	1.885800	3.562400
H	0.040300	1.929400	3.678500
C	3.702800	1.634700	6.911300
H	3.138300	2.542300	7.142800
H	4.575700	1.581300	7.556000
H	3.072100	0.756800	7.079000
C	0.451400	-3.058000	-0.619700
O	4.203300	-1.661400	-5.579100
N	0.836300	-1.954500	-1.131200
C	1.429800	-6.533000	-1.964300
H	1.994000	-7.035300	-2.737400
C	1.416200	-5.116100	-1.949800
H	1.962900	-4.570700	-2.702300
C	0.696600	-4.470600	-0.962500
C	-0.000000	-5.245600	-0.000000
C	0.000000	-6.653300	-0.000000
C	0.748300	-7.287100	-1.027600
H	0.783900	-8.367600	-1.074000
C	1.673000	-1.915700	-2.287200
C	3.063100	-1.825800	-2.143900
H	3.501200	-1.830400	-1.155200
C	3.877400	-1.743900	-3.262800
H	4.952000	-1.685500	-3.165100
C	3.319200	-1.736500	-4.549100
C	1.930500	-1.803000	-4.693400
H	1.471300	-1.791800	-5.669800
C	1.114500	-1.885700	-3.562300
H	0.040300	-1.929300	-3.678500
C	3.702800	-1.634600	-6.911300
H	3.138300	-2.542200	-7.142800
H	4.575700	-1.581100	-7.556000
H	3.072100	-0.756700	-7.079000
C	-0.451300	-3.058000	0.619700
O	-4.203400	-1.661500	5.579100
N	-0.836300	-1.954500	1.131200
C	-1.429800	-6.533000	1.964200
H	-1.994000	-7.035400	2.737300
C	-1.416100	-5.116200	1.949700
H	-1.962900	-4.570800	2.702300
C	-0.696600	-4.470600	0.962500
C	-0.748300	-7.287200	1.027500
H	-0.783900	-8.367600	1.073900
C	-1.673000	-1.915800	2.287200

C	-3.063100	-1.825800	2.143900
H	-3.501200	-1.830500	1.155200
C	-3.877400	-1.744000	3.262900
H	-4.952000	-1.685600	3.165100
C	-3.319200	-1.736600	4.549100
C	-1.930500	-1.803100	4.693400
H	-1.471300	-1.791900	5.669900
C	-1.114500	-1.885800	3.562400
H	-0.040300	-1.929400	3.678500
C	-3.702800	-1.634700	6.911300
H	-3.138300	-2.542300	7.142800
H	-4.575700	-1.581300	7.556000
H	-3.072100	-0.756800	7.079000

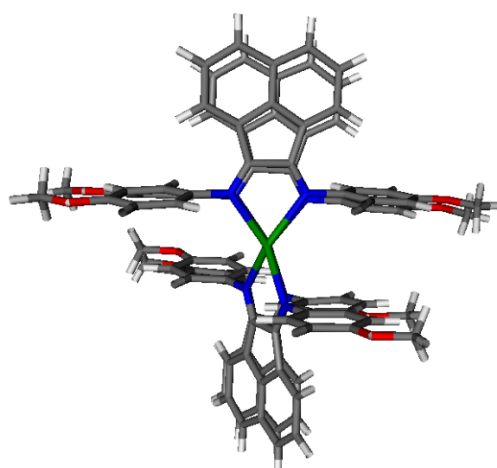


Figure S50: Overlay of the geometry-optimized structure and the molecular structure obtained from X-ray-crystallography of the homoleptic silver(I) N,N'-bis(arylimino)acenaphthene (BIAN) complex.

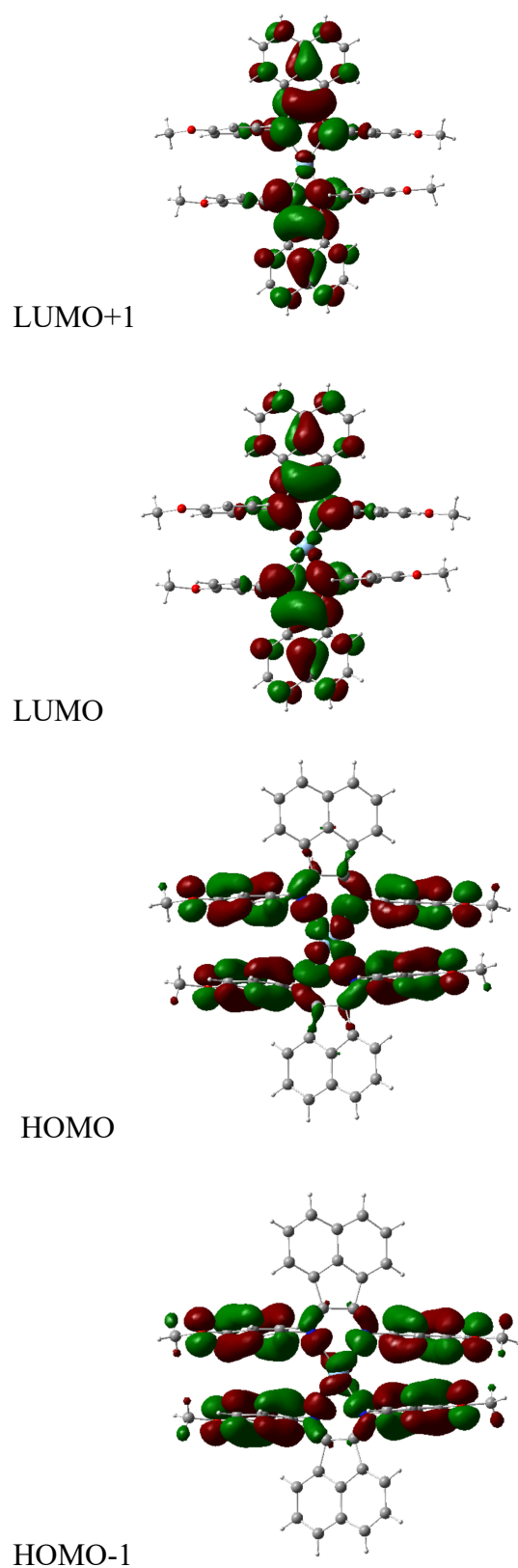


Figure S51: HOMO-1, HOMO, LUMO, and LUMO+1 of the geometry-optimized homoleptic silver(I) N,N'-bis(arylimino)acenaphthene (BIAN) complex, set at isovalues of 0.02. $DE_{\text{HOMO-LUMO}} = 2.7 \text{ eV}$.

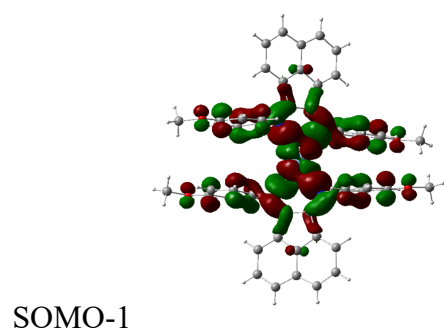
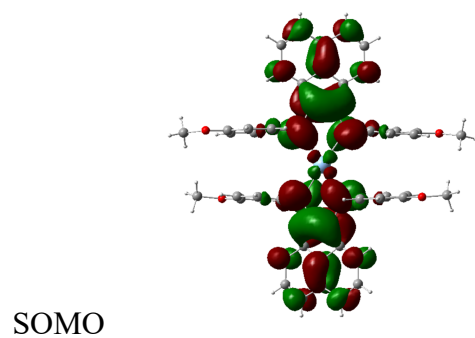
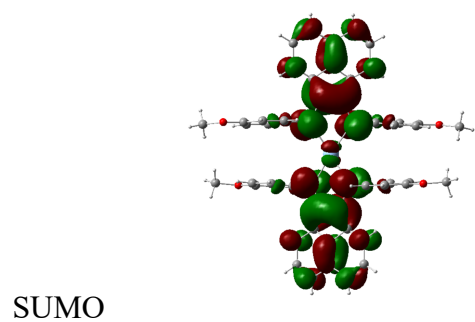
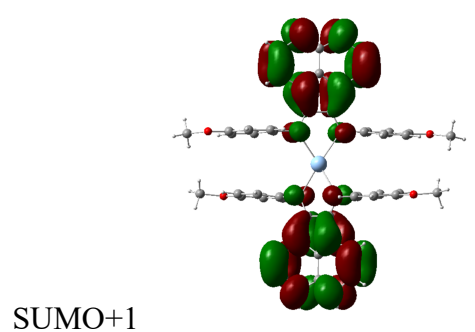


Figure S52: SOMO-1, SOMO, SOMO -1, SUMO, and SUMO+1 of the geometry-optimized two-electron reduced homoleptic silver(I) N,N'-bis(arylimino)acenaphthene (BIAN) complex, set at isovalues of 0.02. $DE_{\text{SOMO-SUMO}} = 0.5 \text{ eV}$.

Comparison of the Ag-BIAN GDEs against the state-of-the-art

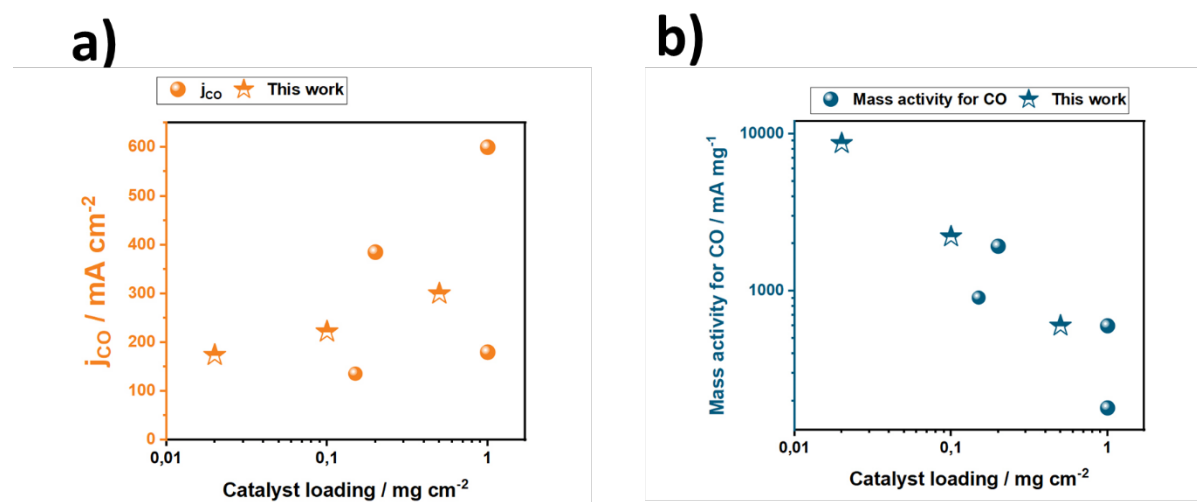


Figure S53 Comparison of the herein presented results against the current state-of-the-art literature in dependence to the employed catalytic loading for the j_{CO} (a) and mass activity for CO (b). References ^{8–11}

Table S5 Critical catalytic parameters for the electrocatalytic reduction of CO₂ achieved with [Ag(4-n-hexyloxy-BIAN)₂]BF₄ **Ag-OC₆** compared with the state-of-the-art for molecular CO₂R catalyst CoPc prior to this work. Values are typically obtained for 1 h of galvanostatic electrolysis, 40 μm membrane between anode and cathode and 2 cm² WE area unless otherwise noted. Single-pass conversions have only been determined for selected experiments.

Catalyst	Loading / mg cm ⁻²	j / mA cm ⁻²	FE _{CO} / %	SPC / %	Reference
CoPc	0.4	150	95	3.9	¹²
CoPc	0.5	300	7	-	¹³
Ag-OC ₆	0.5	300	90	-	This work
Ag-OC ₆	0.1	300	74	7.5	This work
Ag-OC ₆	0.1	300	68	40.3	This work
Ag-OC ₆	0.02	300	59	-	This work
Ag-OC ₆	0.5	300	79	-	This work
Ag-OC ₆	0.5	600	51	-	This work
Ag-OC ₆	0.5	900	30	-	This work

Table S6 Comparison of the achieved energy efficiency in the herein investigation against literature reports.

Catalyst	Catalytic Loading / mg cm ⁻²	EE _{CO} / %	j _{CO} / %	Reference
Ag-NPs	1	40	180	10
Ag-NPs	1	40	200	14
Ag-NPs	1	37	420	15
Ag-NPs	1	33	400	8
Ag-NPs	1	29	195	16
Ag-NPs	2	37	558	17
Ag-NPs	3	38	255	16
Ag-NPs	3	29	195	16
Au-NPs	0.4	40	450	12
CoPc	0.2	50	200	12
Ag-OC₆	0.5	51	300	This work
Ag-OC₆	0.1	31	221	This work
Ag-OC₆	0.02	30	176	This work

Scaling-up experiments and cost scenarios

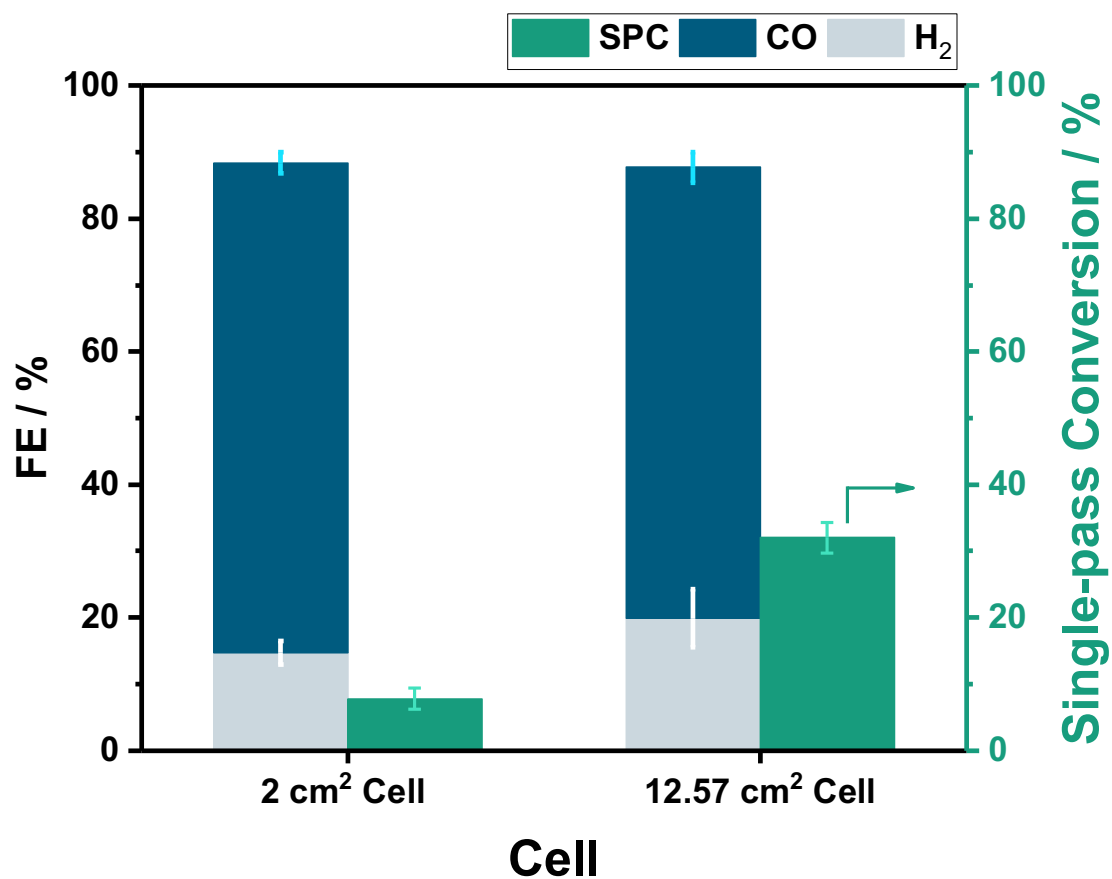


Figure S54 Comparison of the achieved FE_{CO} and single-pass conversion achieved in a 2 cm² and 12.57 cm² cell at 300 mA cm⁻² and 240 mA cm⁻² respectively after 1 h of electrolysis at 60°C. All investigated electrodes possessed a catalytic Ag-OC₆ loading of 0.1 mg cm⁻².

Table S7. Comparison of the required catalytic loadings between Ag and Ag-OC₆-based electrolyzers in different output scenarios with the associated cost improvements.

Scenario 1	FE _{CO} : 90% - j: 300 mA cm ⁻²			
Catalyst	Loading / mg cm ⁻²	Catalyst re- quired for electrolyzer / kg	Total catalyst price for the cathode / \$	Improvement
Ag-NPs	1	13.9	567,953	4.7
Ag-OC ₆	0.5	6.9	118,906	
Scenario 2	FE _{CO} : 33% at j: 300 mA cm ⁻²			
Ag-NPs	1	40.2	1,079,262	78.8
Ag-OC ₆	0.02	0.80	5,637	
Scenario 3	FE _{CO} : 33% at j: 900 mA cm ⁻²			
Ag-NPs	1	13.4	545,014	4.7
Ag-OC ₆	0.5	6.71	114,104	

Spectral Data

Spectral Data of 4-Methoxy-BIAN

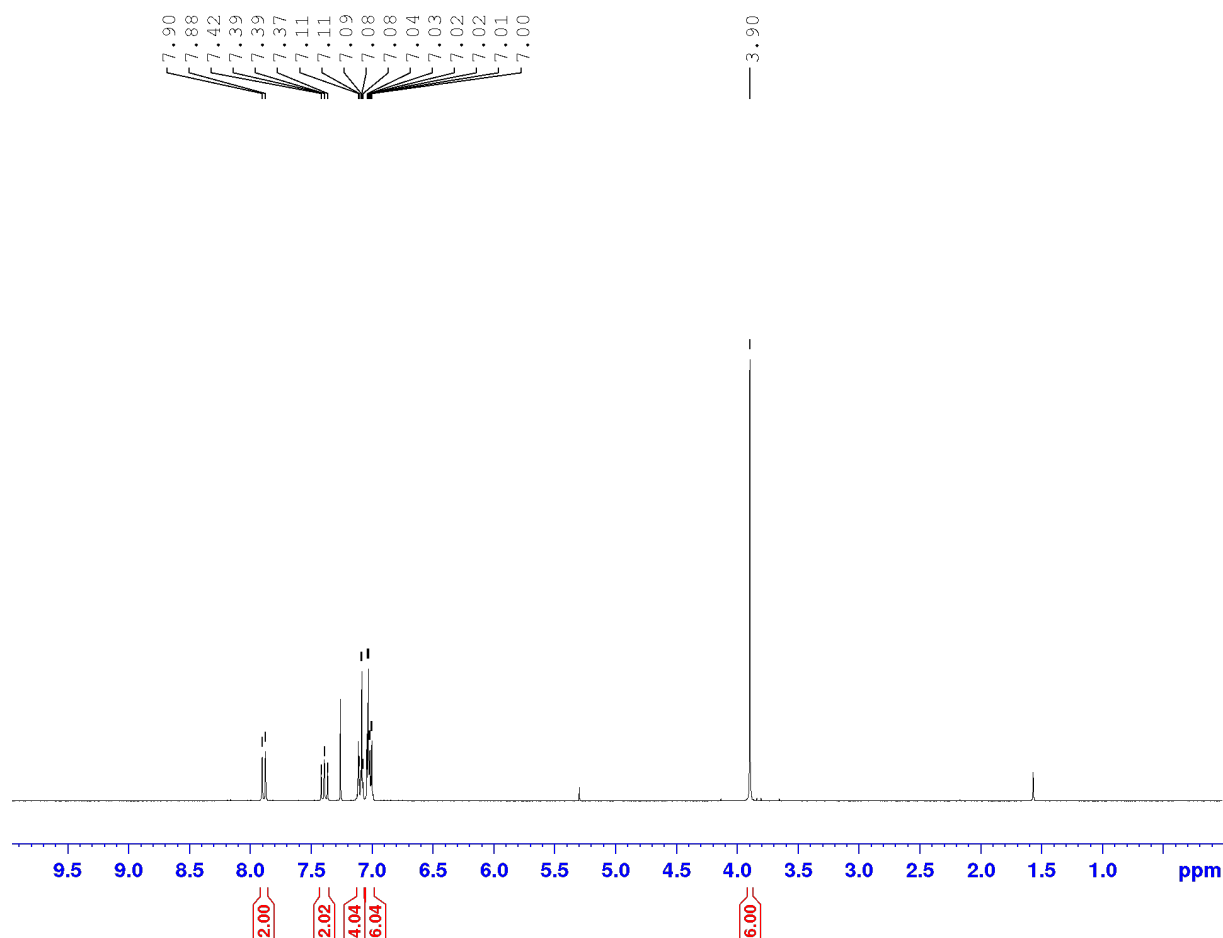


Figure S55: ¹H NMR (300 MHz, CDCl₃, 25 °C) of *N*¹,*N*²-bis(4-methoxyphenyl)acenaphthylene-1,2-diimine **L1**.

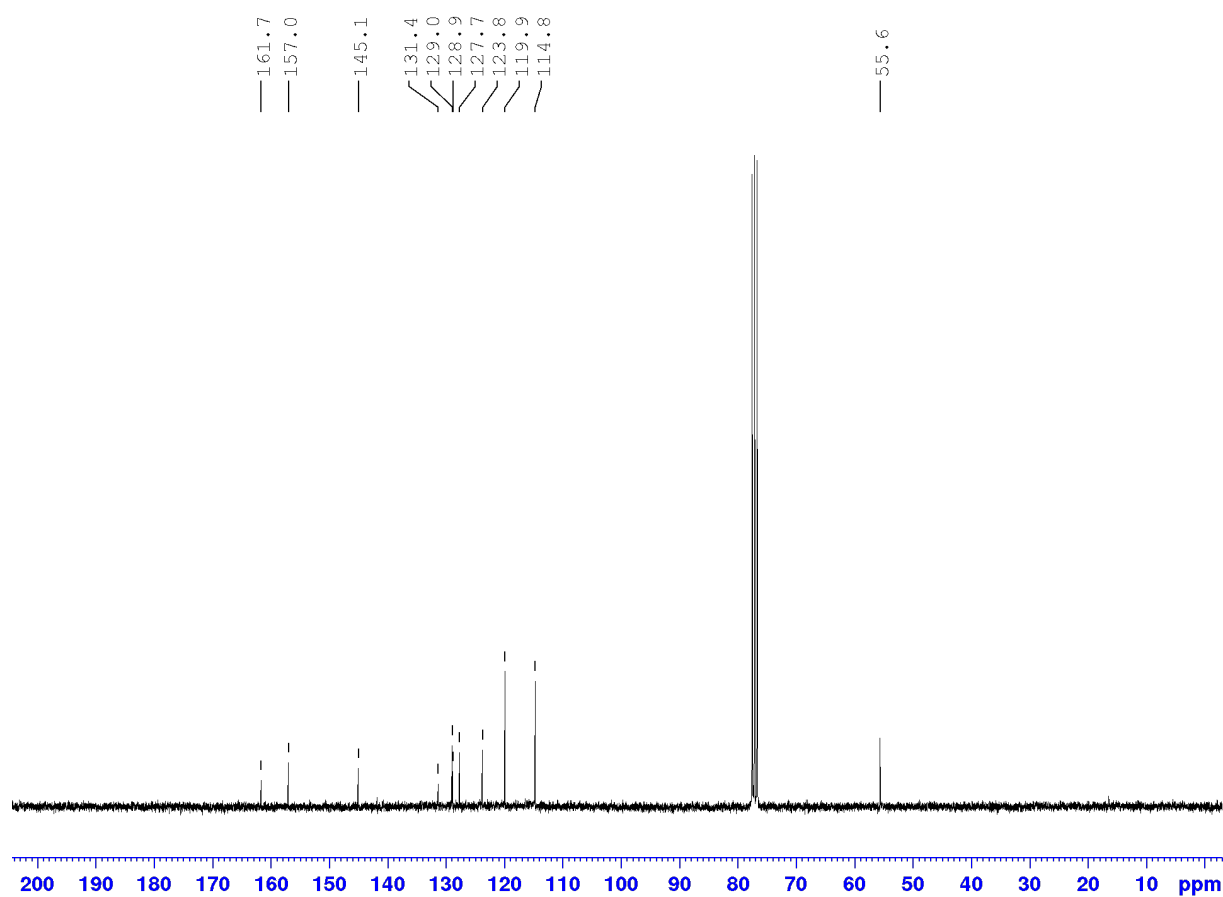


Figure S56: ^{13}C NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$) of N^1,N^2 -bis(4-methoxyphenyl)acenaphthylene-1,2-diimine **L1**.

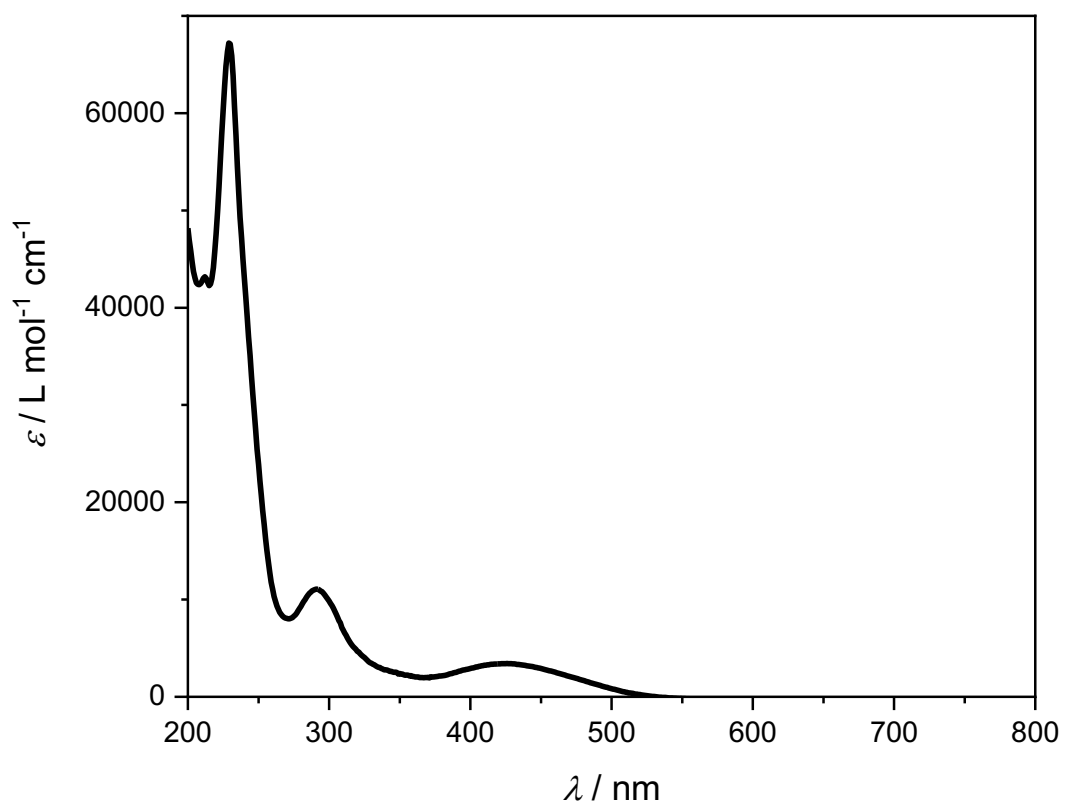


Figure S57: UV-vis absorption spectrum of N^1, N^2 -bis(4-methoxyphenyl)acenaphthylene-1,2-diimine **L1** in ACN.

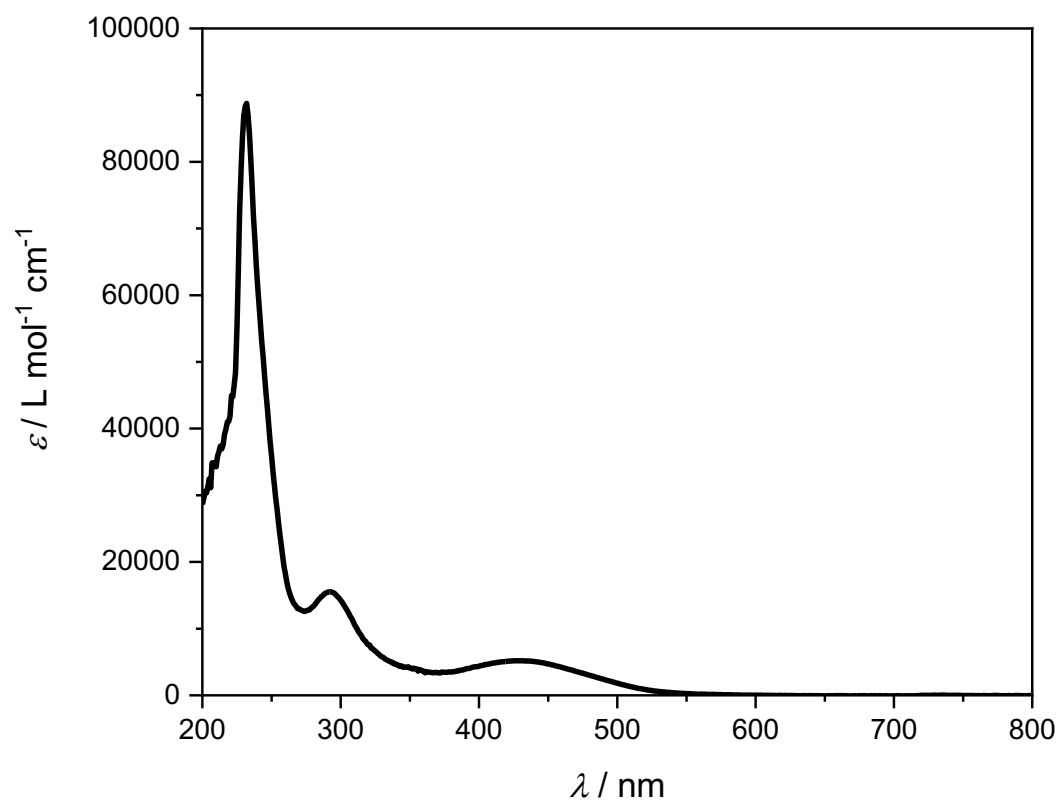


Figure S58: UV-vis absorption spectrum of N^1, N^2 -bis(4-n-methoxyphenyl)acenaphthylene-1,2-diimine **L1** in DCM.

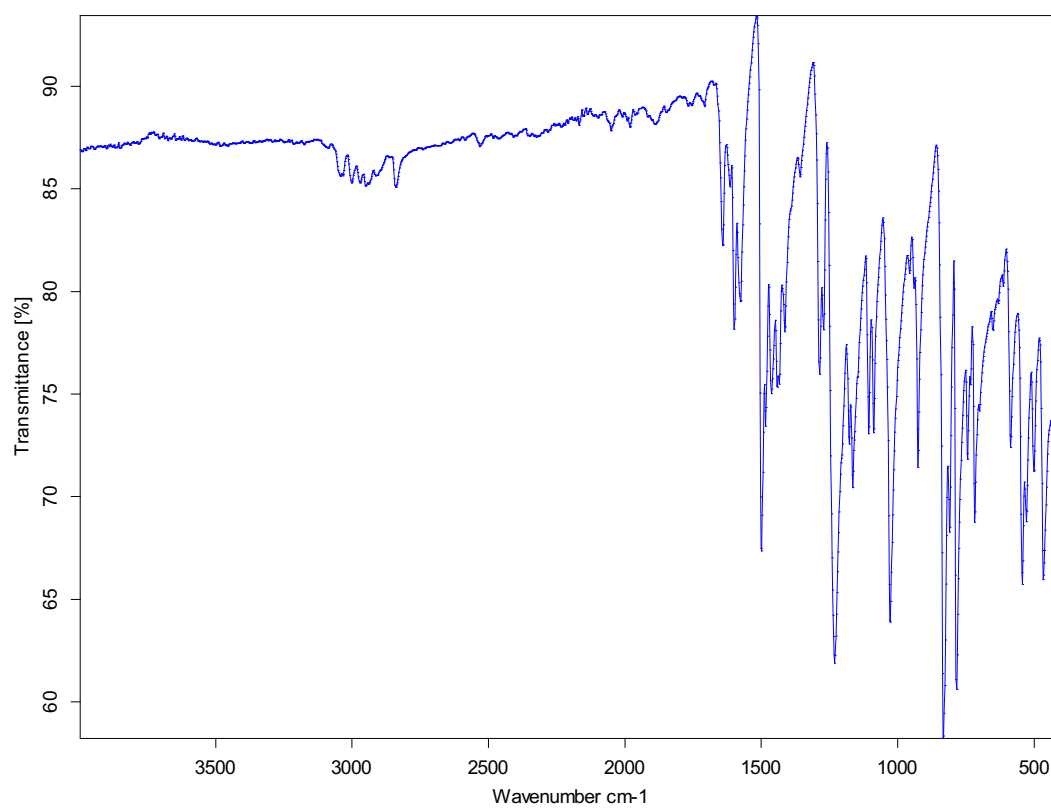


Figure S59: IR absorption spectrum of N¹,N²-bis(4-methoxyphenyl)acenaphthylene-1,2-diimine **L1**.

Spectral Data of 4-n-Hexyloxy-BIAN

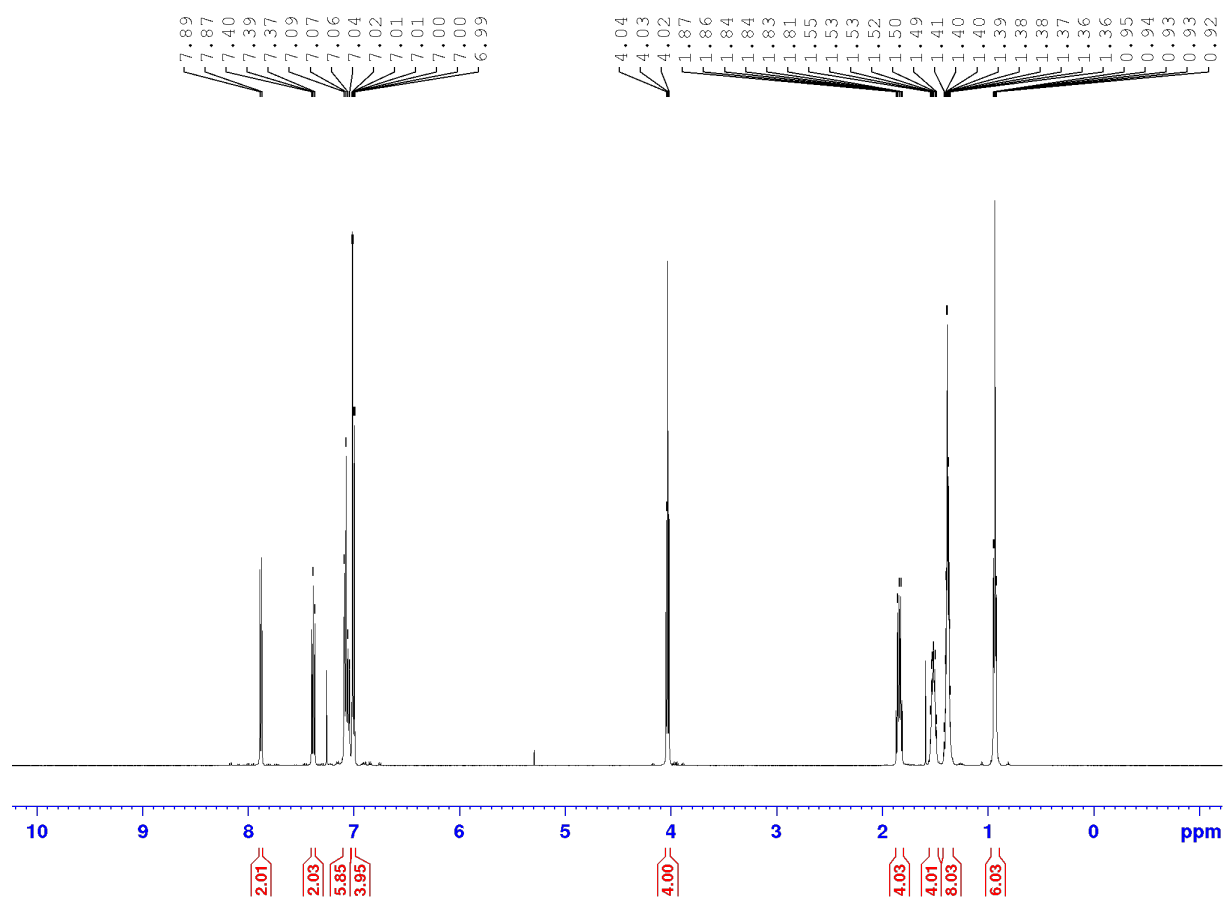


Figure S60: ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of N^1,N^2 -bis(4-n-hexyloxyphenyl)acenaphthylene-1,2-diimine .

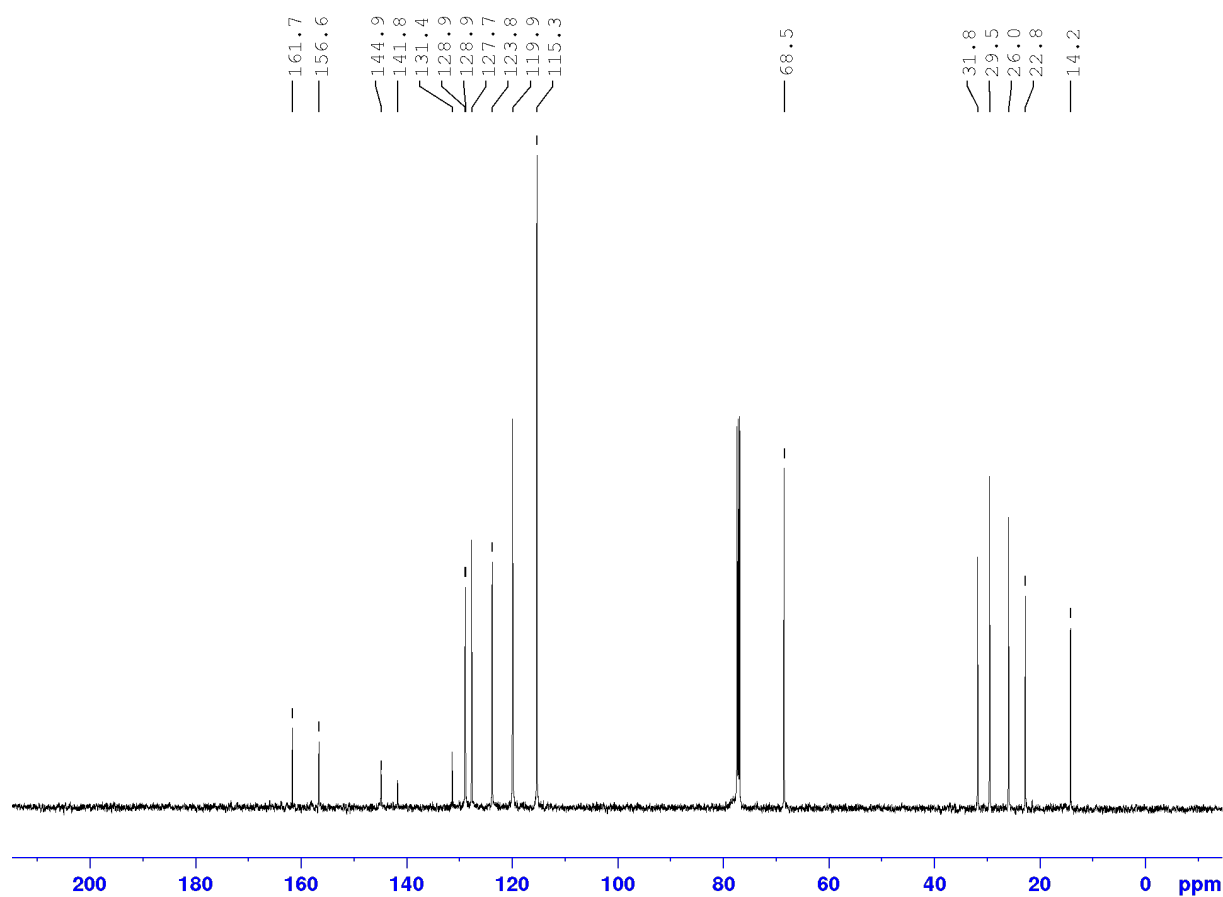


Figure S61: ^{13}C NMR (126 MHz, CDCl_3 , 25 $^\circ\text{C}$) of N^1,N^2 -bis(4-n-hexyloxyphenyl)acenaphthylene-1,2-diimine .

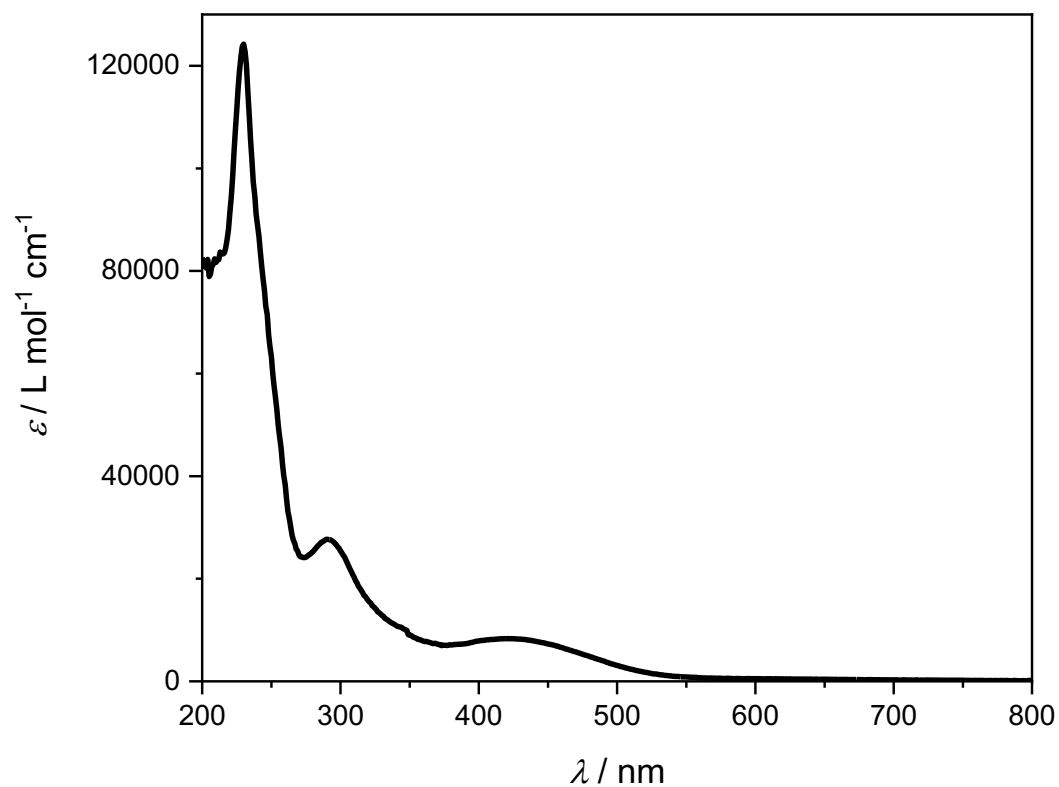


Figure S62: UV-vis absorption spectrum of N¹,N²-bis(4-n-hexyloxyphenyl)acenaphthylene-1,2-diimine in ACN.

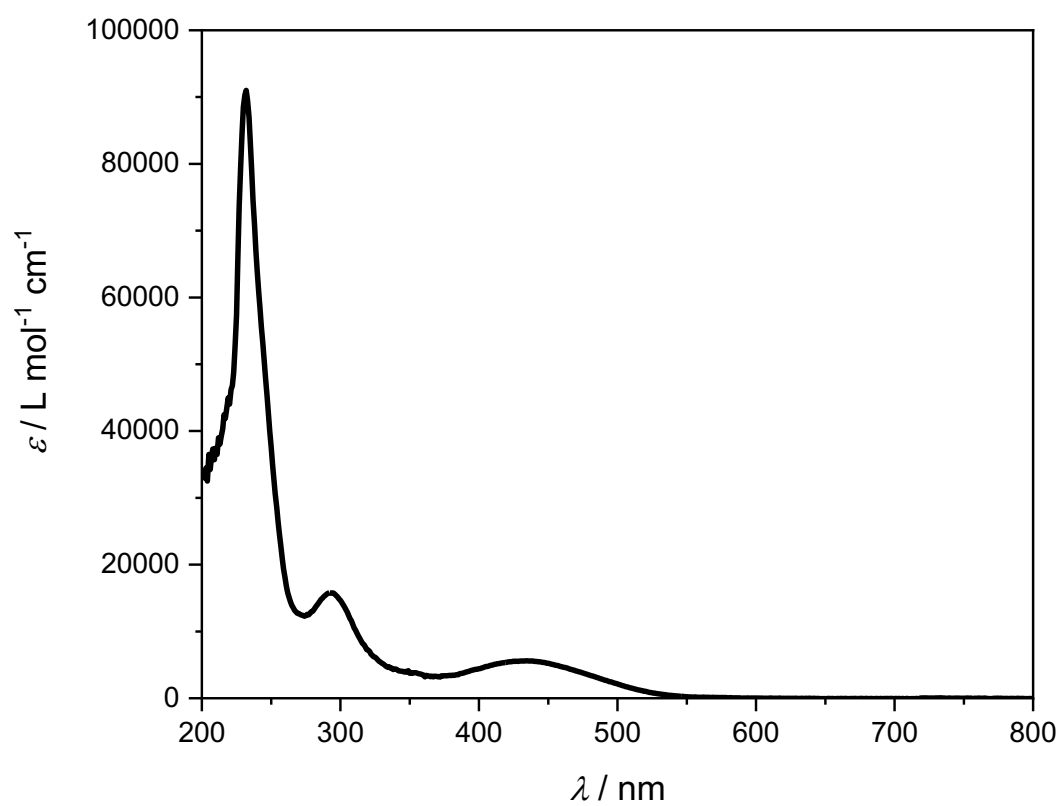


Figure S63: UV-vis absorption spectrum of N¹,N²-bis(4-n-hexyloxyphenyl)acenaphthylene-1,2-diimine in DCM.

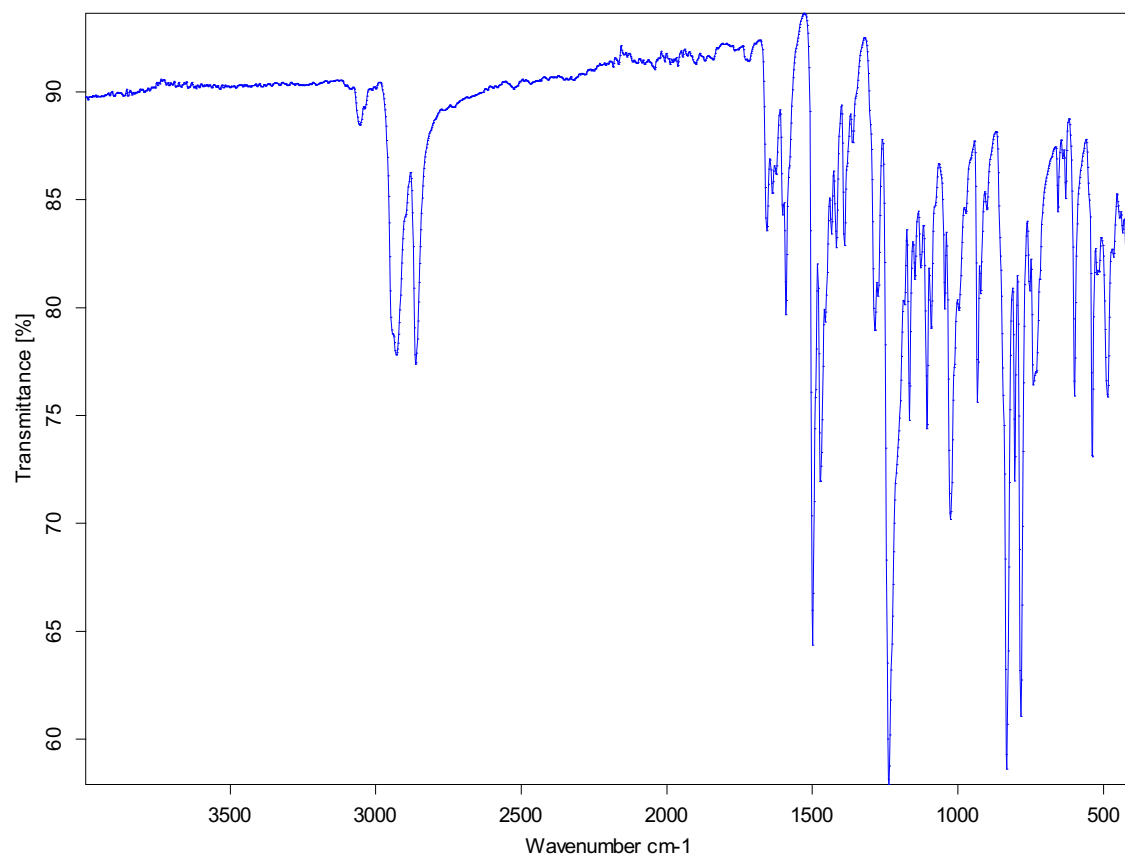


Figure S64: IR absorption spectrum of N¹,N²-bis(4-n-hexyloxyphenyl)acenaphthylene-1,2-diimine .

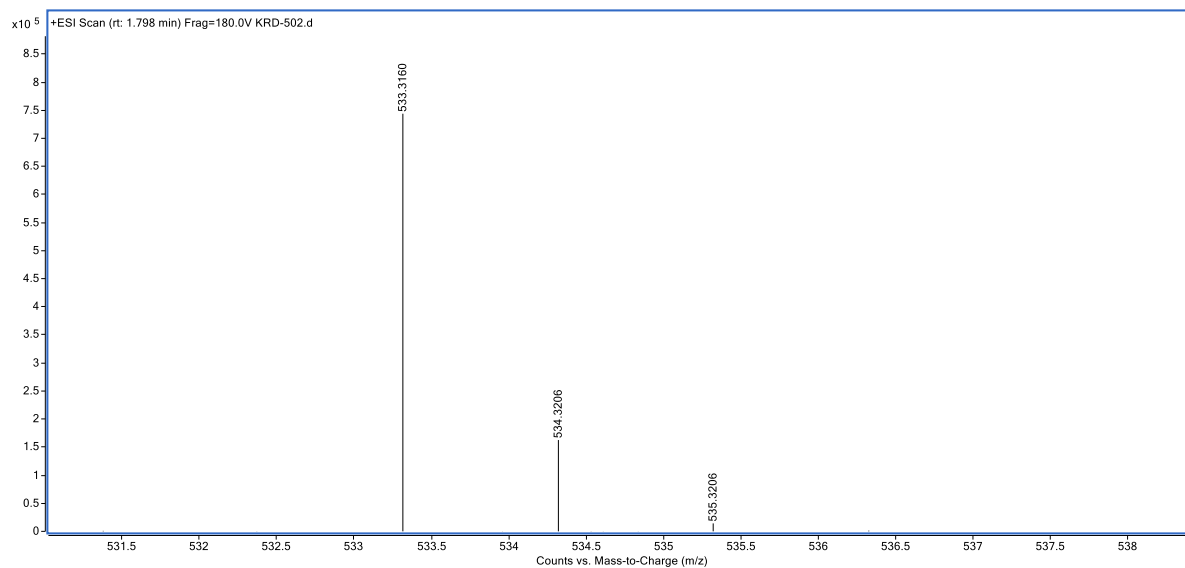


Figure S65: HRMS spectrum of N¹,N²-bis(4-n-hexyloxyphenyl)acenaphthylene-1,2-diimine .

Spectral Data of 4-n-Hexadecyloxy-BIAN

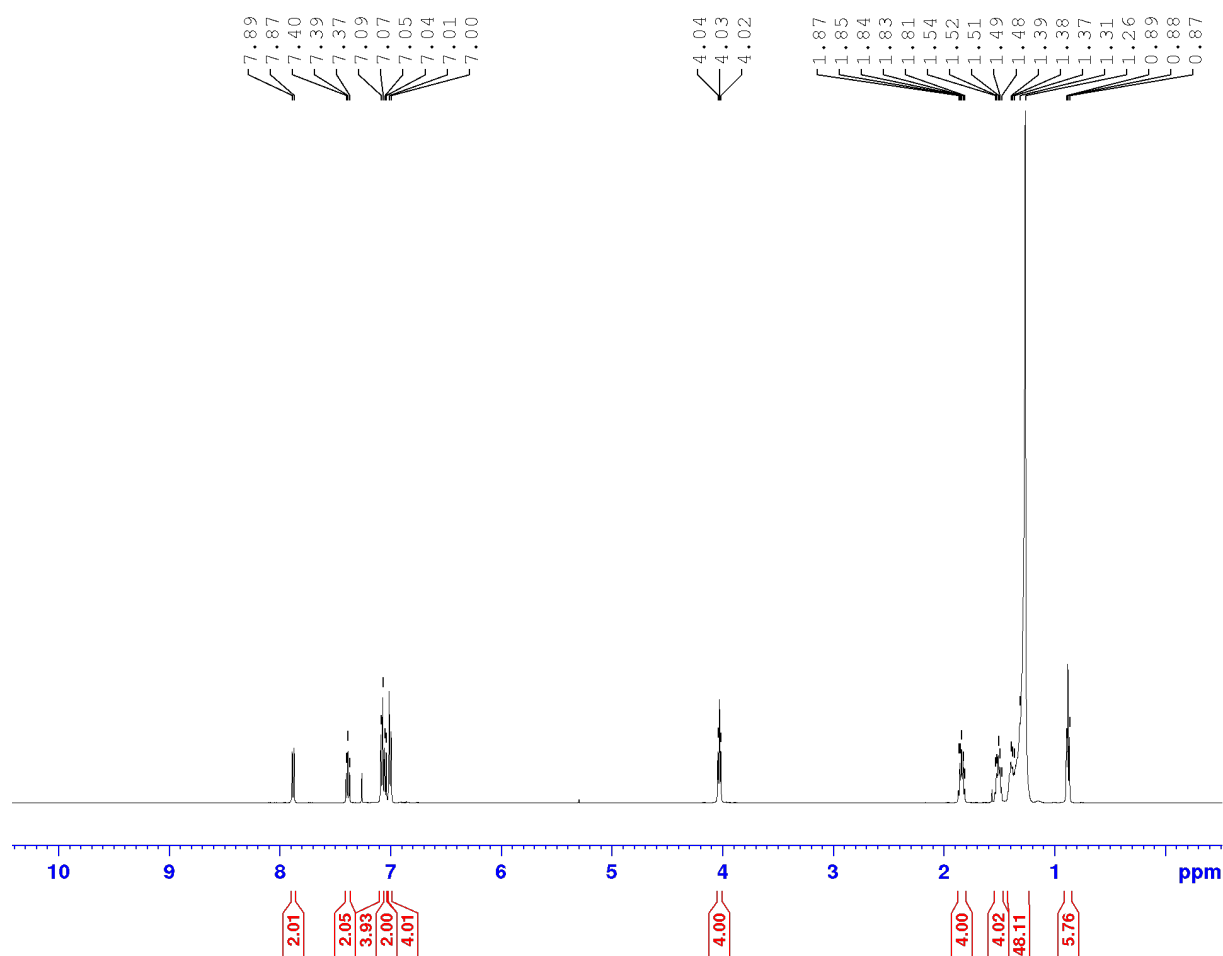


Figure S66: ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of N^1, N^2 -bis(4-n-hexadecyloxyphenyl)acenaphthylene-1,2-diimine L3.

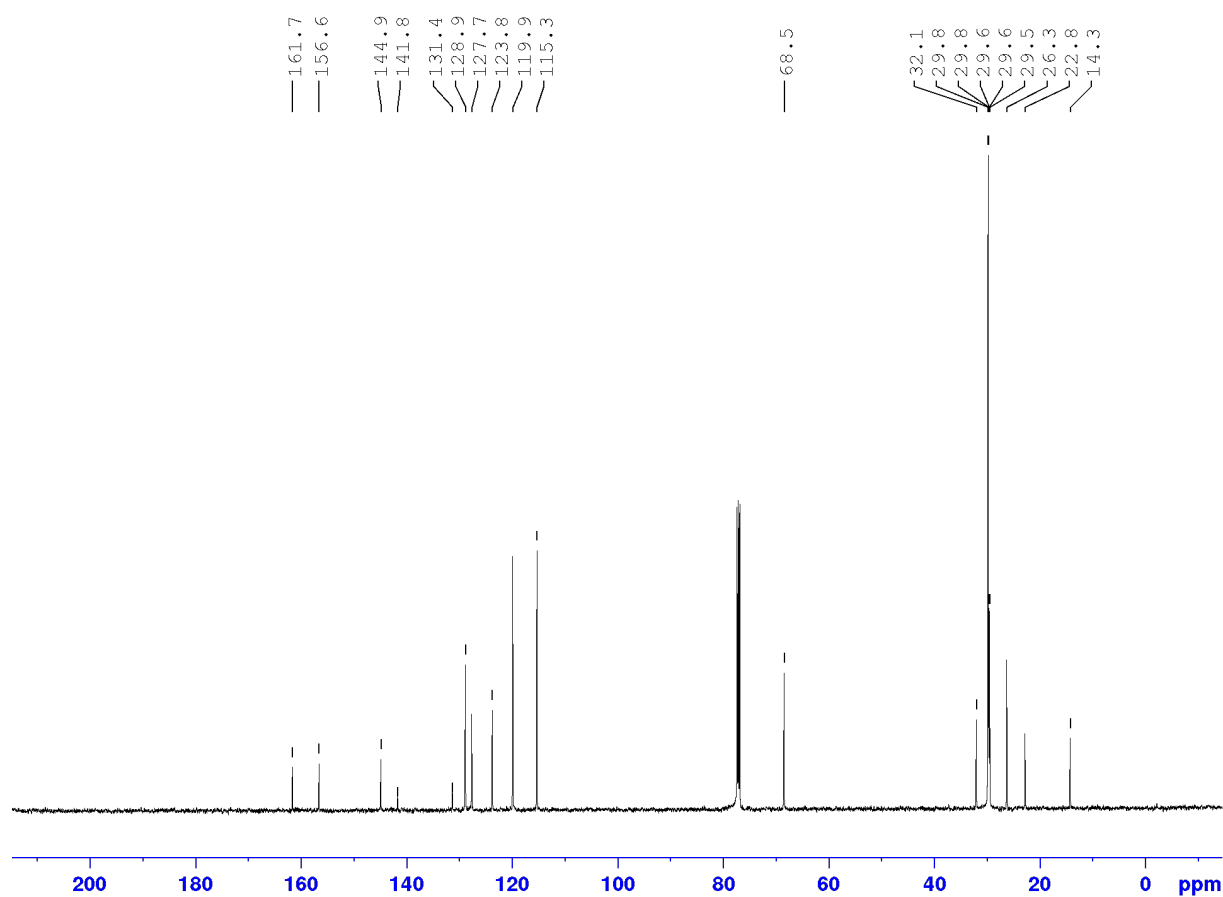


Figure S67: ^{13}C NMR (126 MHz, CDCl_3 , 25 $^\circ\text{C}$) of N^1,N^2 -bis(4-n-hexadecyloxyphenyl)acenaphthylene-1,2-diimine L3.

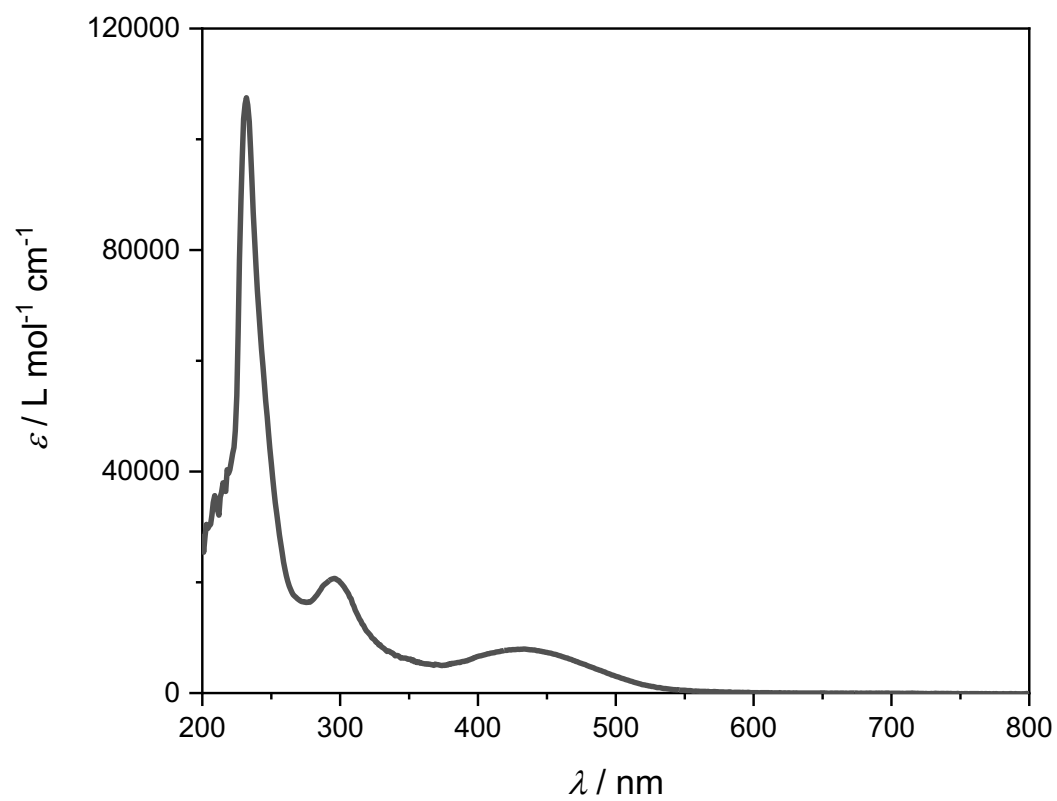


Figure S68: UV-vis absorption spectrum of N^1, N^2 -bis(4-n-hexadecyloxyphenyl)acenaphthylene-1,2-diimine L3 in DCM.

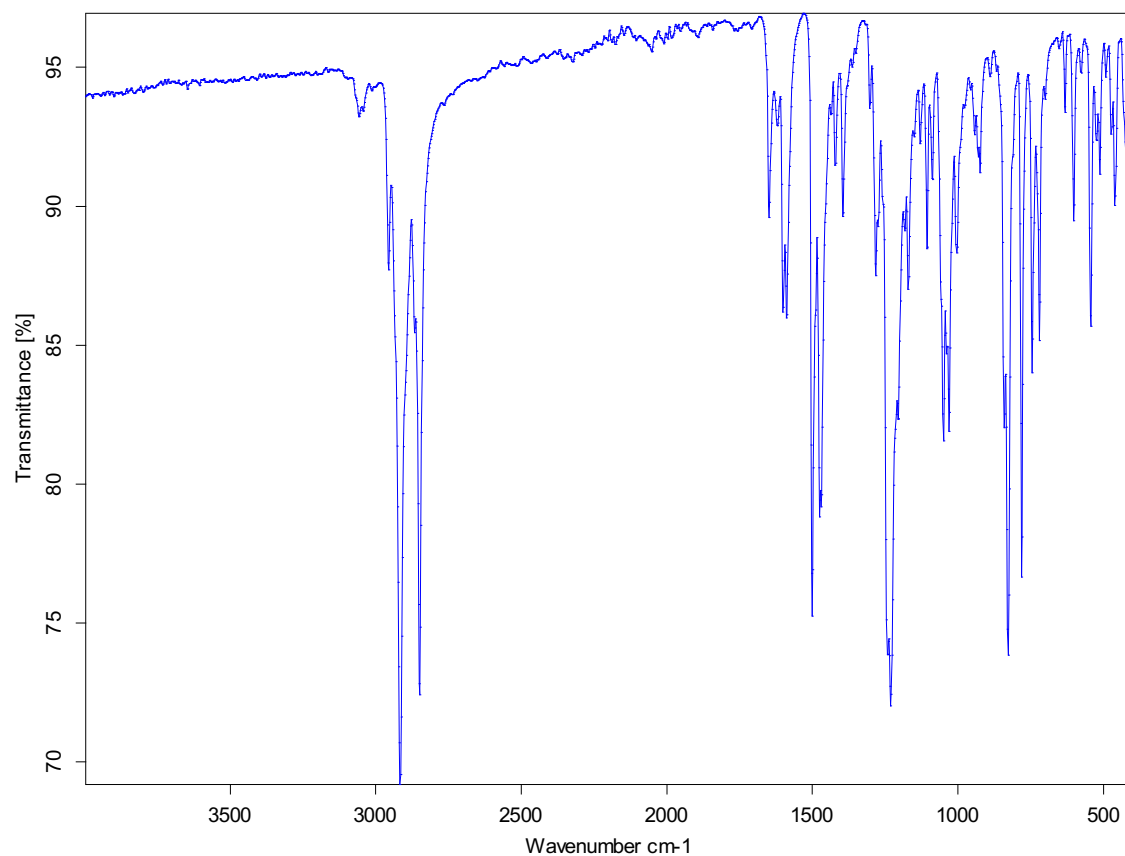


Figure S69: IR absorption spectrum of N¹,N²-bis(4-n-hexadecyloxyphenyl)acenaphthylene-1,2-diimine L3.

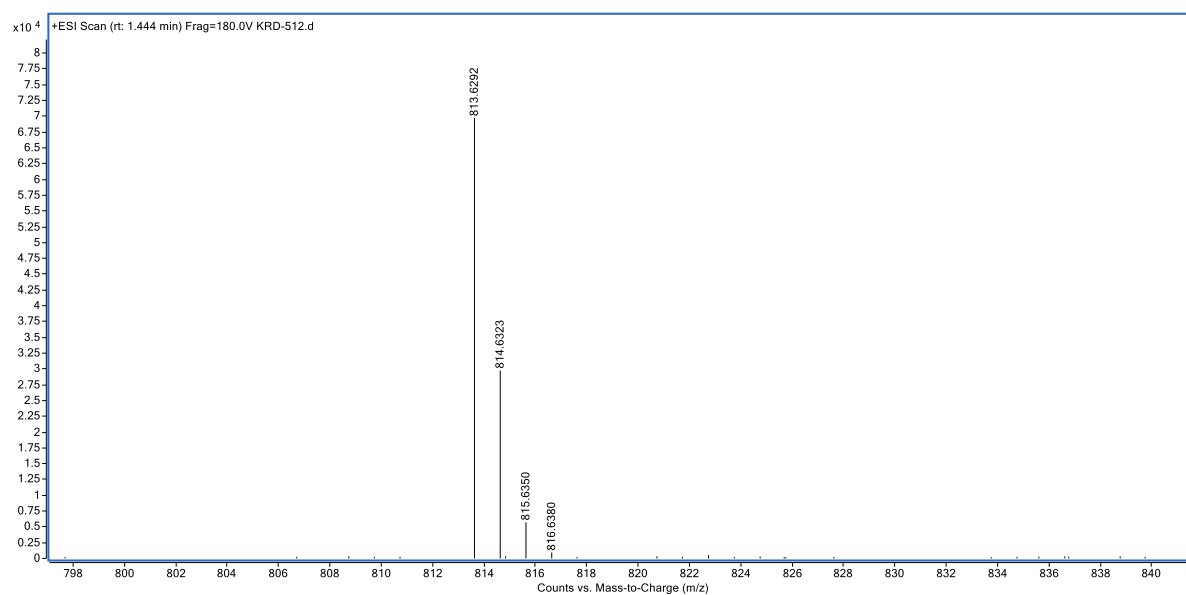


Figure S70: HRMS spectrum of N¹,N²-bis(4-n-hexadecyloxyphenyl)acenaphthylene-1,2-diimine L3.

Spectral Data of [Ag(4-OMe-BIAN)₂]BF₄ (Ag-OMe)

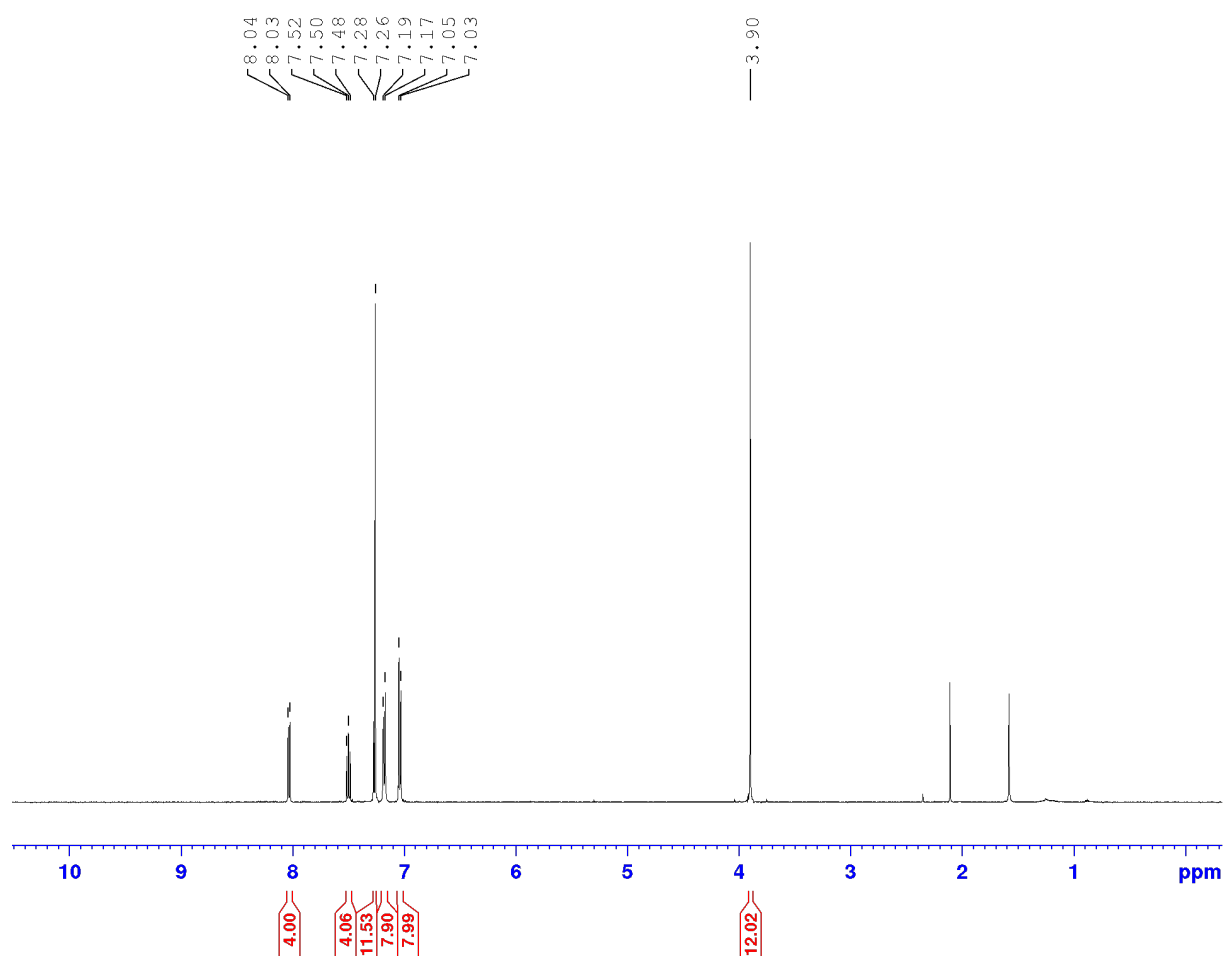


Figure S71: ¹H NMR (500 MHz, CDCl₃, 25 °C) of [Ag(4-OMe-BIAN)₂]BF₄ Ag-OMe.

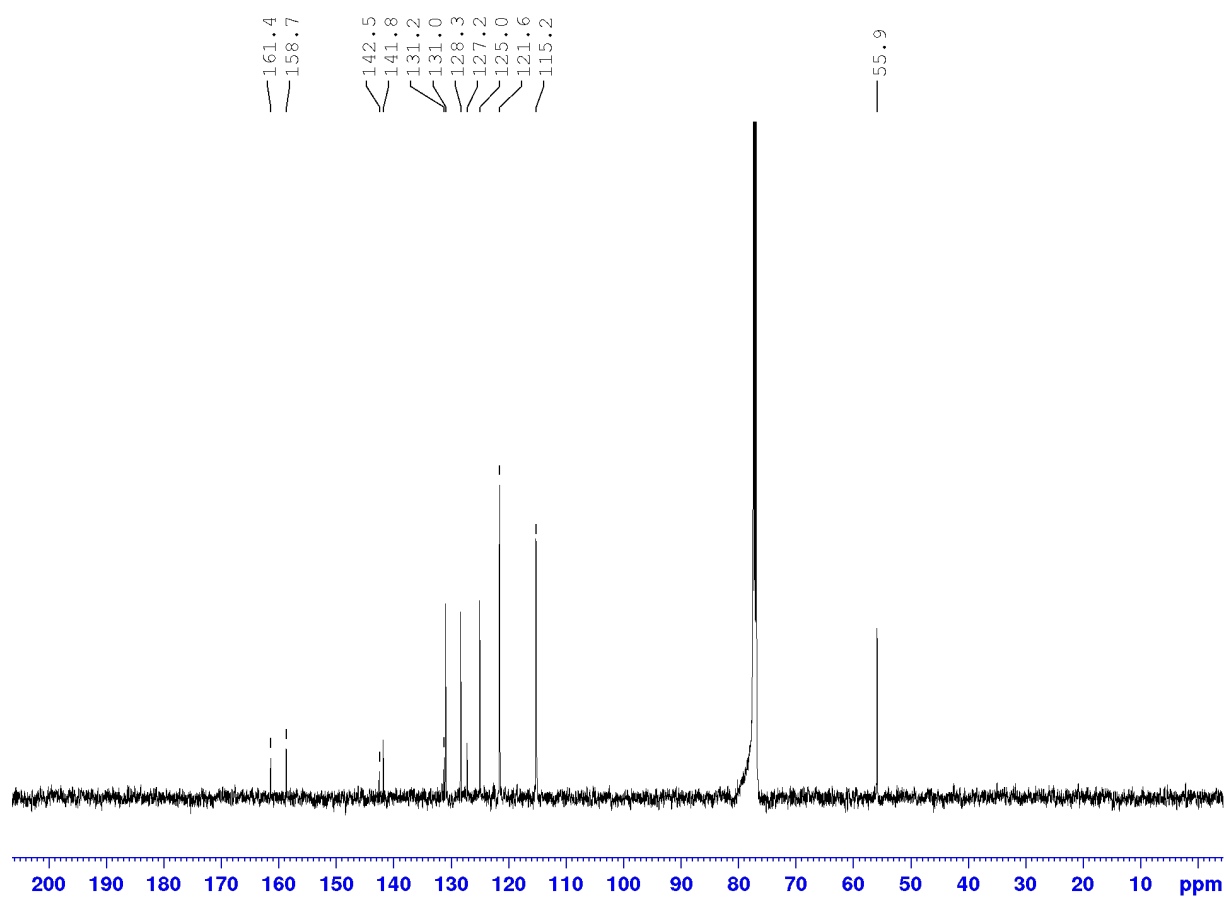


Figure S72: ^{13}C NMR (126 MHz, CDCl_3 , 25 $^\circ\text{C}$) of $[\text{Ag}(\text{4-OMe-BIAN})_2]\text{BF}_4 \cdot \text{Ag-OMe}$.

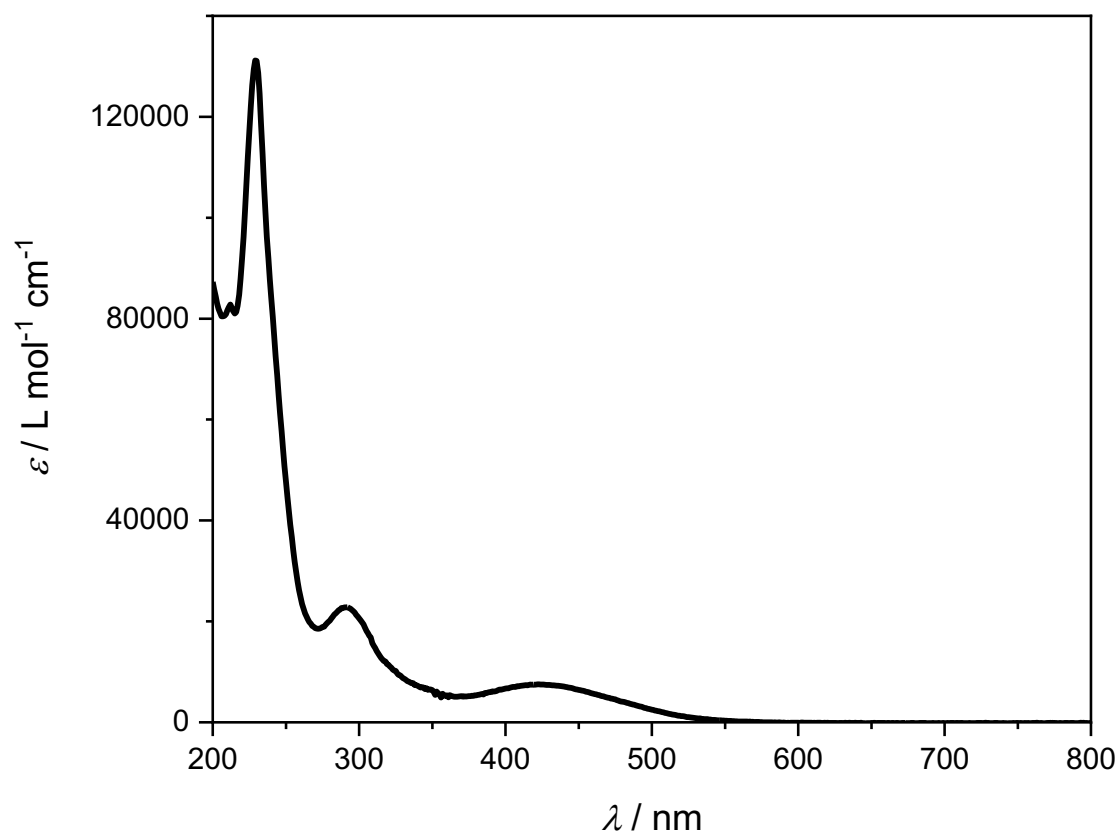


Figure S73: UV-vis absorption spectrum of [Ag(4-OMe-BIAN)₂]BF₄ Ag-OMe in ACN.

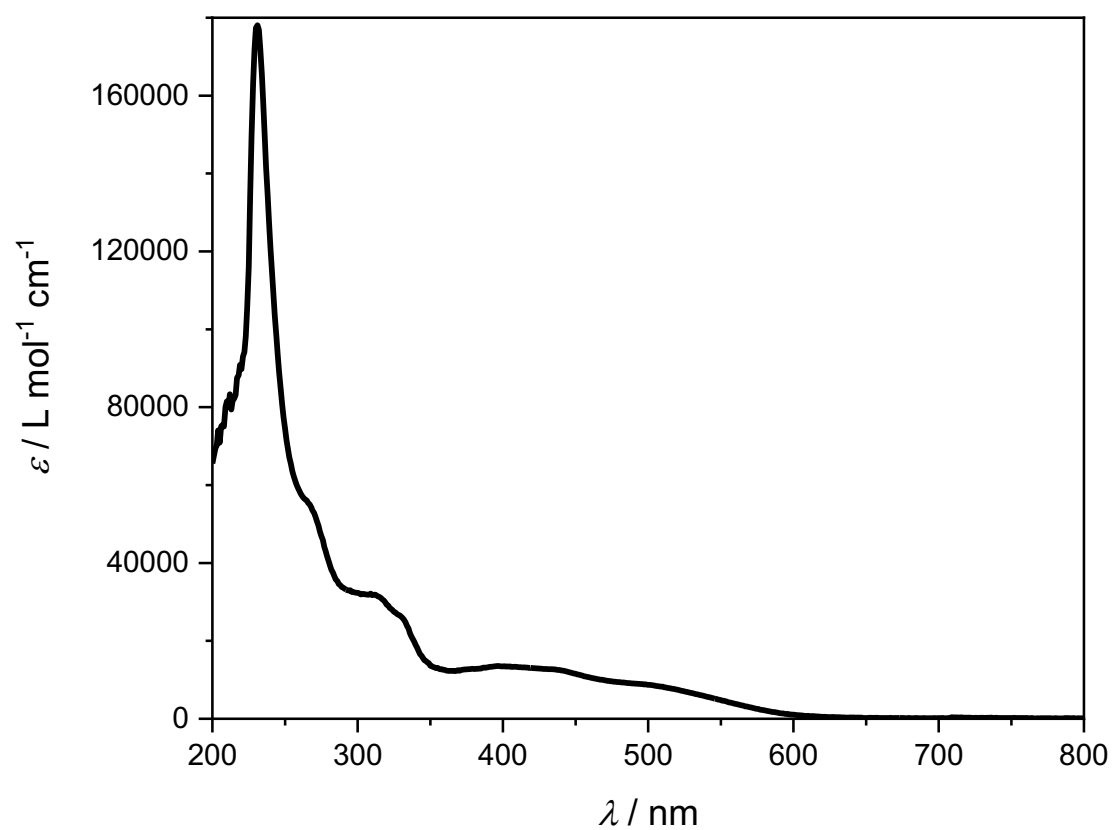


Figure S74: UV-vis absorption spectrum of [Ag(4-OMe-BIAN)₂]BF₄ Ag-OMe in DCM.

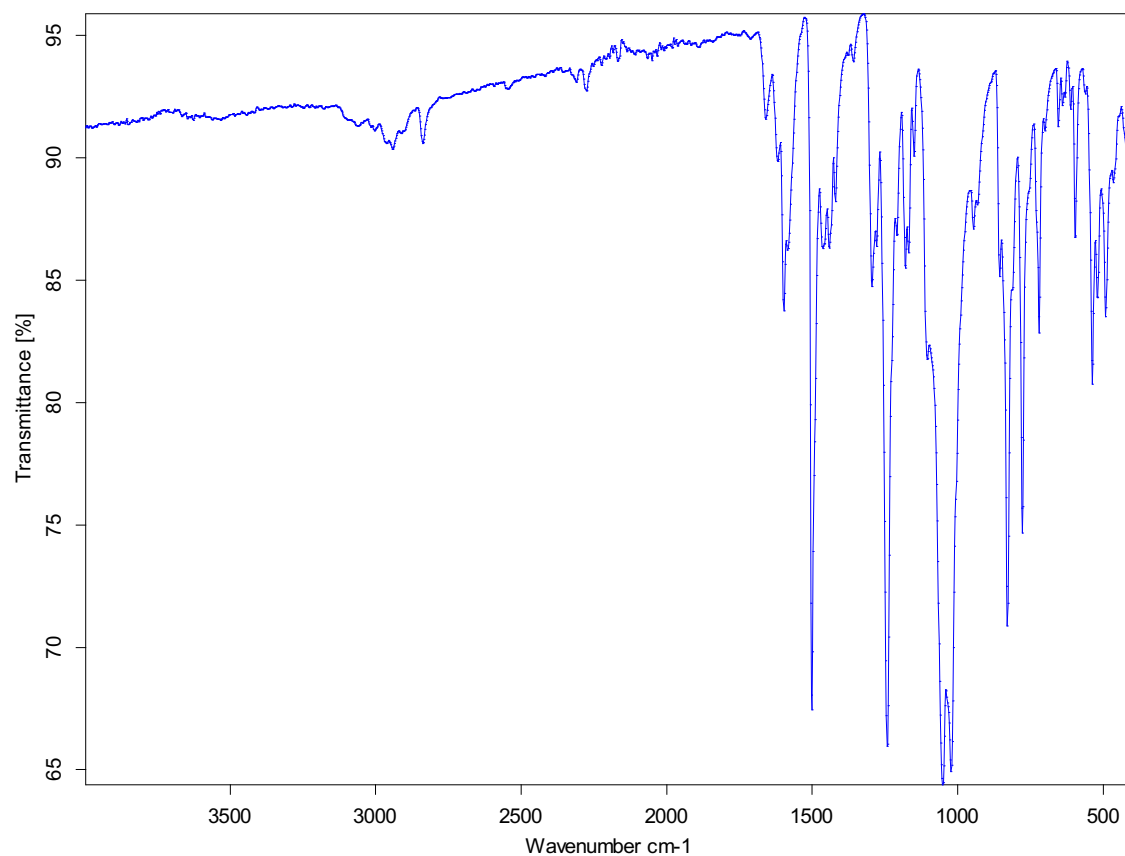


Figure S75: IR absorption spectrum of $[\text{Ag}(\text{4-OMe-BIAN})_2]\text{BF}_4 \text{ Ag-OMe}$.

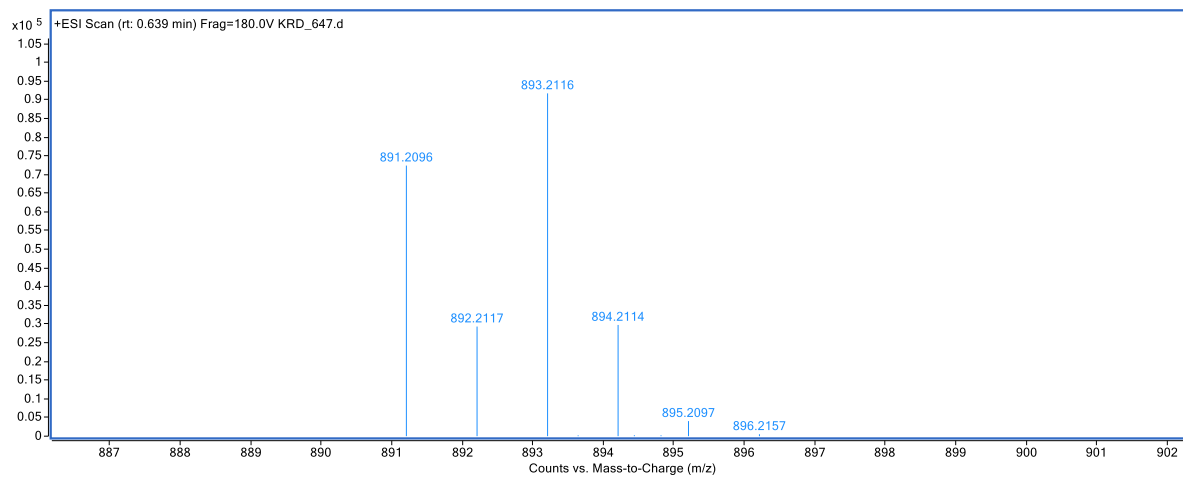


Figure S76: HRMS spectrum of $[\text{Ag}(\text{4-OMe-BIAN})_2]\text{BF}_4 \text{ Ag-OMe}$.

Spectral Data of [Ag(4-n-hexyloxy-BIAN)₂]BF₄ (Ag-OC₆)

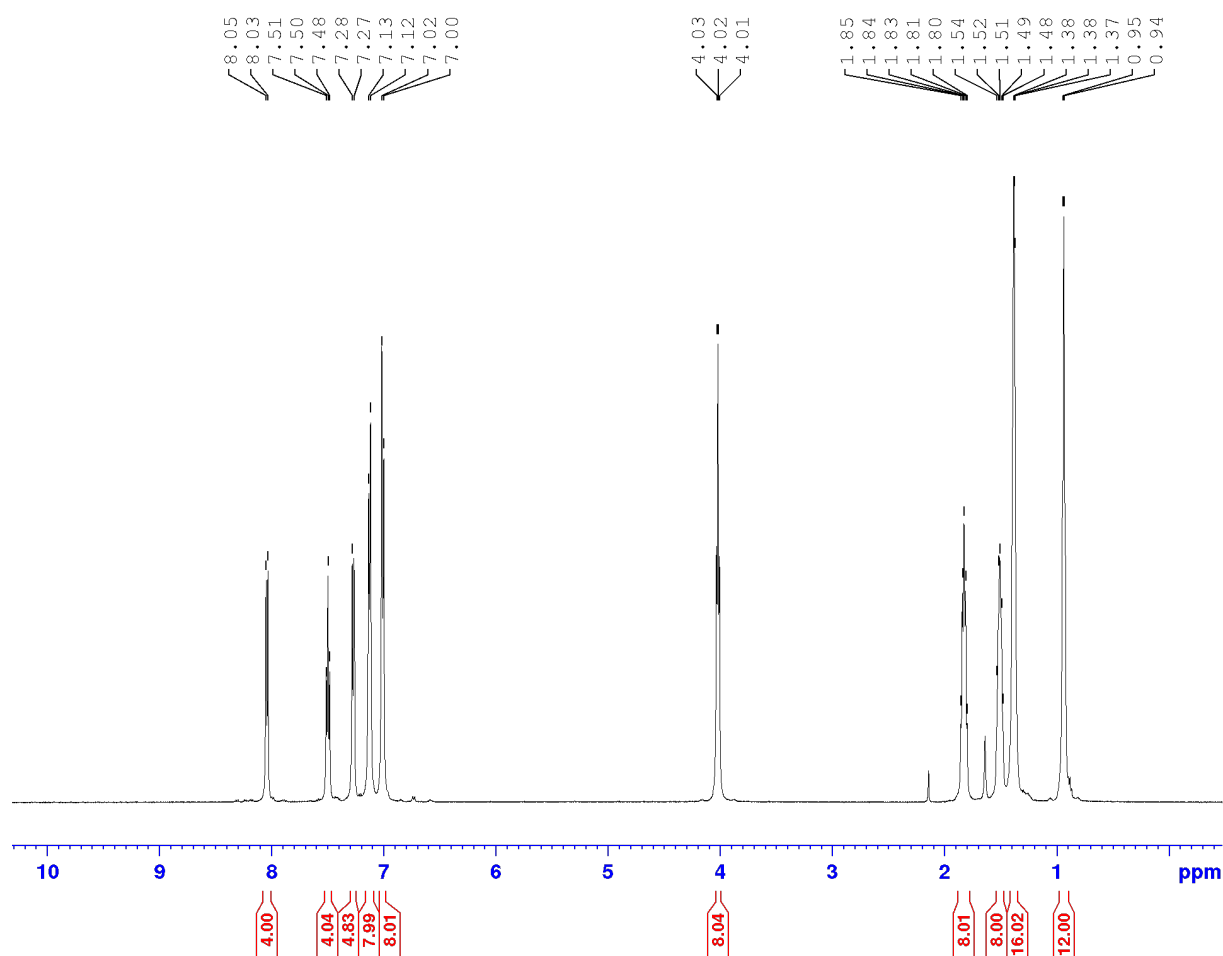


Figure S77: ¹H NMR (500 MHz, CDCl₃, 25 °C) of [Ag(4-n-hexyloxy-BIAN)₂]BF₄ Ag-OC₆.

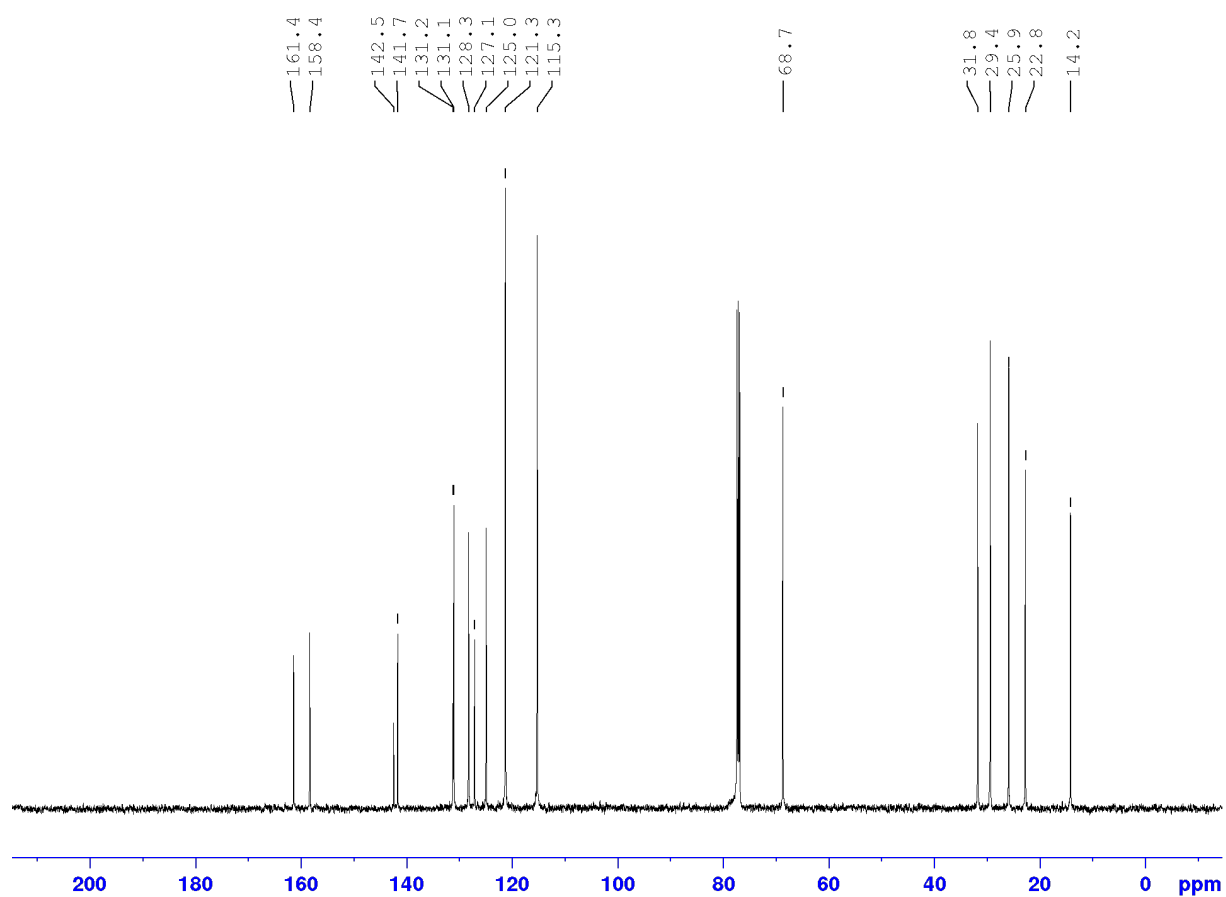


Figure S78: ^{13}C NMR (126 MHz, CDCl_3 , 25 °C) of $[\text{Ag}(\text{4-n-hexyloxy-BIAN})_2]\text{BF}_4 \text{ Ag-OC}_6$.

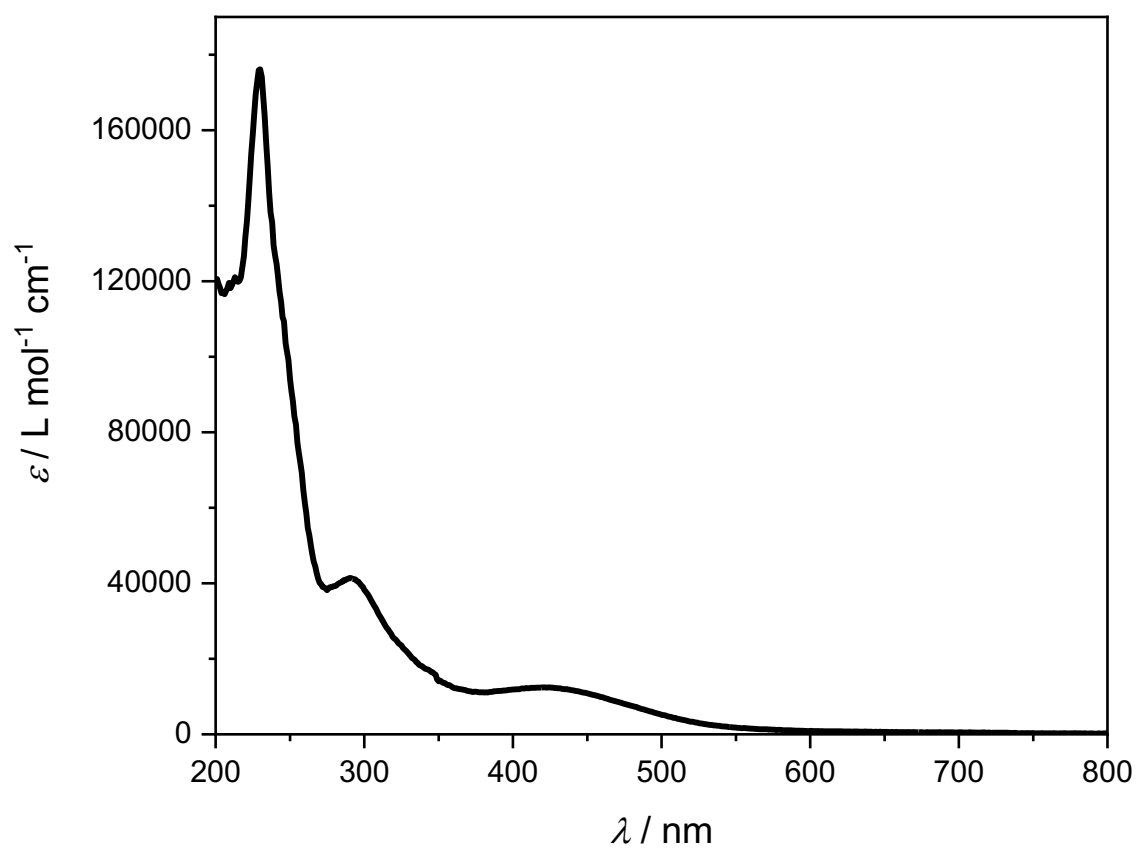


Figure S79: UV-vis absorption spectrum of [Ag(4-n-hexyloxy-BIAN)₂]BF₄ Ag-OC₆ in ACN.

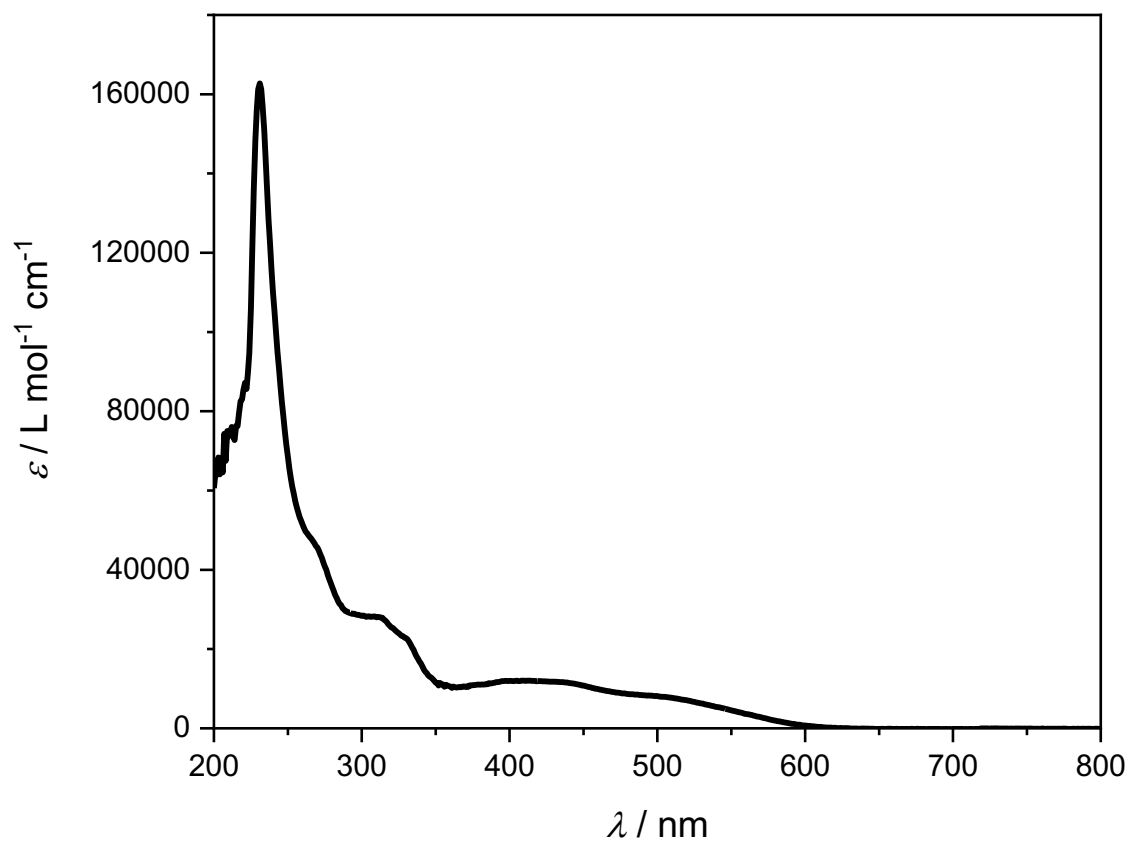


Figure S80: UV-vis absorption spectrum of [Ag(4-n-hexyloxy-BIAN)₂]BF₄ Ag-OC₆ in DCM.

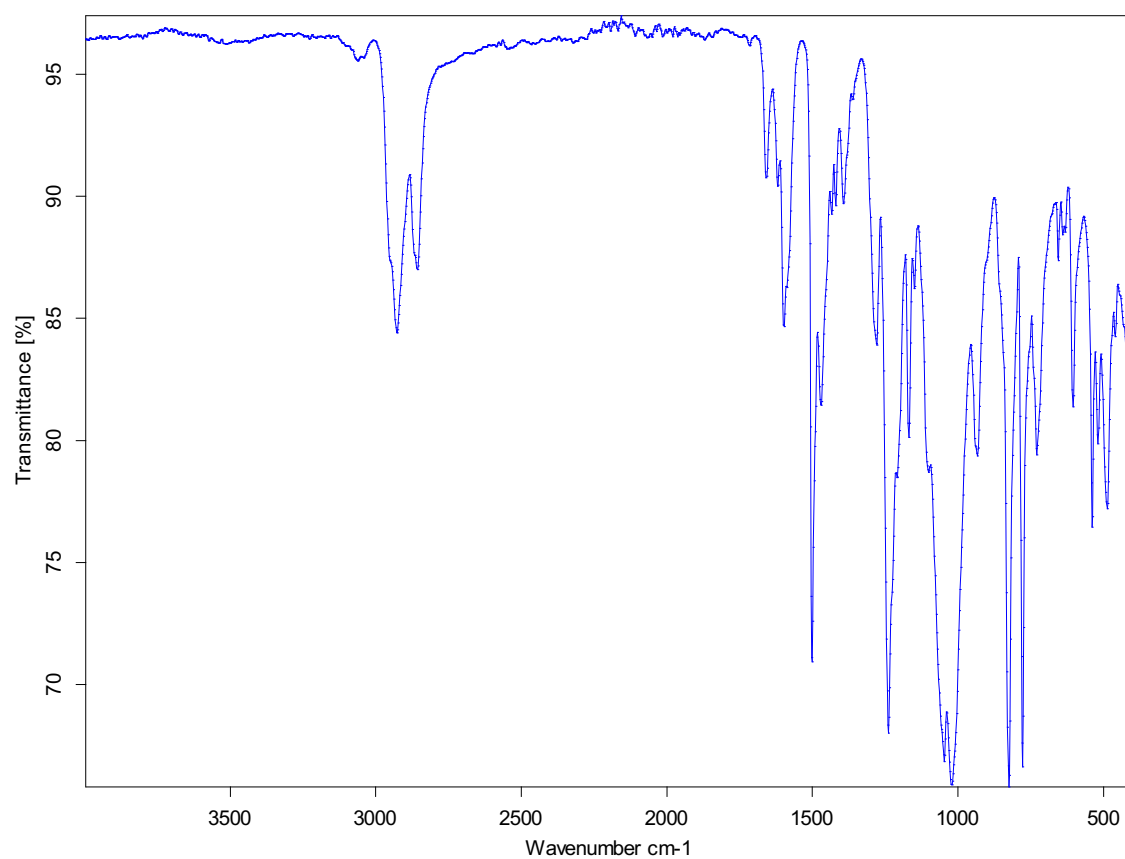


Figure S81: IR absorption spectrum of $[\text{Ag}(\text{4-n-hexyloxy-BIAN})_2]\text{BF}_4 \text{ Ag-OC}_6$.

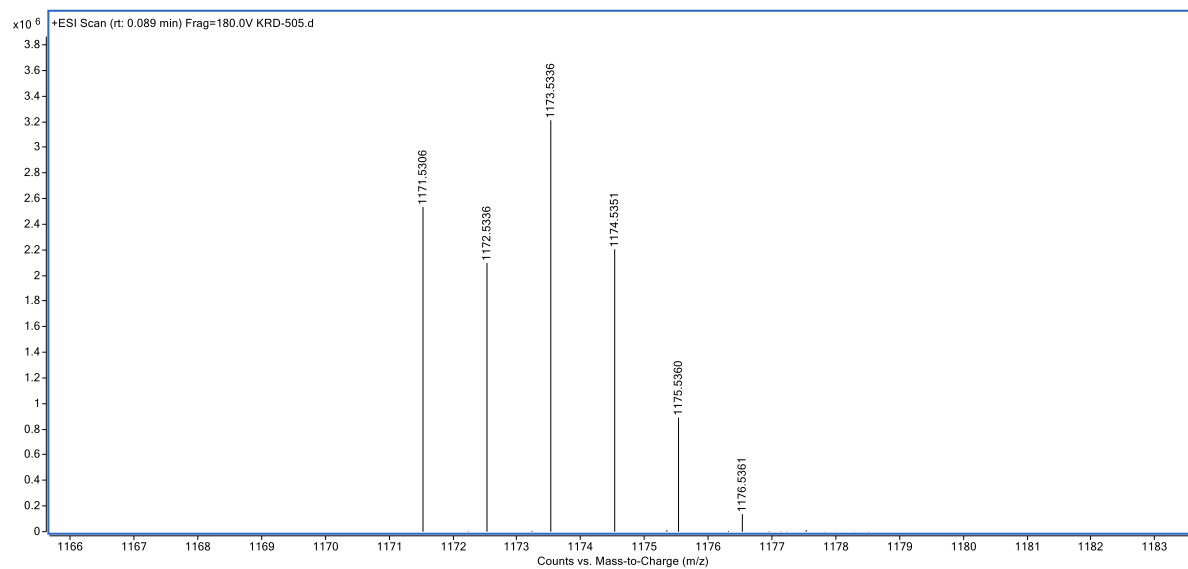


Figure S82: HRMS spectrum of $[\text{Ag}(\text{4-n-hexyloxy-BIAN})_2]\text{BF}_4 \text{ Ag-OC}_6$.

Spectral Data of [Ag(4-n-hexadecyloxy-BIAN)₂]BF₄ (Ag-OC₁₆)

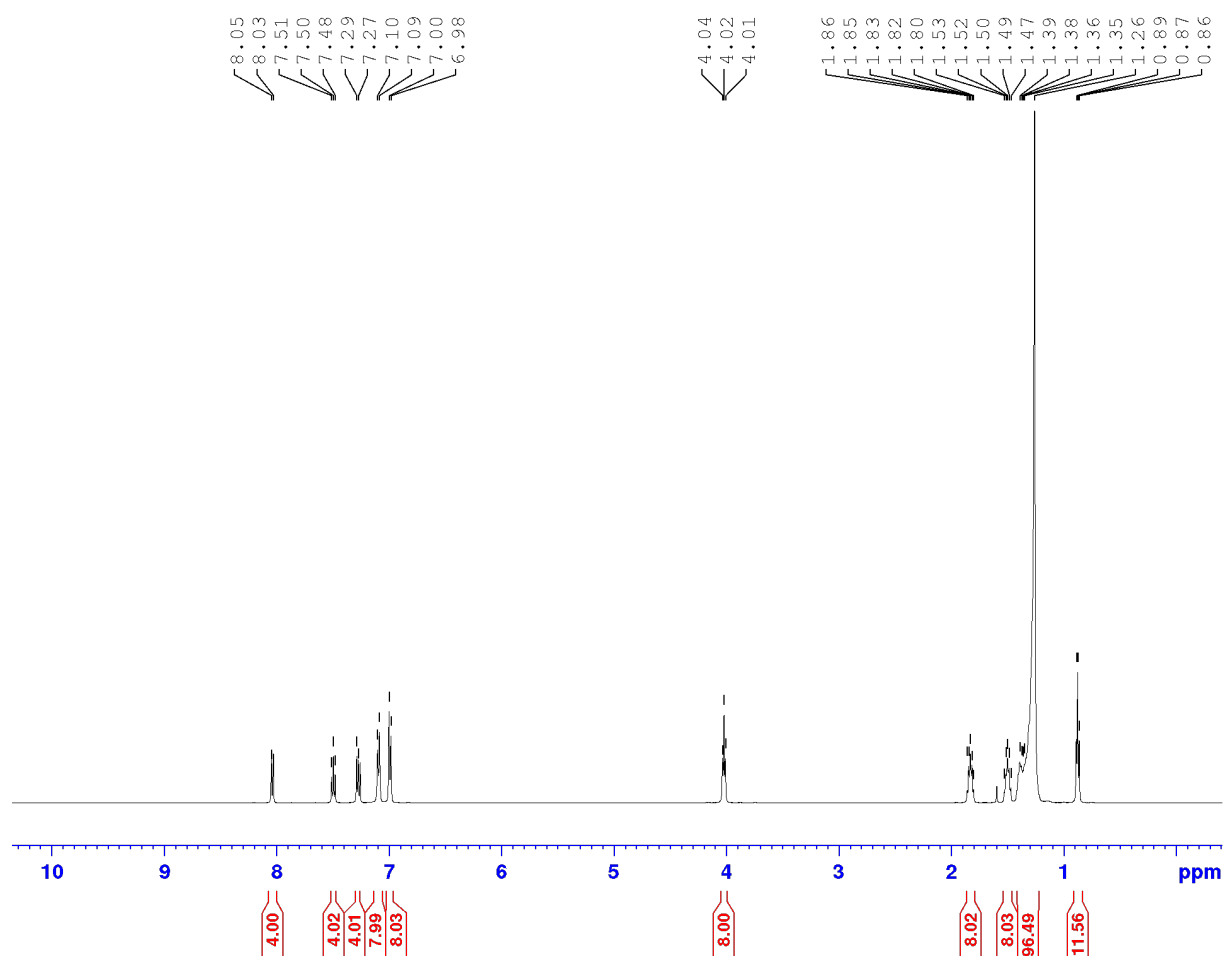


Figure S83: ¹H NMR (500 MHz, CDCl₃, 25 °C) of [Ag(4-n-hexadecyloxy-BIAN)₂]BF₄ Ag-OC₁₆.

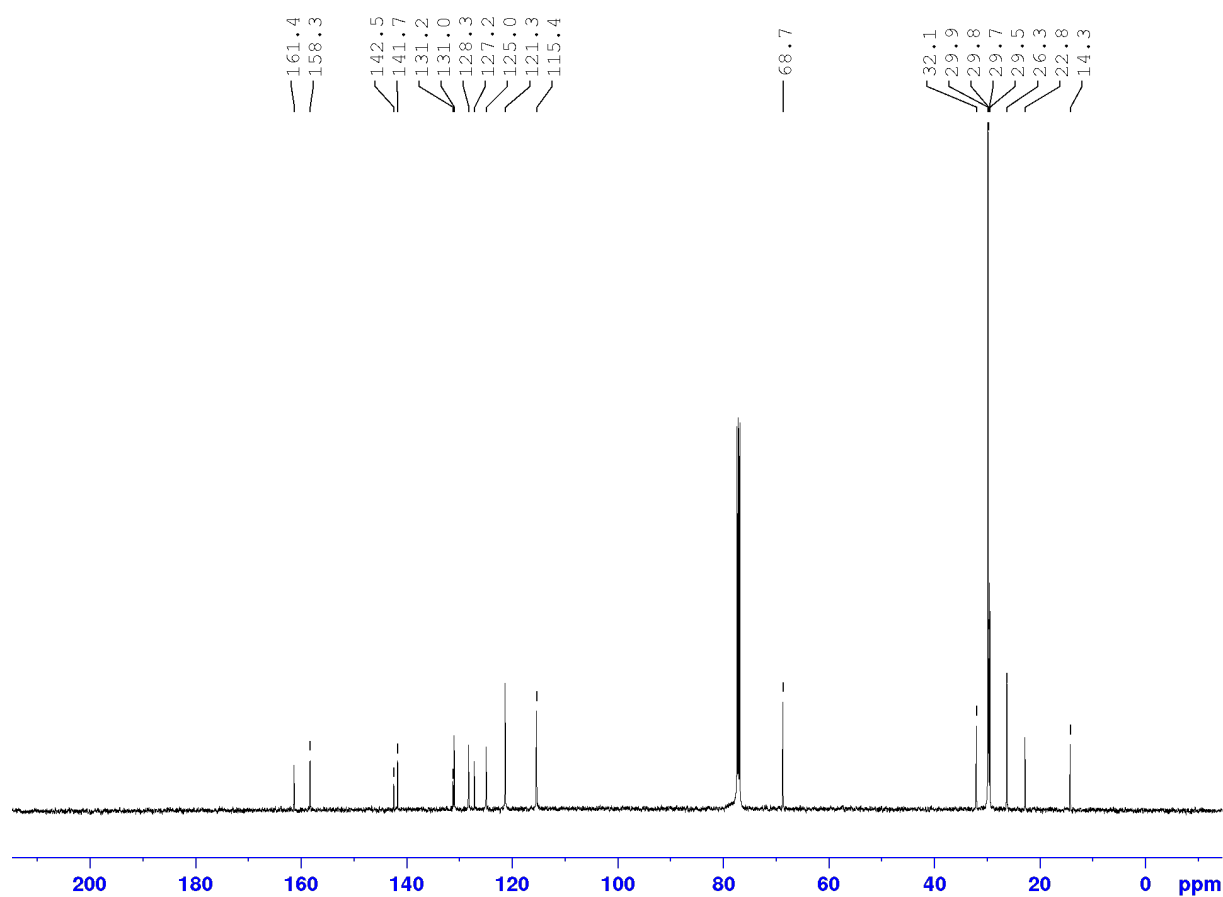


Figure S84: ^{13}C NMR (126 MHz, CDCl_3 , 25 °C) of $[\text{Ag}(4\text{-n-hexadecyloxy-BIAN})_2]\text{BF}_4$ Ag-OC₁₆.

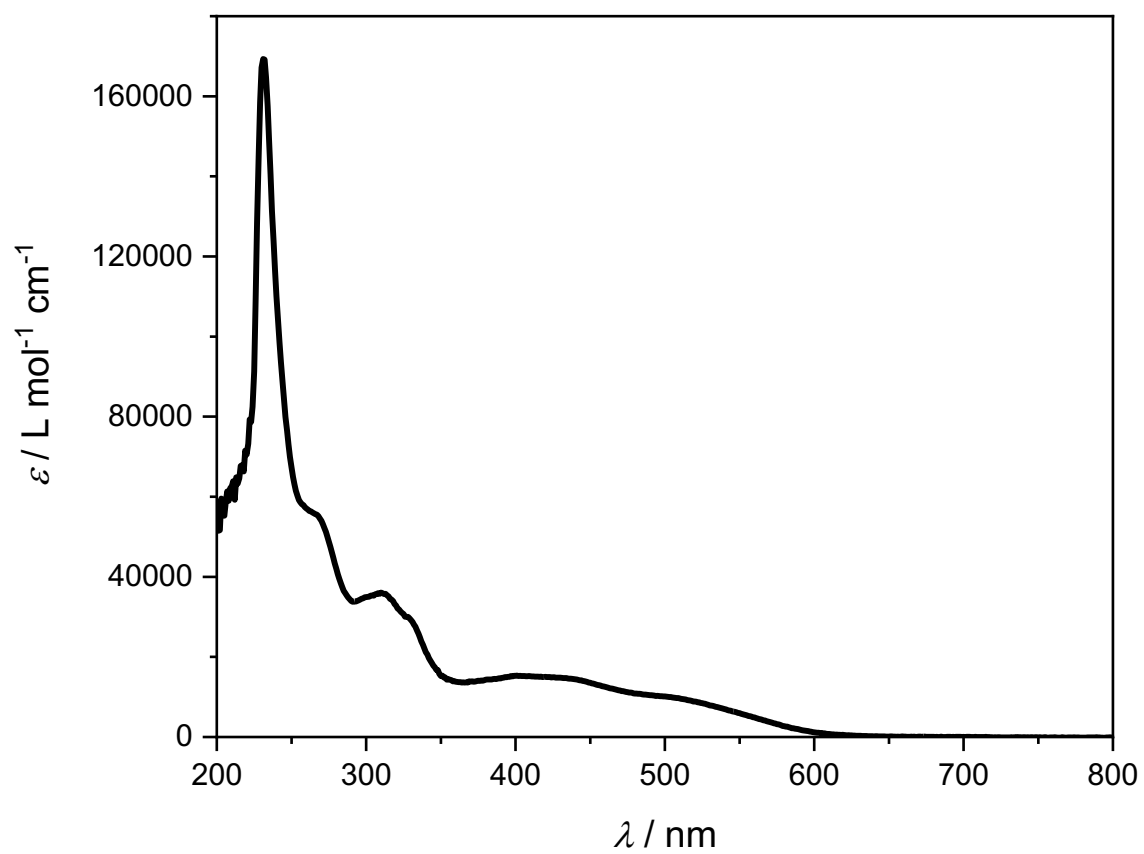


Figure S85: UV-vis absorption spectrum of [Ag(4-n-hexadecyloxy-BIAN)₂]BF₄ Ag-OC₁₆ in DCM.

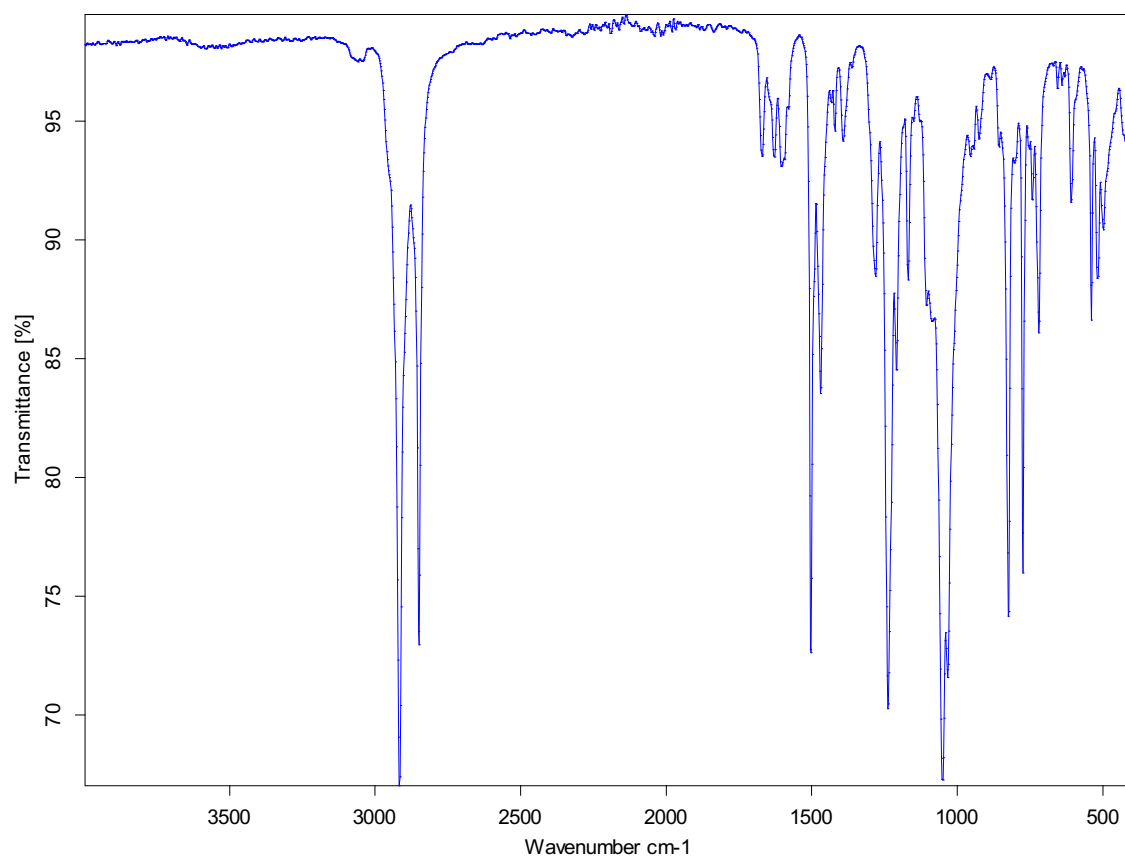


Figure S86: IR absorption spectrum of $[\text{Ag}(\text{4-n-hexadecyloxy-BIAN})_2]\text{BF}_4 \text{ Ag-OC}_{16}$.

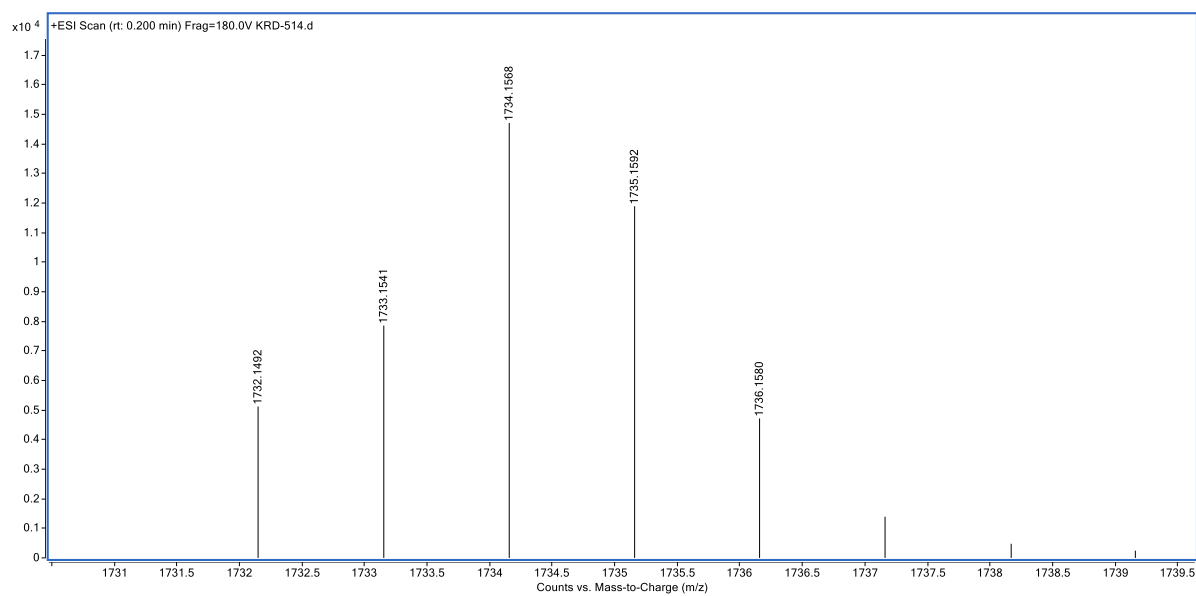


Figure S87: HRMS spectrum of $[\text{Ag}(\text{4-n-hexadecyloxy-BIAN})_2]\text{BF}_4 \text{ Ag-OC}_{16}$.

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