Supporting Information for:

Novel Copper(II) Complexes with BIAN Ligands: Synthesis, Structure and Catalytic Properties of the Oxidation of Isopropylbenzene

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Table S1. Crystal data and structure refinement for **2**.

Chemical formula	$C_{26}H_{20}Br_2CuN_2$
M_r	583.80
Crystal system, space group	Monoclinic, $P2_1/n$
a, b, c (Å)	11.544 (2), 10.6495 (19), 18.722 (4)
α, β, γ (°)	90, 90.549 (7), 90
V (Å^3)	2301.4 (8)
Z	4
μ (mm^{-1})	4.44
Crystal size (mm)	0.10 × 0.08 × 0.05
T_{min}, T_{max}	0.626, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34785, 7663, 5729
R_{int}	0.047
θ values (°)	θ_{max} = 31.5, θ_{min} = 2.1
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.736
Range of h, k, l	$-16 \le h \le 16$, $-13 \le k \le 15$, $-27 \le l \le 27$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.098, 1.03
No. of reflections	7663
No. of parameters	280
No. of restraints	0
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 4.529P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.41, -0.62

Table S2. Cartesian atomic coordinates for optimized model structures.

Atom	X	Y	Z
1			
C	-3.388118	-1.093245	0.692623
H	-2.840989	-1.261578	1.625099
C	-3.370957	-0.398816	-1.629686
C	-4.728699	-0.699964	-1.724644
H	-5.242906	-0.553069	-2.680254
C	-5.440646	-1.187897	-0.622090
C	-4.746502	-1.379365	0.580542
H	-5.278703	-1.770298	1.454153
C	-2.708097	-0.582159	-0.414899
C	-0.933884	0.951903	-0.250588
C	-1.646185	2.234422	-0.132103
C	-2.975895	2.601075	-0.085059
H	-3.776683	1.866935	-0.198603
C	-3.288765	3.970861	0.118873
H	-4.341324	4.265446	0.153012
C	-2.311776	4.933902	0.284061
H	-2.595153	5.978615	0.447957
C	-0.934370	4.578248	0.256034
C	0.175258	5.447386	0.451839
H	0.003337	6.514290	0.626325
C	1.461954	4.946579	0.435481
H	2.301951	5.627171	0.600091
C	1.739402	3.571197	0.210706
H	2.772445	3.217006	0.210357
C	-0.640889	3.223666	0.034766
C	0.683129	2.710325	0.000846
C	0.551152	1.250345	-0.207283
C	2.751817	0.345728	-0.317118
C	3.459390	-0.503619	0.542608
H	2.902413	-1.179419	1.198686
C	4.848276	-0.469061	0.548594
H	5.393843	-1.125498	1.234555
C	5.563044	0.365637	-0.323375
C	4.837467	1.172759	-1.206934
H	5.372209	1.812676	-1.916858
C	3.443345	1.170006	-1.208412
N	-1.320067	-0.268341	-0.315217
N	1.344082	0.255650	-0.310214

Cu	0.157058	-1.660102	-0.094976
Br	-0.138808	-2.075621	2.215927
Br	1.412877	-3.321583	-1.010263
H	2.889073	1.787782	-1.921838
H	-2.821790	-0.018252	-2.496383
C	7.069707	0.355700	-0.327971
H	7.473275	0.500982	0.688331
H	7.453686	-0.611249	-0.697724
H	7.477823	1.148527	-0.974572
C	-6.902042	-1.539681	-0.730678
H	-7.377353	-1.036224	-1.587564
H	-7.031506	-2.627673	-0.869897
H	-7.451550	-1.257841	0.182414
2			
C	2.691010	-0.038625	2.216772
H	3.408549	-0.178152	3.039133
H	1.745161	0.334629	2.645646
H	2.485885	-1.031466	1.776046
C	3.004259	2.043308	-0.971621
H	2.402981	2.234404	-1.865479
C	3.242078	0.896120	1.175955
C	4.522995	1.446256	1.279690
H	5.130131	1.203589	2.157912
C	5.045234	2.274882	0.286338
H	6.055651	2.680565	0.392230
C	4.289217	2.566166	-0.849450
H	4.702233	3.189459	-1.647450
C	2.485364	1.237142	0.042517
C	0.132514	1.399621	-0.133018
C	-0.173247	2.839959	-0.021471
C	0.574981	3.982937	0.167247
H	1.664299	3.945550	0.238775
C	-0.104440	5.227114	0.263752
H	0.488041	6.133866	0.413253
C	-1.479081	5.328488	0.169108
H	-1.962118	6.308086	0.242647
C	-2.275363	4.163596	-0.017775
C	-3.693822	4.100993	-0.121684
H	-4.279187	5.024645	-0.068700
C	-4.333938	2.887204	-0.286343
H	-5.424285	2.864718	-0.365481
C	-3.624977	1.658226	-0.351238
H	-4.163012	0.714560	-0.470830

C	-1.588703	2.943140	-0.101203
C	-2.249572	1.696022	-0.254905
C	-1.188813	0.677549	-0.259861
C	-2.407391	-1.318688	-0.350067
C	-2.867903	-1.788299	-1.578405
H	-2.269099	-1.615423	-2.477377
C	-4.080507	-2.473190	-1.643550
H	-4.446850	-2.841954	-2.605639
C	-4.809564	-2.694914	-0.475835
H	-5.757947	-3.238497	-0.514892
C	-4.319684	-2.241088	0.749844
H	-4.885529	-2.437400	1.666468
C	-3.111276	-1.544888	0.843722
C	-2.573568	-1.057760	2.161423
H	-3.169672	-1.453902	2.997107
H	-1.530357	-1.393378	2.290195
H	-2.594052	0.045402	2.225732
N	1.186348	0.677977	-0.084206
N	-1.174892	-0.599951	-0.307556
Cu	0.757594	-1.403567	-0.223988
Br	2.726156	-1.961485	-1.334216
Br	0.237099	-3.341362	0.977903

Table S3. Cartesian atomic coordinates for model supramolecular associate based on the obtained experimental X-ray geometry of **2**.

Atom	X	Y	Z
C	4.064647	10.278897	10.360279
H	4.054652	11.254157	10.261226
H	3.406393	10.013235	11.036468
H	4.957442	9.989071	10.642894
C	3.404389	7.634627	7.703749
H	3.433489	6.687417	7.634125
C	3.721658	9.638862	9.048863
C	3.408205	10.392847	7.907810
H	3.414172	11.341281	7.959742
C	3.091765	9.787955	6.717145
H	2.865241	10.322763	5.965005
C	3.099821	8.416300	6.599202
H	2.897828	8.006912	5.765194
C	3.665283	8.260817	8.908455
C	2.851799	6.967968	10.677228
C	1.412488	6.932825	10.412698
C	0.589901	7.381168	9.396702
H	0.946641	7.852068	8.652649
C	-0.792836	7.122386	9.492742
H	-1.363009	7.408378	8.788302
C	-1.349236	6.467441	10.574823
H	-2.286502	6.314802	10.604609
C	-0.532843	6.023357	11.634814
C	-0.962202	5.387582	12.831470
H	-1.886193	5.209565	12.963735
C	-0.059464	5.029759	13.795608
H	-0.375958	4.602256	14.583881
C	1.335188	5.273632	13.660816
H	1.942171	5.032315	14.351177
C	0.842036	6.267231	11.515561
C	1.777979	5.866810	12.508156
C	3.086301	6.270426	11.985836
C	4.666385	5.499402	13.582187
C	5.375611	4.224657	13.417441
H	5.522773	3.852158	12.556194
C	5.811726	3.601661	14.527605
H	6.252599	2.762374	14.469045
C	5.601097	4.216137	15.787538
H	5.936946	3.780700	16.561039
C	4.970460	5.348179	15.942923

H	4.844564	5.708004	16.812371
C	4.462120	6.057436	14.780340
C	3.793172	7.302362	14.958191
H	3.755070	7.519090	15.913101
H	4.280721	8.006805	14.482356
H	2.882190	7.237965	14.601516
N	3.873291	7.468494	10.090695
N	4.305221	6.160736	12.360446
Cu	5.605456	6.936658	10.995487
Br	6.884738	6.951781	9.022279
Br	7.293998	7.386387	12.549529
C	7.299964	0.370603	8.360861
H	7.309959	-0.604657	8.459915
H	7.958218	0.636265	7.684672
H	6.407170	0.660429	8.078247
C	7.960222	3.014873	11.017391
H	7.931122	3.962083	11.087015
C	7.642953	1.010638	9.672277
C	7.956406	0.256653	10.813331
H	7.950439	-0.691781	10.761398
C	8.272846	0.861545	12.003995
H	8.499371	0.326737	12.756136
C	8.264790	2.233200	12.121939
H	8.466784	2.642588	12.955947
C	7.699328	2.388683	9.812686
C	8.512812	3.681532	8.043912
C	9.952123	3.716676	8.308442
C	10.774710	3.268332	9.324438
H	10.417971	2.797432	10.068491
C	12.157447	3.527114	9.228399
H	12.727620	3.241122	9.932838
C	12.713847	4.182059	8.146317
H	13.651113	4.334698	8.116532
C	11.897454	4.626143	7.086326
C	12.326813	5.261918	5.889671
H	13.250804	5.439935	5.757406
C	11.424076	5.619741	4.925532
H	11.740569	6.047244	4.137260
C	10.029423	5.375868	5.060324
H	9.422440	5.617185	4.369964
C	10.522575	4.382269	7.205580
C	9.586633	4.782690	6.212985
C	8.278310	4.379074	6.735305

C	6.698226	5.150098	5.138953
C	5.989000	6.424843	5.303699
H	5.841838	6.797342	6.164946
C	5.552885	7.047839	4.193535
H	5.112013	7.887126	4.252095
C	5.763515	6.433363	2.933603
H	5.427666	6.868800	2.160101
C	6.394152	5.301321	2.778217
H	6.520047	4.941496	1.908770
C	6.902491	4.592064	3.940800
C	7.571439	3.347138	3.762949
H	7.609541	3.130410	2.808040
H	7.083890	2.642695	4.238784
H	8.482421	3.411535	4.119624
N	7.491320	3.181006	8.630446
N	7.059390	4.488764	6.360695
Cu	5.759155	3.712842	7.725653
Br	4.479873	3.697719	9.698861
Br	4.070613	3.263113	6.171611

Table S4. Conversion of IPBHP and products obtained in CH_3CN solutions of **1** and **2**. Conditions: 0.001 mmol of **1** or **2**, 4 mmol of IPBHP in 2.5 ml CH_3CN, 30 ^{0}C, 130 min, Ar.

Complex	Conversion of IPBHP, %	PP/mmol	AP/mmol
1	18	0.60	0.12
2	11	0.35	0.08

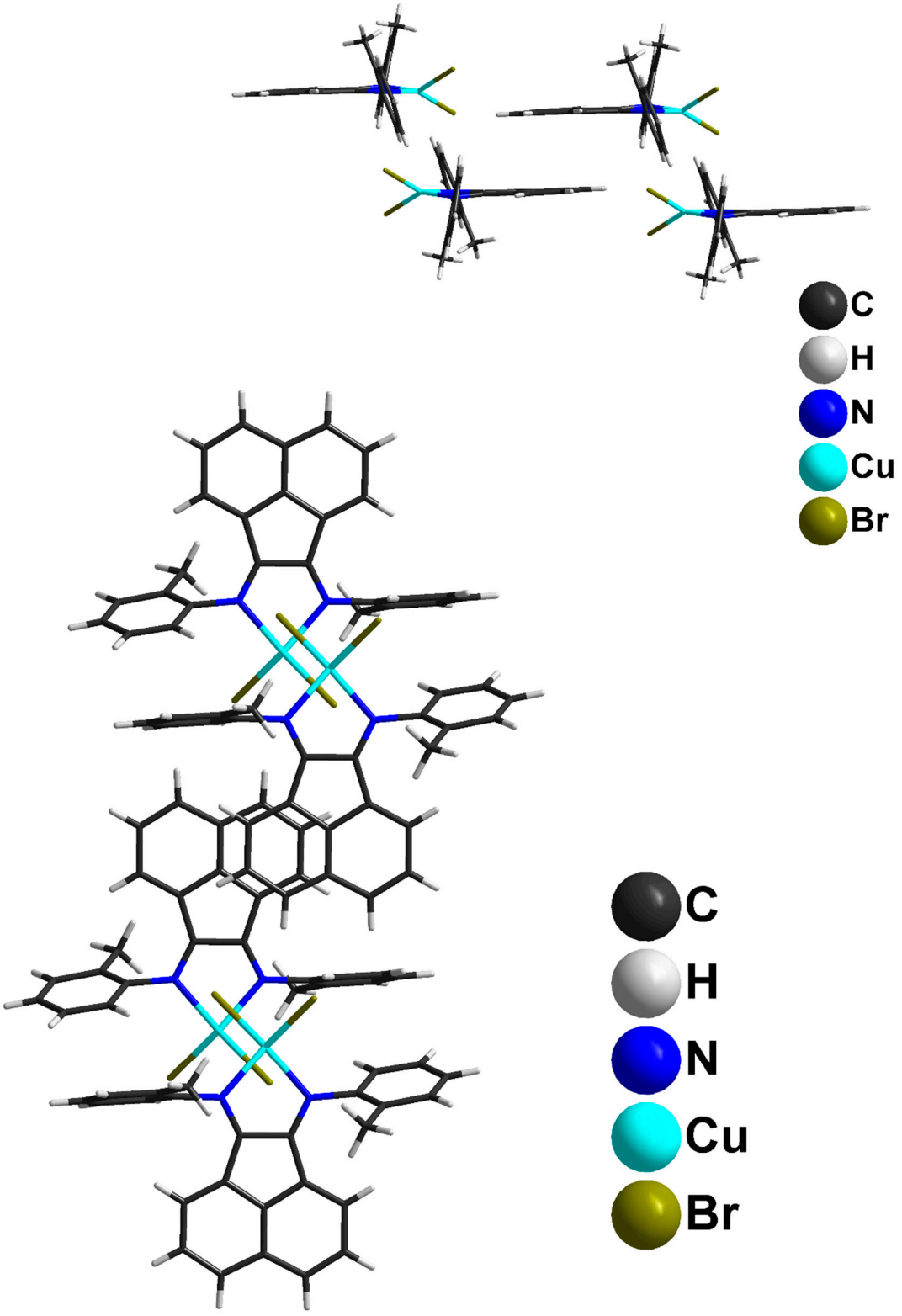


Figure S1. Formation of π-π interactions between the dimers in the crystal structure of **2**.

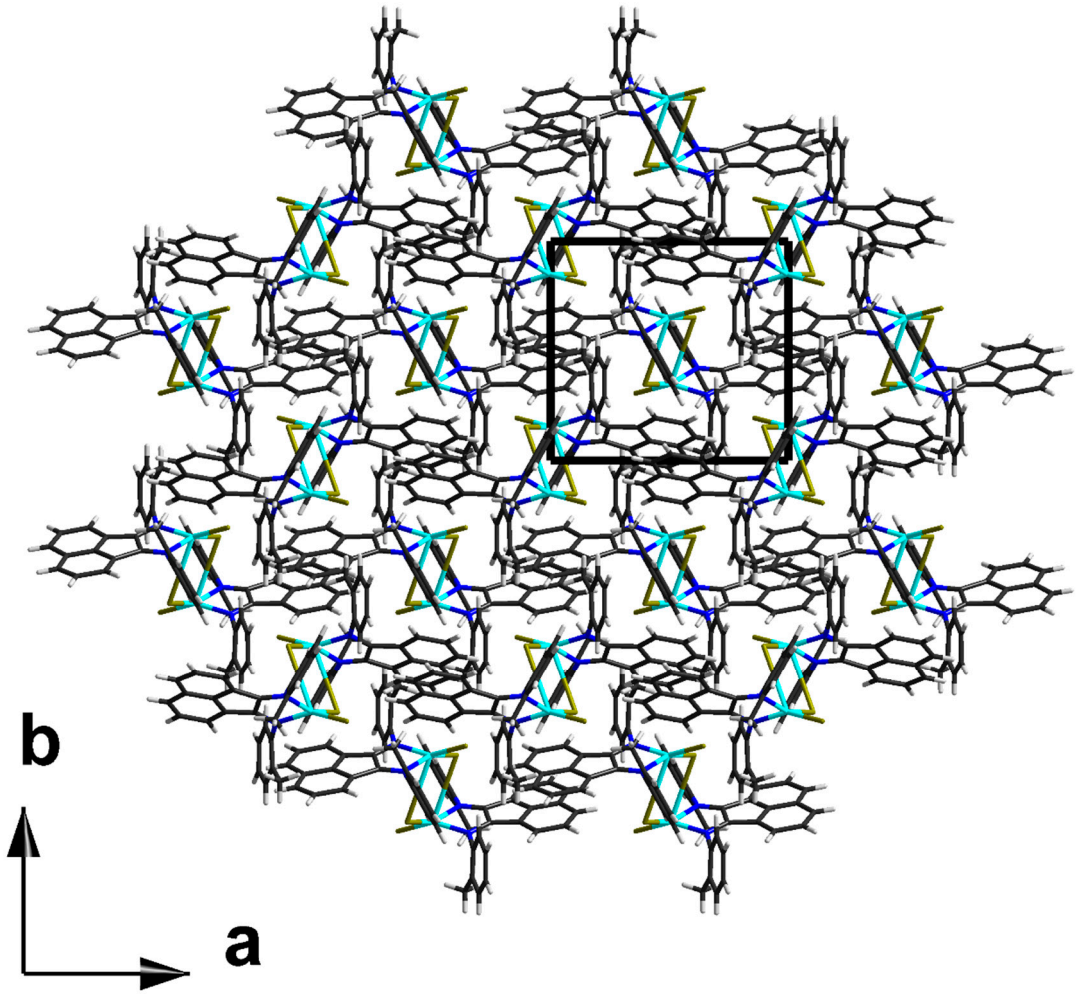


Figure S2. Crystal packing of **2**.

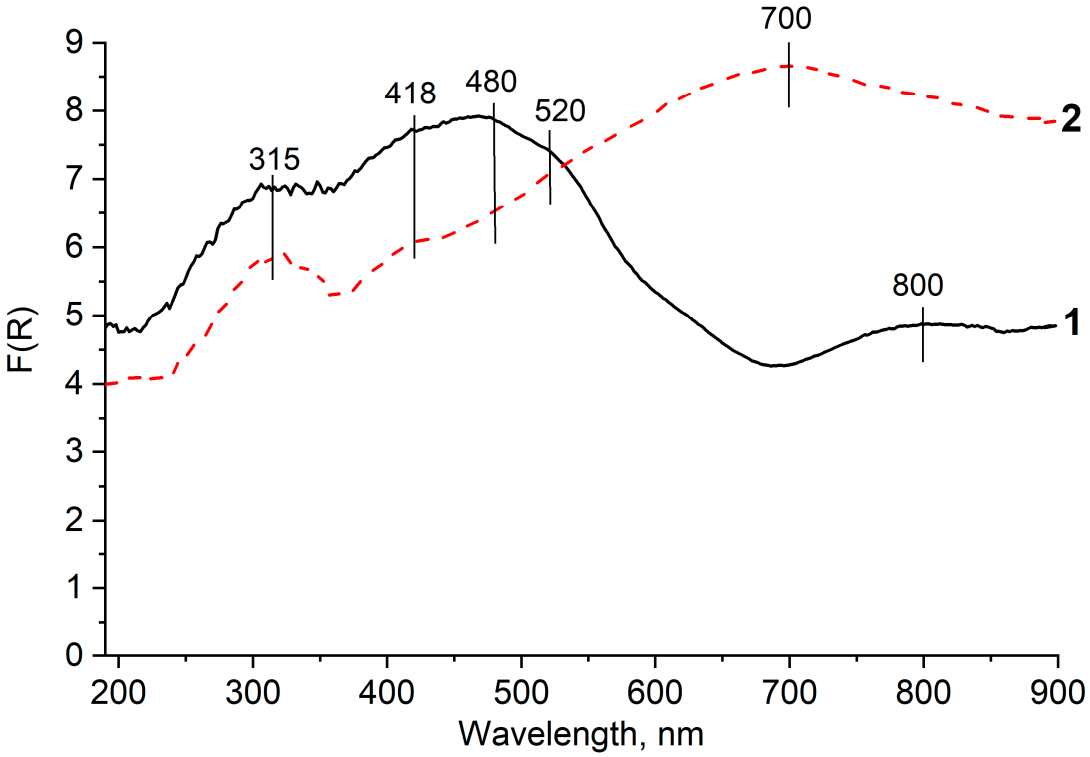


Figure S3. UV-Vis diffuse reflectance spectra of complexes **1** and **2** in solid state.

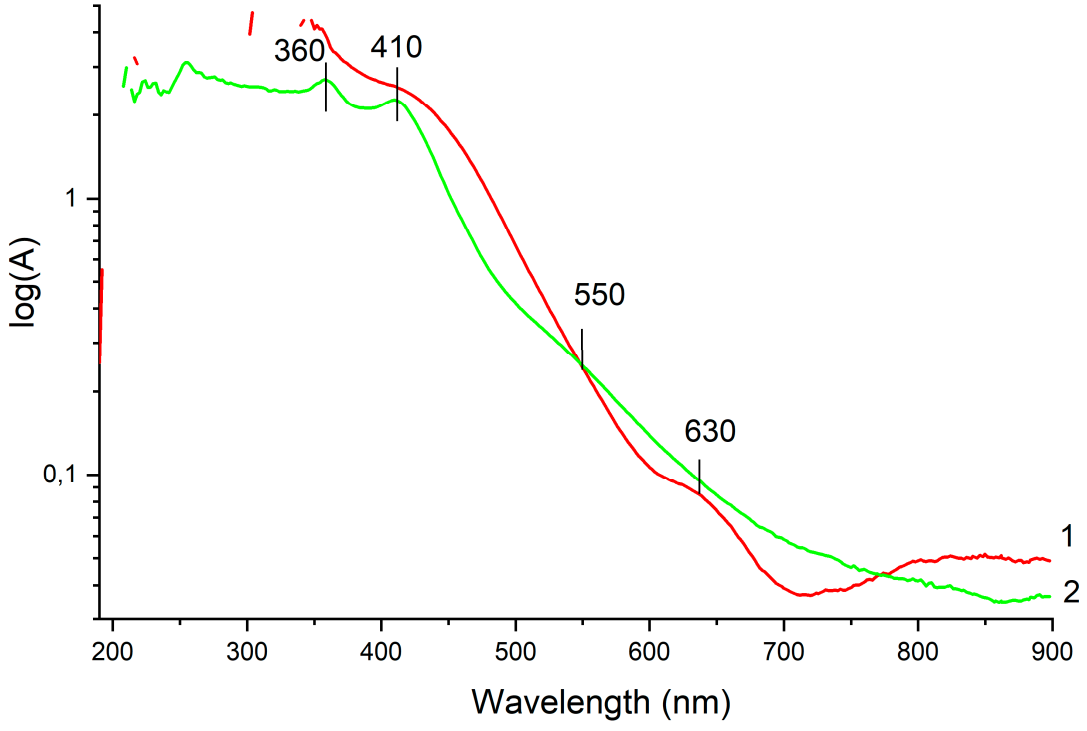
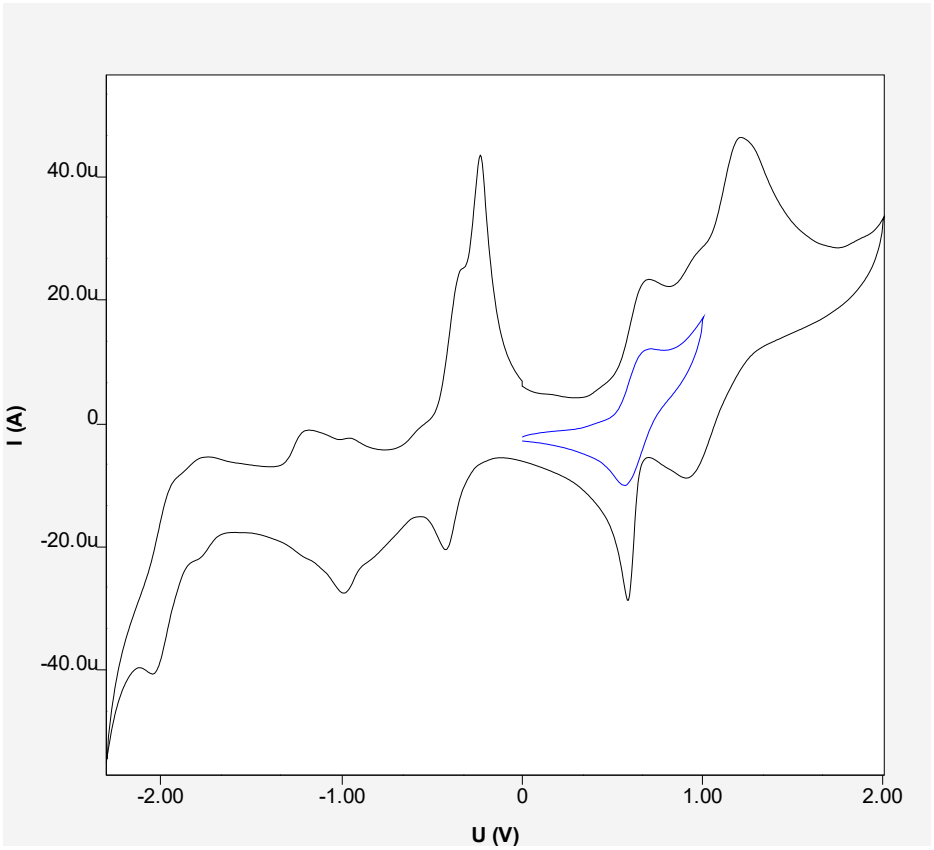
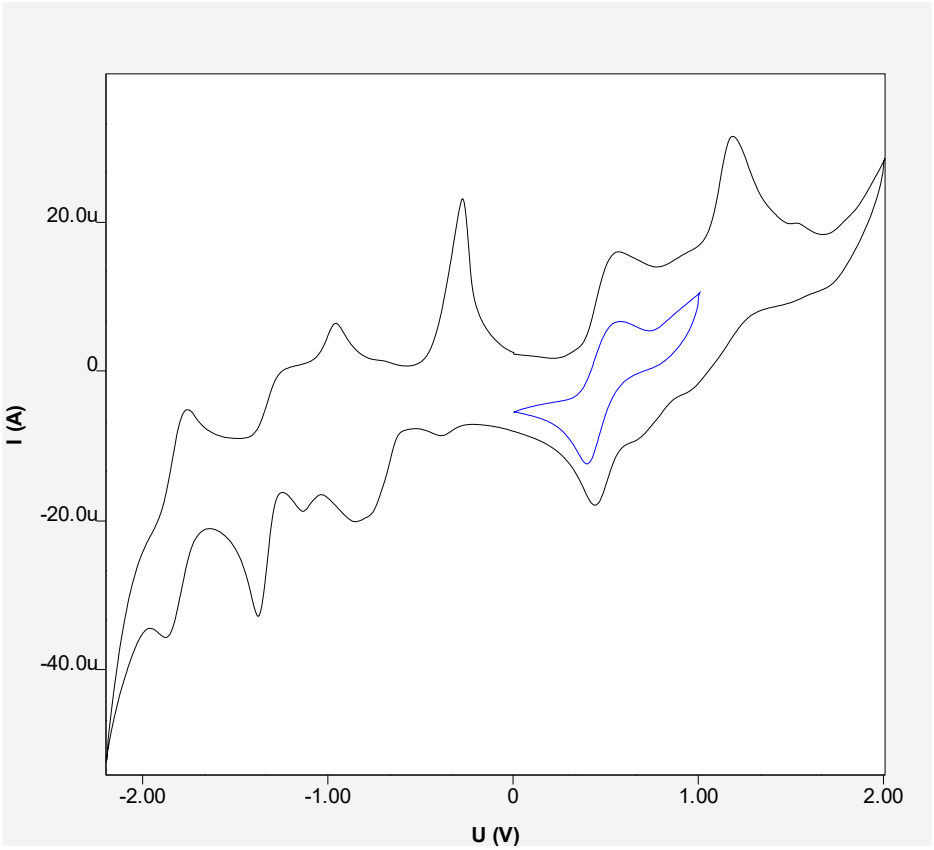


Figure S4. UV-Vis absorption spectra of CH_3CN solutions of complexes **1** and **2** ($5 \bullet 10^{-4}$ M).


40.0u
20.0u
0
-20.0u
-40.0u
I (A)
-2.00
-1.00
0
1.00
2.00
U (V)

A


20.0u
0
-20.0u
-40.0u
I (A)
-2.00
-1.00
0
1.00
2.00
U (V)

B

Figure S5. Cyclic voltammograms of **1** (A) and **2** (B) in CH_3CN in the -2.3–2.0 V region (black line) and the 0–1.0 V region (blue line) at a potential scan rate of 100 mV/s.

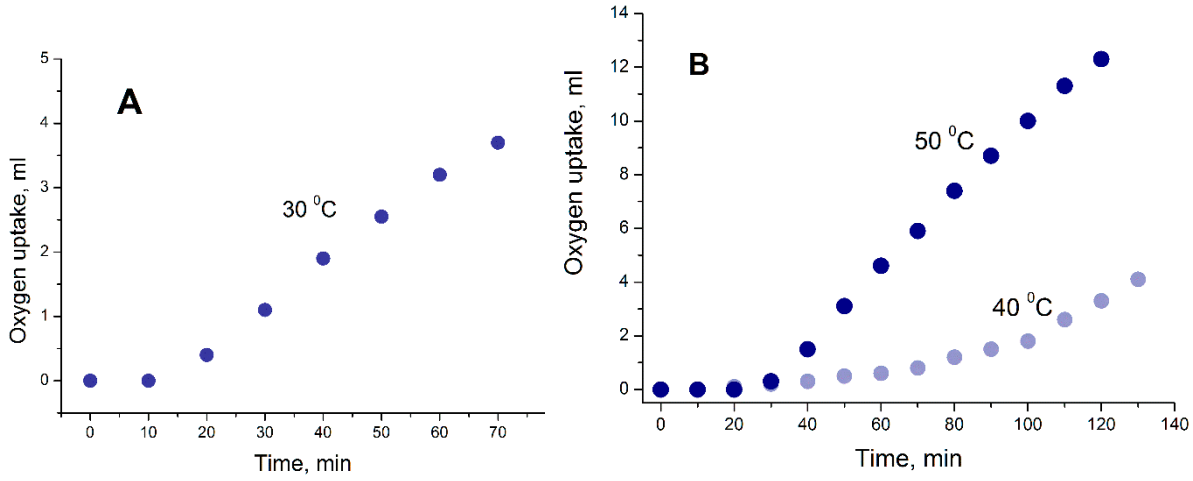


Figure S6. Kinetic curves of oxygen uptake by $CuBr_2$ (A) and $CuCl_2$ (B) solutions. Conditions: 1 mL of IPB, 1.5 mL of CH_3CN, $5 \cdot 10^{-4}$ M of catalyst.

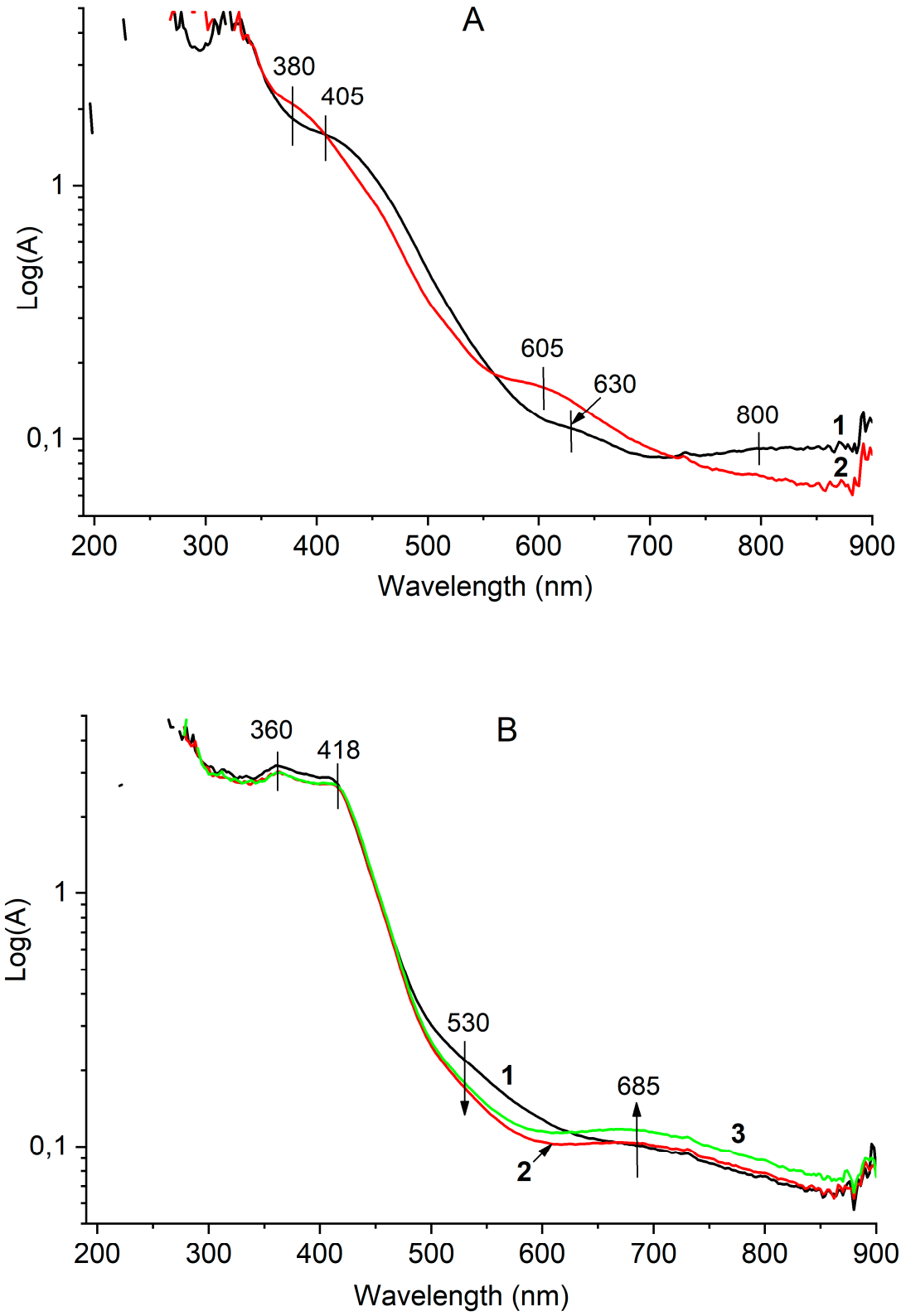


Figure S7. UV-Vis spectra of **1** (A) and **2** (B) ($3 \bullet 10^{-4}$ M) in CH_3CN solution (1), 10 min after addition of IPBHP (2), 40 min after addition of IPBHP (3).