Supporting Information for

Gas-Phase Synthesis and Deposition of Metal-bipyridine Complex $[M\text{-}bpy_{1\text{-}2}]^+$ (M=Ag, Cu)

Mengdi Guo,[ab] Benben Huang,[ab] Qiuhao Yi,[ab] and Zhixun Luo[a]*

a. Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences. Beijing 100190, China

b. University of Chinese Academy of Sciences, Beijing 100049, China

*Correspondence. Email: zxluo@iccas.ac.cn

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S1. Thermodynamics

Table S1. DFT-calculated Energetics

Ag^+	+	$C_{10}H_8N_2^0$	→	$[Ag\text{-}C_{10}H_8N_2]^+$				ΔE = **-3.062 eV** (1)
Ag_2^+	+	$C_{10}H_8N_2^0$	→	$[Ag\text{-}C_{10}H_8N_2]^+$	+	Ag^0		ΔE = -1.238 eV (2)
Ag_3^+	+	$C_{10}H_8N_2^0$	→	$[Ag\text{-}C_{10}H_8N_2]^+$	+	Ag_2^0		ΔE = -0.060 eV (3)
Ag^+	+	$2C_{10}H_8N_2^0$	→	$[Ag\text{-}(C_{10}H_8N_2)_2]^+$				ΔE = **-5.074 eV** (4)
Ag_2^+	+	$2C_{10}H_8N_2^0$	→	$[Ag\text{-}(C_{10}H_8N_2)_2]^+$	+	Ag^0		ΔE = -3.250 eV (5)
Ag_3^+	+	$2C_{10}H_8N_2^0$	→	$[Ag\text{-}(C_{10}H_8N_2)_2]^+$	+	Ag_2^0		ΔE = -2.072 eV (6)
Cu^+	+	$C_{10}H_8N_2^0$	→	$[Cu\text{-}C_{10}H_8N_2]^+$				ΔE = **-2.733 eV** (7)
Cu_2^+	+	$C_{10}H_8N_2^0$	→	$[Cu\text{-}C_{10}H_8N_2]^+$	+	Cu^0		ΔE = -0.441 eV (8)
Cu_3^+	+	$C_{10}H_8N_2^0$	→	$[Cu\text{-}C_{10}H_8N_2]^+$	+	Cu_2^0		ΔE = 0.832 eV (9)
Cu^+	+	$2C_{10}H_8N_2^0$	→	$[Cu\text{-}(C_{10}H_8N_2)_2]^+$				ΔE = **-5.264 eV** (10)
Cu_2^+	+	$2C_{10}H_8N_2^0$	→	$[Cu\text{-}(C_{10}H_8N_2)_2]^+$	+	Cu^0		ΔE = -2.971 eV (11)
Cu_3^+	+	$2C_{10}H_8N_2^0$	→	$[Cu\text{-}(C_{10}H_8N_2)_2]^+$	+	Cu_2^0		ΔE = -1.698 eV (12)
Ag^+	+	$C_{10}H_8N_2^0$	→	Ag^0	+	$C_{10}H_8N_2^+$		ΔE = 0.231 eV (13)
Cu^+	+	$C_{10}H_8N_2^0$	→	Cu^0	+	$C_{10}H_8N_2^+$		ΔE = -0.077 eV (14)
Ar^+	+	$C_{10}H_8N_2^0$	→	Ar^0	+	$C_{10}H_8N_2^+$		ΔE = -7.482 eV (15)
Ag^0	+	$C_{10}H_8N_2^+$	→	$[Ag\text{-}C_{10}H_8N_2]^+$				ΔE = -3.293 eV (16)
Cu^0	+	$C_{10}H_8N_2^+$	→	$[Cu\text{-}C_{10}H_8N_2]^+$				ΔE = -2.656 eV (17)

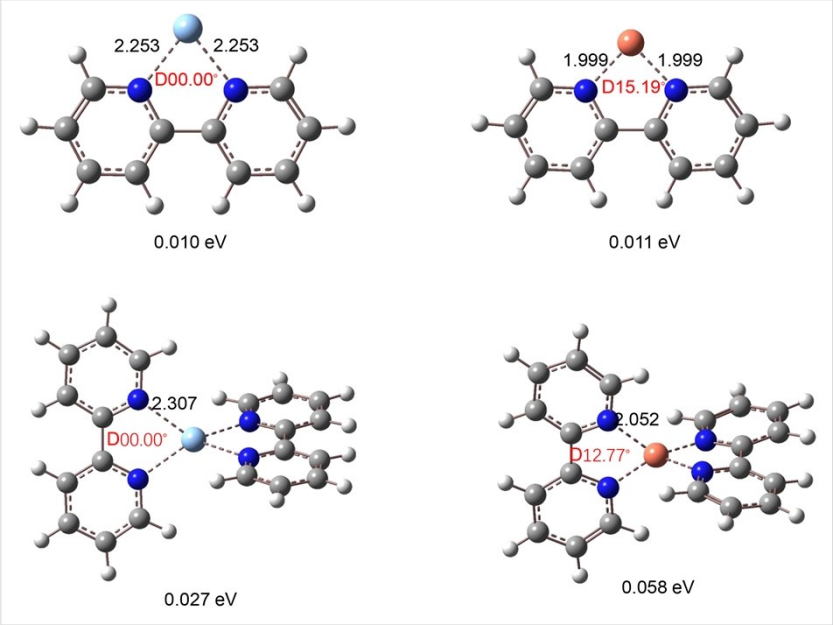

Fig. S1 Structures and relative energies of $[Ag\text{-}bpy_{1\text{-}2}]^+$ and $[Cu\text{-}bpy_{1\text{-}2}]^+$ with numerical exchange of the N-C-C-N dihedral angles.

S2. Charge distribution analysis

Table S2 Positive charge distribution on metal part.

	Mulliken	NPA	Hirshfeld	ADCH
$[Ag\text{-}bpy]^+$	0.664	0.822	0.697	0.849
$[Ag\text{-}bpy_2]^+$	0.624	0.633	0.536	0.619
$[Cu\text{-}bpy]^+$	0.586	0.799	0.664	0.767
$[Cu\text{-}bpy_2]^+$	0.520	0.568	0.525	0.475

S3. Topological analysis

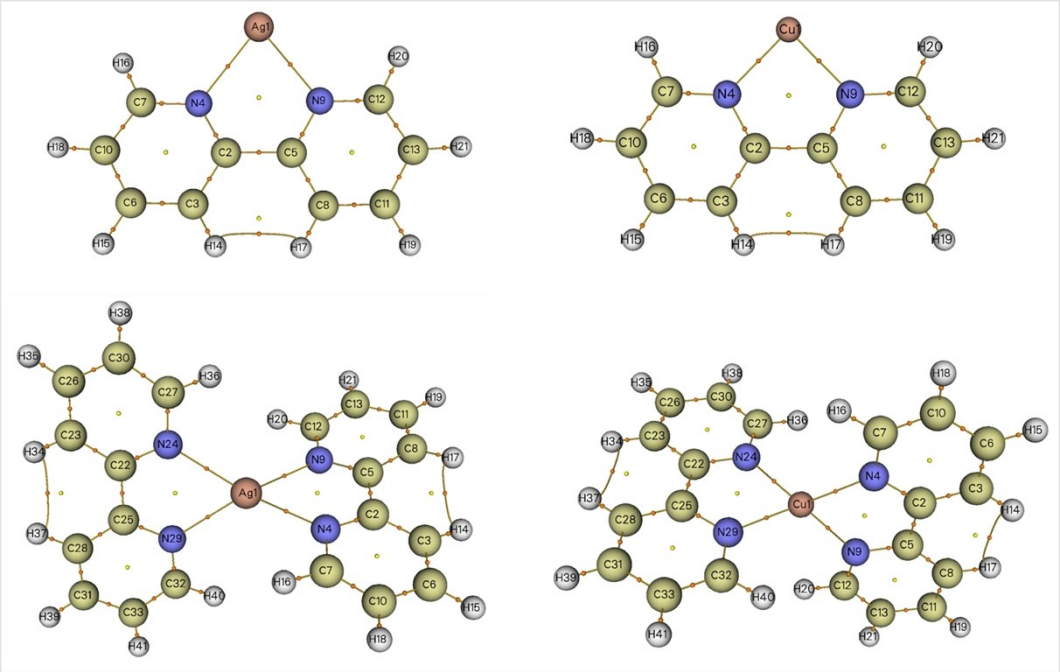

Fig. S2 Topological analysis within the theory of atoms in molecules (AIM), the bond critical points (BCPs) are indicated by orange dots.

Table S3 Energy density (H), electron density (ρ), potential energy density (V), Lagrangian kinetic energy (G), Laplacian of electron density ($\nabla 2\rho$), eta index (η), and bond ellipticity (εr) of $[M\text{-}bpy_{1\text{-}2}]^+$ (M=Ag, Cu).

BCP	ρ(BCP)	V(BCP)	G(BCP)	$\nabla 2\rho$(BCP)	λ1	λ2	λ3	$\eta(r)=\lvert\lambda_1\rvert/\lambda_3$	$\varepsilon(r)=[\lambda_1/\lambda_2]-1$
Ag1-N4	0.065	-0.084	0.076	0.270	-0.073	-0.069	0.411	0.177	0.058
Ag1-N9	0.065	-0.084	0.076	0.270	-0.073	-0.069	0.411	0.177	0.058
H14-H17	0.013	-0.0077	0.010	0.050	-0.012	-0.0071	0.070	0.176	0.690
Ag1-N4	0.058	-0.074	0.067	0.243	-0.062	-0.057	0.362	0.172	0.088
Ag1-N9	0.058	-0.074	0.067	0.243	-0.062	-0.057	0.362	0.172	0.088
Ag1-N24	0.058	-0.074	0.067	0.243	-0.062	-0.057	0.362	0.172	0.088
Ag1-N29	0.058	-0.074	0.067	0.243	-0.062	-0.057	0.362	0.172	0.088
H14-H17	0.012	-0.007	0.010	0.047	-0.0117	-0.0066	0.065	0.178	0.773
H34-H37	0.0123	-0.0072	0.0095	0.047	-0.0117	-0.0066	0.066	0.178	0.773
Cu1-N4	0.088	-0.138	0.127	0.464	-0.117	-0.112	0.693	0.169	0.045
Cu1-N9	0.088	-0.138	0.127	0.464	-0.117	-0.112	0.693	0.169	0.045
H14-H17	0.128	-0.742	0.974	0.483	-0.013	-0.008	0.070	0.190	0.625
Cu1-N4	0.076	-0.115	0.110	0.416	-0.096	-0.088	0.599	0.160	0.091
Cu1-N9	0.076	-0.115	0.110	0.416	-0.096	-0.088	0.599	0.160	0.091
Cu1-N24	0.076	-0.115	0.110	0.416	-0.096	-0.088	0.599	0.160	0.091
Cu1-N29	0.076	-0.115	0.110	0.416	-0.096	-0.088	0.599	0.160	0.091
H14-H17	0.012	-0.0067	0.0088	0.044	-0.0114	-0.0064	0.062	0.185	0.781
H34-H37	0.0116	-0.0067	0.0088	0.044	-0.0114	-0.0064	0.0618	0.185	0.781

Table S3-1 Detailed topological analysis of $[Ag\text{-}bpy]^+$.

BCP	ρ(BCP)	V(BCP)	G(BCP)	∇2ρ(BCP)	λ1	λ2	λ3	η(r)=|λ1|/λ3	ε(r)=[λ1/λ2]-1
Ag1-N4	0.065	-0.084	0.076	0.270	-0.073	-0.069	0.411	0.177	0.058
Ag1-N9	0.065	-0.084	0.076	0.270	-0.073	-0.069	0.411	0.177	0.058
C2-N4	0.331	-0.744	0.263	-0.875	-0.693	-0.621	0.439	1.580	0.116
C7-N4	0.332	-0.791	0.298	-0.786	-0.691	-0.632	0.537	1.286	0.093
C2-C3	0.310	-0.423	0.103	-0.871	-0.643	-0.531	0.303	2.123	0.211
C7-C10	0.316	-0.436	0.105	-0.909	-0.661	-0.548	0.301	2.199	0.206
C3-C6	0.313	-0.430	0.103	-0.894	-0.646	-0.546	0.298	2.168	0.183
C6-C10	0.314	-0.431	0.103	-0.901	-0.648	-0.551	0.298	2.176	0.176
C2-C5	0.264	-0.289	0.061	-0.668	-0.537	-0.479	0.348	1.542	0.121
C5-N9	0.331	-0.744	0.263	-0.875	-0.693	-0.621	0.439	1.580	0.116
C12-N9	0.332	-0.791	0.298	-0.786	-0.691	-0.632	0.537	1.286	0.093
C5-C8	0.310	-0.423	0.103	-0.871	-0.643	-0.531	0.303	2.123	0.211
C12-C13	0.316	-0.436	0.105	-0.909	-0.661	-0.548	0.301	2.199	0.206
C8-C11	0.313	-0.430	0.103	-0.894	-0.646	-0.546	0.298	2.168	0.183
C11-C13	0.314	-0.431	0.103	-0.901	-0.648	-0.551	0.298	2.176	0.176
H14-H17	0.013	-0.0077	0.010	0.050	-0.012	-0.0071	0.070	0.176	0.690

Table S3-2 Detailed topological analysis of $[Ag\text{-}bpy_2]^+$.

BCP	ρ(BCP)	V(BCP)	G(BCP)	∇2ρ(BCP)	λ1	λ2	λ3	η(r)=|λ1|/λ3	ε(r)=[λ1/λ2]-1
Ag1-N4	0.058	-0.074	0.067	0.243	-0.062	-0.057	0.362	0.172	0.088
Ag1-N9	0.058	-0.074	0.067	0.243	-0.062	-0.057	0.362	0.172	0.088
C2-N4	0.335	-0.750	0.262	-0.902	-0.704	-0.633	0.435	1.620	0.112
C7-N4	0.336	-0.792	0.293	-0.826	-0.703	-0.641	0.518	1.357	0.097
C2-C3	0.309	-0.421	0.102	-0.868	-0.642	-0.531	0.305	2.106	0.209
C7-C10	0.315	-0.434	0.104	-0.902	-0.659	-0.545	0.302	2.180	0.209
C3-C6	0.313	-0.430	0.104	-0.892	-0.646	-0.543	0.298	2.172	0.190
C6-C10	0.313	-0.429	0.103	-0.894	-0.646	-0.547	0.298	2.167	0.181
C2-C5	0.267	-0.295	0.621	-0.684	-0.546	-0.487	0.349	1.565	0.121
C5-N9	0.335	-0.750	0.262	-0.902	-0.704	-0.633	0.435	1.620	0.112

C12-N9	0.336	-0.792	0.293	-0.826	-0.703	-0.641	0.518	1.357	0.097
C5-C8	0.309	-0.421	0.102	-0.868	-0.642	-0.531	0.305	2.106	0.209
C12-C13	0.315	-0.434	0.104	-0.902	-0.659	-0.545	0.302	2.180	0.209
C8-C11	0.313	-0.430	0.104	-0.892	-0.646	-0.543	0.298	2.172	0.190
C11-C13	0.313	-0.429	0.103	-0.894	-0.646	-0.547	0.298	2.166	0.181
H14-H17	0.012	-0.007	0.010	0.047	-0.0117	-0.0066	0.065	0.178	0.773
Ag1-N24	0.058	-0.074	0.067	0.243	-0.062	-0.057	0.362	0.172	0.088
Ag1-N29	0.058	-0.074	0.067	0.243	-0.062	-0.057	0.362	0.172	0.088
C22-N24	0.335	-0.750	0.262	-0.902	-0.704	-0.633	0.435	1.620	0.112
C27-N24	0.336	-0.792	0.293	-0.826	-0.703	-0.641	0.518	1.357	0.097
C22-C23	0.309	-0.421	0.101	-0.868	-0.642	-0.531	0.305	2.106	0.209
C27-C30	0.315	-0.434	0.104	-0.902	-0.659	-0.545	0.302	2.180	0.209
C23-C26	0.313	-0.430	0.104	-0.892	-0.646	-0.543	0.298	2.172	0.190
C26-C30	0.313	-0.429	0.103	-0.894	-0.646	-0.547	0.298	2.166	0.181
C22-C25	0.267	-0.295	0.062	-0.684	-0.546	-0.487	0.349	1.565	0.121
C25-N29	0.335	-0.750	0.262	-0.902	-0.704	-0.633	0.435	1.620	0.112
C32-N29	0.336	-0.792	0.293	-0.826	-0.703	-0.641	0.518	1.357	0.097
C25-C28	0.309	-0.421	0.102	-0.868	-0.642	-0.531	0.305	2.106	0.209
C32-C33	0.315	-0.434	0.104	-0.902	-0.659	-0.545	0.302	2.180	0.209
C28-C31	0.313	-0.430	0.104	-0.892	-0.646	-0.543	0.298	2.172	0.190
C31-C33	0.313	-0.429	0.103	-0.894	-0.646	-0.547	0.298	2.166	0.181
H34-H37	0.0123	-0.0072	0.0095	0.047	-0.0117	-0.0066	0.066	0.178	0.773

Table S3-3 Detailed topological analysis of $[Cu\text{-}bpy]^{+}$.

BCP	ρ(BCP)	V(BCP)	G(BCP)	∇2ρ(BCP)	λ1	λ2	λ3	η(r)=|λ1|/λ3	ε(r)=[λ1/λ2]-1
Cu1-N4	0.088	-0.138	0.127	0.464	-0.117	-0.112	0.693	0.169	0.045
Cu1-N9	0.088	-0.138	0.127	0.464	-0.117	-0.112	0.693	0.169	0.045
C2-N4	0.328	-0.727	0.255	-0.873	-0.683	-0.610	0.420	1.626	0.120
C7-N4	0.331	-0.794	0.301	-0.766	-0.687	-0.630	0.551	1.247	0.090
C2-C3	0.311	-0.428	0.104	-0.880	-0.647	-0.533	0.300	2.153	0.214
C7-C10	0.316	-0.437	0.105	-0.911	-0.662	-0.549	0.300	2.207	0.206

C3-C6	0.312	-0.428	0.103	-0.891	-0.644	-0.545	0.299	2.157	0.182
C6-C10	0.314	-0.432	0.103	-0.902	-0.648	-0.551	0.298	2.179	0.176
C2-C5	0.264	-0.288	0.610	-0.664	-0.535	-0.476	0.347	1.543	0.124
C5-N9	0.328	-0.727	0.255	-0.873	-0.683	-0.610	0.420	1.626	0.120
C12-N9	0.331	-0.794	0.301	-0.766	-0.687	-0.630	0.551	1.247	0.090
C5-C8	0.311	-0.428	0.104	-0.880	-0.647	-0.533	0.300	2.153	0.214
C12-C13	0.316	-0.437	0.105	-0.911	-0.662	-0.549	0.300	2.207	0.206
C8-C11	0.312	-0.428	0.103	-0.891	-0.644	-0.545	0.299	2.157	0.182
C11-C13	0.314	-0.432	0.103	-0.902	-0.648	-0.551	0.298	2.179	0.176
H14-H17	0.128	-0.742	0.974	0.483	-0.013	-0.008	0.070	0.190	0.625

Table S3-4 Detailed topological analysis of $[Cu\text{-}bpy_2]^+$.

BCP	ρ(BCP)	V(BCP)	G(BCP)	∇2ρ(BCP)	λ1	λ2	λ3	η(r)=|λ1|/λ3	ε(r)=[λ1/λ2]-1
Cu1-N4	0.076	-0.115	0.110	0.416	-0.096	-0.088	0.599	0.160	0.091
Cu1-N9	0.076	-0.115	0.110	0.416	-0.096	-0.088	0.599	0.160	0.091
C2-N4	0.332	-0.736	0.256	-0.898	-0.696	-0.624	0.421	1.652	0.115
C7-N4	0.334	-0.789	0.292	-0.816	-0.699	-0.637	0.520	1.345	0.097
C2-C3	0.310	-0.423	0.102	-0.874	-0.644	-0.533	0.303	2.127	0.208
C7-C10	0.315	-0.435	0.104	-0.905	-0.660	-0.545	0.301	2.192	0.211
C3-C6	0.313	-0.430	0.104	-0.890	-0.646	-0.542	0.297	2.171	0.192
C6-C10	0.312	-0.428	0.102	-0.891	-0.644	-0.546	0.298	2.158	0.179
C2-C5	0.270	-0.302	0.064	-0.697	-0.554	-0.490	0.347	1.596	0.131
C5-N9	0.332	-0.736	0.256	-0.898	-0.696	-0.624	0.421	1.652	0.115
C12-N9	0.334	-0.789	0.292	-0.816	-0.699	-0.637	0.520	1.345	0.097
C5-C8	0.310	-0.423	0.102	-0.874	-0.644	-0.533	0.303	2.127	0.208
C12-C13	0.315	-0.435	0.104	-0.905	-0.660	-0.545	0.301	2.192	0.211
C8-C11	0.313	-0.430	0.104	-0.890	-0.646	-0.542	0.297	2.171	0.192
C11-C13	0.312	-0.428	0.102	-0.891	-0.644	-0.546	0.298	2.158	0.179
H14-H17	0.012	-0.0067	0.0088	0.044	-0.0114	-0.0064	0.062	0.185	0.781
Cu1-N24	0.076	-0.115	0.110	0.416	-0.096	-0.088	0.599	0.160	0.091
Cu1-N29	0.076	-0.115	0.110	0.416	-0.096	-0.088	0.599	0.160	0.091

C22-N24	0.331	-0.736	0.256	-0.898	-0.696	-0.624	0.421	1.652	0.115
C27-N24	0.334	-0.789	0.292	-0.816	-0.699	-0.637	0.520	1.345	0.097
C22-C23	0.310	-0.423	0.102	-0.874	-0.644	-0.533	0.303	2.127	0.208
C27-C30	0.315	-0.435	0.104	-0.905	-0.660	-0.545	0.301	2.192	0.211
C23-C26	0.313	-0.430	0.104	-0.890	-0.646	-0.542	0.297	2.171	0.192
C26-C30	0.312	-0.428	0.102	-0.891	-0.644	-0.546	0.298	2.158	0.179
C22-C25	0.270	-0.302	0.064	-0.697	-0.554	-0.490	0.347	1.596	0.131
C25-N29	0.332	-0.736	0.256	-0.898	-0.696	-0.624	0.421	1.652	0.115
C32-N29	0.334	-0.789	0.292	-0.816	-0.699	-0.637	0.520	1.345	0.097
C25-C28	0.310	-0.423	0.102	-0.874	-0.644	-0.533	0.303	2.127	0.208
C32-C33	0.315	-0.435	0.104	-0.905	-0.660	-0.545	0.301	2.192	0.211
C28-C31	0.313	-0.430	0.104	-0.890	-0.646	-0.542	0.297	2.171	0.192
C31-C33	0.312	-0.428	0.102	-0.891	-0.644	-0.546	0.298	2.158	0.179
H34-H37	0.0116	-0.0067	0.0088	0.044	-0.0114	-0.0064	0.0618	0.185	0.781