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Supporting Information

Gas-phase Synthesis of Ag-centred Phenylenediamine Clusters

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S1. Mass spectrometry observation

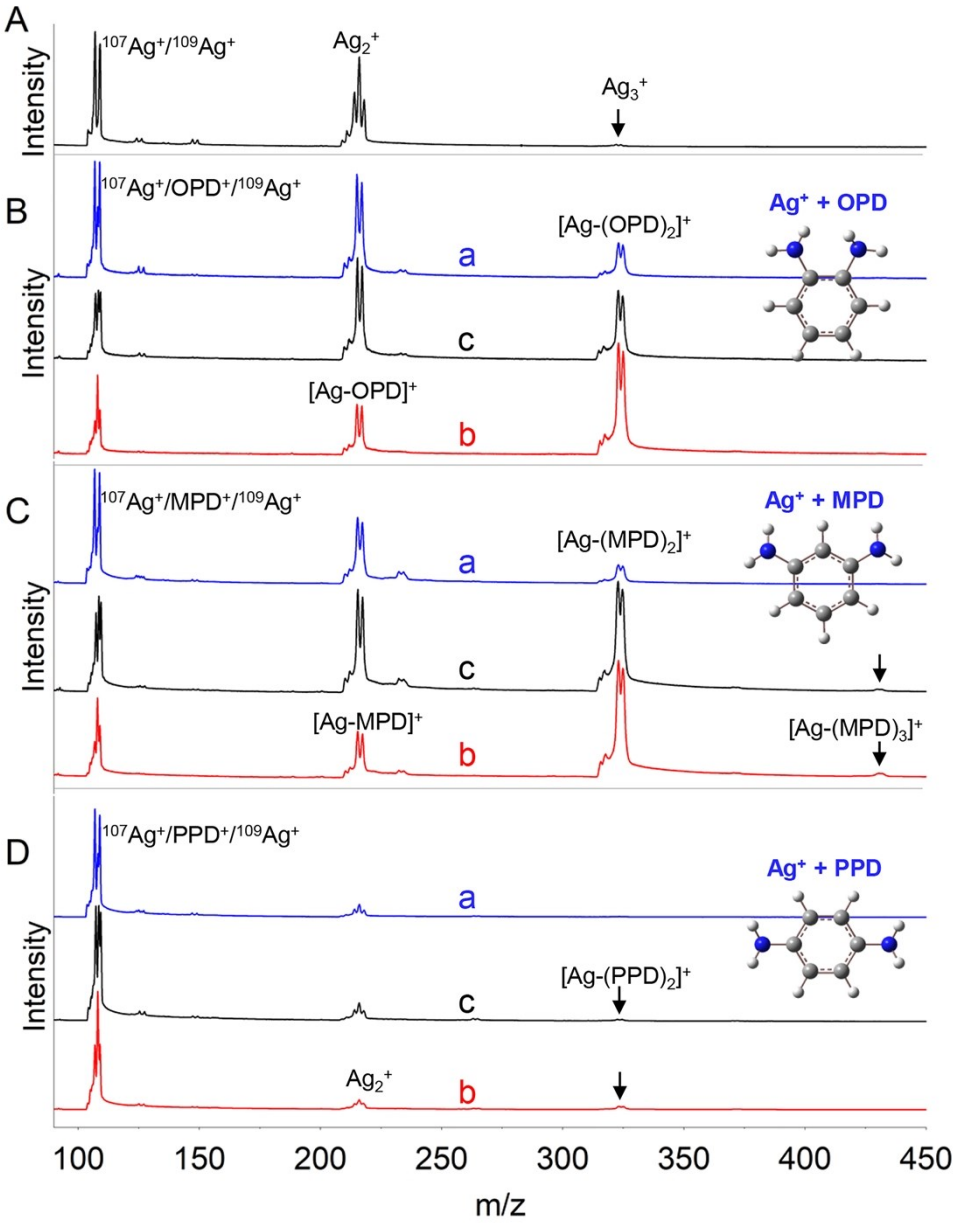


Fig. S1 Mass spectra of (A) $Ag_{1\text{-}3}^+$, (B) $[Ag\text{-}(OPD)_{1\text{-}2}]^+$, (C) $[Ag\text{-}(MPD)_{1\text{-}3}]^+$ and (D) $[Ag\text{-}(PPD)_2]^+$. (a-c-b) Small to large amounts of PD vapors were introduced into the compact reaction tube. Mass spectra (a) and (b) are the same as that in Fig. 1.

Table S1 The intensity ratios of $[Ag\text{-}(PD)_n]^+$ to the corresponding PD in Fig. S1.

line	n	$[Ag\text{-}(OPD)_n^+]$/OPD	$[Ag\text{-}(MPD)_n^+]$/MPD	$[Ag\text{-}(PPD)_n^+]$/PPD
Curve a	1	1.468	1.183	0.000
(blue)	2	0.486	0.328	0.004
	3	0.000	0.000	0.000
Curve c	1	1.464	1.081	0.000
(black)	2	0.985	1.158	0.009
	3	0.000	0.019	0.000
Curve b	1	0.629	0.570	0.000
(red)	2	1.403	1.480	0.025
	3	0.003	0.042	0.000

line	Ag^+/OPD	Ag^+/MPD	Ag^+/PPD
a-blue	1.653	2.074	1.689
c-black	0.973	0.938	0.989
b-red	0.558	0.645	0.537

S2. DFT-calculated Energetics

$Ag^+ + OPD \rightarrow Ag + OPD^+$	ΔE= -1.042 eV	(S1)
$Ag^+ + MPD \rightarrow Ag + MPD^+$	ΔE= -1.087 eV	(S2)
$Ag^+ + PPD \rightarrow Ag + PPD^+$	ΔE= -1.553 eV	(S3)
$Ar^+ + OPD \rightarrow Ar + OPD^+$	ΔE= -8.770 eV	(S4)
$Ar^+ + MPD \rightarrow Ar + MPD^+$	ΔE= -8.815 eV	(S5)
$Ar^+ + PPD \rightarrow Ar + PPD^+$	ΔE= -9.281 eV	(S6)
$Ag^+ + OPD \rightarrow [Ag\text{-}OPD]^+$	ΔE= -2.905 eV	(S6)
$Ag^+ + 2\ OPD \rightarrow [Ag\text{-}(OPD)_2]^+$	ΔE= -4.933 eV	(S7)
$Ag^+ + 3\ OPD \rightarrow [Ag\text{-}(OPD)_3]^+$	ΔE= -6.273 eV	(S8)
$Ag_2^+ + OPD \rightarrow [Ag\text{-}OPD]^+ + Ag$	ΔE= -1.119 eV	(S9)
$Ag_2^+ + 2\ OPD \rightarrow [Ag\text{-}(OPD)_2]^+ + Ag$	ΔE= -3.147 eV	(S10)
$Ag_2^+ + 3\ OPD \rightarrow [Ag\text{-}(OPD)_3]^+ + Ag$	ΔE= -4.487 eV	(S11)
$Ag_3^+ + OPD \rightarrow [Ag\text{-}OPD]^+ + Ag_2$	ΔE= 0.023 eV	(S12)
$Ag_3^+ + 2\ OPD \rightarrow [Ag\text{-}(OPD)_2]^+ + Ag_2$	ΔE= -2.005eV	(S13)
$Ag_3^+ + 3\ OPD \rightarrow [Ag\text{-}(OPD)_3]^+ + Ag_2$	ΔE= -3.345 eV	(S14)
$Ag^+ + MPD \rightarrow [Ag\text{-}MPD]^+$	ΔE= -2.798 eV	(S15)
$Ag^+ + 2\ MPD \rightarrow [Ag\text{-}(MPD)_2]^+$	ΔE= -4.973 eV	(S16)
$Ag^+ + 3\ MPD \rightarrow [Ag\text{-}(MPD)_3]^+$	ΔE= -6.365 eV	(S17)
$Ag_2^+ + MPD \rightarrow [Ag\text{-}MPD]^+ + Ag$	ΔE= -1.012 eV	(S18)
$Ag_2^+ + 2\ MPD \rightarrow [Ag\text{-}(MPD)_2]^+ + Ag$	ΔE= -3.187 eV	(S19)
$Ag_2^+ + 3\ MPD \rightarrow [Ag\text{-}(MPD)_3]^+ + Ag$	ΔE= -4.579 eV	(S20)
$Ag_3^+ + MPD \rightarrow [Ag\text{-}MPD]^+ + Ag_2$	ΔE= 0.130 eV	(S21)
$Ag_3^+ + 2\ MPD \rightarrow [Ag\text{-}(MPD)_2]^+ + Ag_2$	ΔE= -2.045 eV	(S22)
$Ag_3^+ + 3\ MPD \rightarrow [Ag\text{-}(MPD)_3]^+ + Ag_2$	ΔE= -3.437 eV	(S23)
$Ag^+ + PPD \rightarrow [Ag\text{-}PPD]^+$	ΔE= -2.570 eV	(S24)
$Ag^+ + 2\ PPD \rightarrow [Ag\text{-}(PPD)_2]^+$	ΔE= -4.895 eV	(S25)
$Ag^+ + 3\ PPD \rightarrow [Ag\text{-}(PPD)_3]^+$	ΔE= -6.331 eV	(S26)
$Ag_2^+ + PPD \rightarrow [Ag\text{-}PPD]^+ + Ag$	ΔE= -0.785 eV	(S27)
$Ag_2^+ + 2\ PPD \rightarrow [Ag\text{-}(PPD)_2]^+ + Ag$	ΔE= -3.109 eV	(S28)
$Ag_2^+ + 3\ PPD \rightarrow [Ag\text{-}(PPD)_3]^+ + Ag$	ΔE= -4.545 eV	(S29)
$Ag_3^+ + PPD \rightarrow [Ag\text{-}PPD]^+ + Ag_2$	ΔE= 0.358eV	(S30)
$Ag_3^+ + 2\ PPD \rightarrow [Ag\text{-}(PPD)_2]^+ + Ag_2$	ΔE= -1.967 eV	(S31)
$Ag_3^+ + 3\ PPD \rightarrow [Ag\text{-}(PPD)_3]^+ + Ag_2$	ΔE= -3.403 eV	(S32)

S3. Electrostatic potentials (ESP)

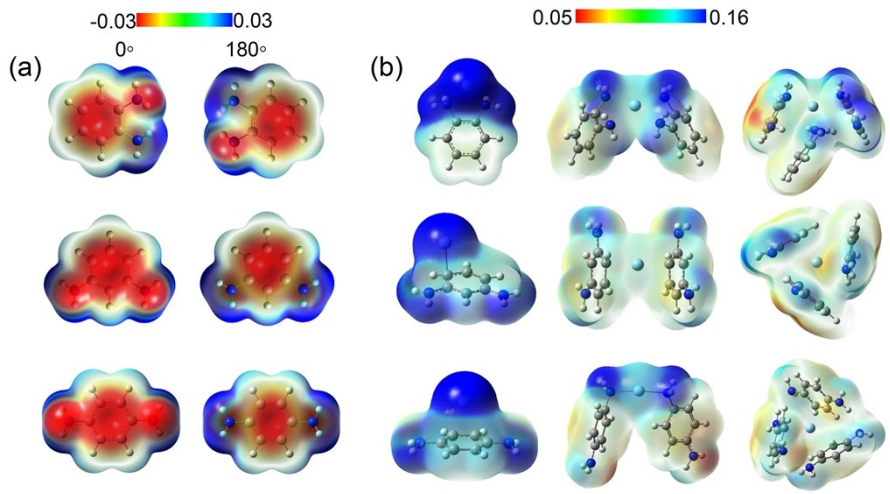


Fig. S2 Electrostatic potentials (ESP) on van der Waals surface. **(a)** ESP patterns of neutral PDs, where positive and negative parts are represented by blue and red with maxima and minima corresponding to 0.03 au and -0.03 au. 180◦ and 0◦ mean molecules flip 180◦ vertically and before flip, respectively. **(b)** ESP patterns of $[Ag\text{-}(PD)_n]^+$ (n=1-3) with minima and maxima corresponding to 0.05 au and 0.16 au.

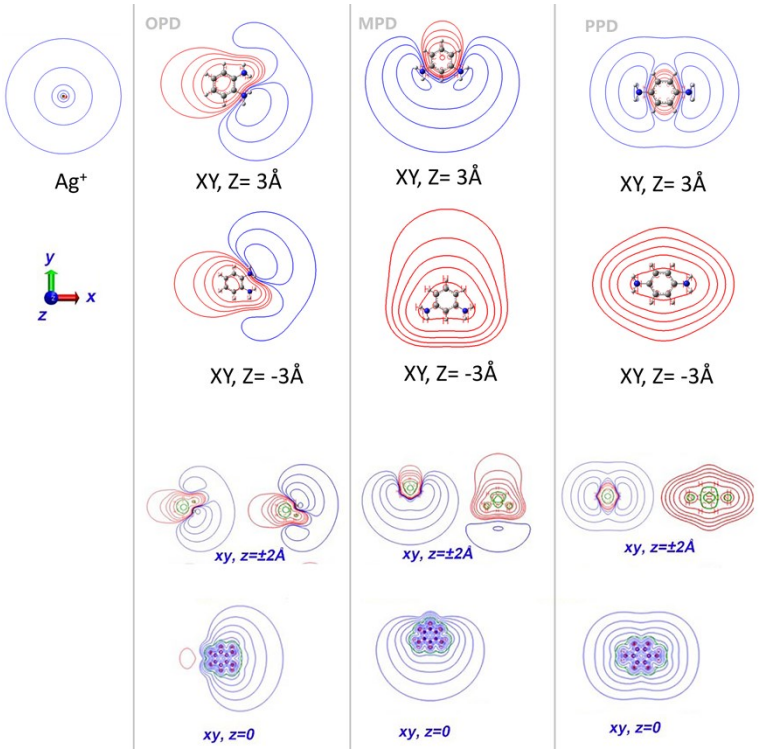


Fig. S3 ESP maps of neutral OPD, MPD and PPD on different coordinate plane. Positive and negative parts are represented by blue and red lines, respectively.

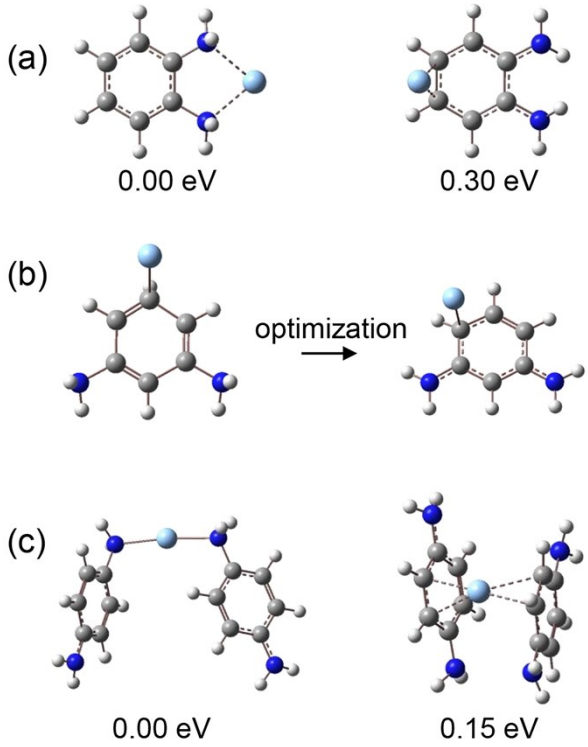


Fig. S4 The typical structures of (a) $[Ag\text{-}OPD]^+$, (b) $[Ag\text{-}MPD]^+$ and (c) $[Ag\text{-}(PPD)_2]^+$

S4. Topological analysis

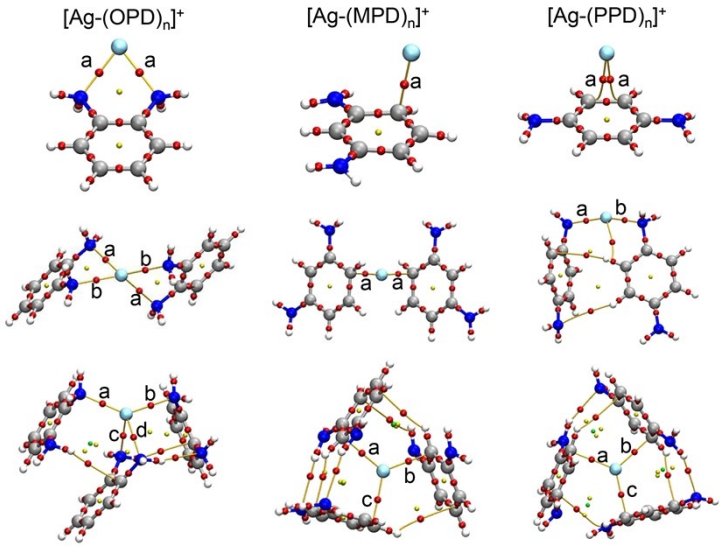


Fig. S5 Topological analysis within the theory of atoms in molecules (AIM), the bond critical points (BCPs) are indicated by red dots.

S5. NBO analysis

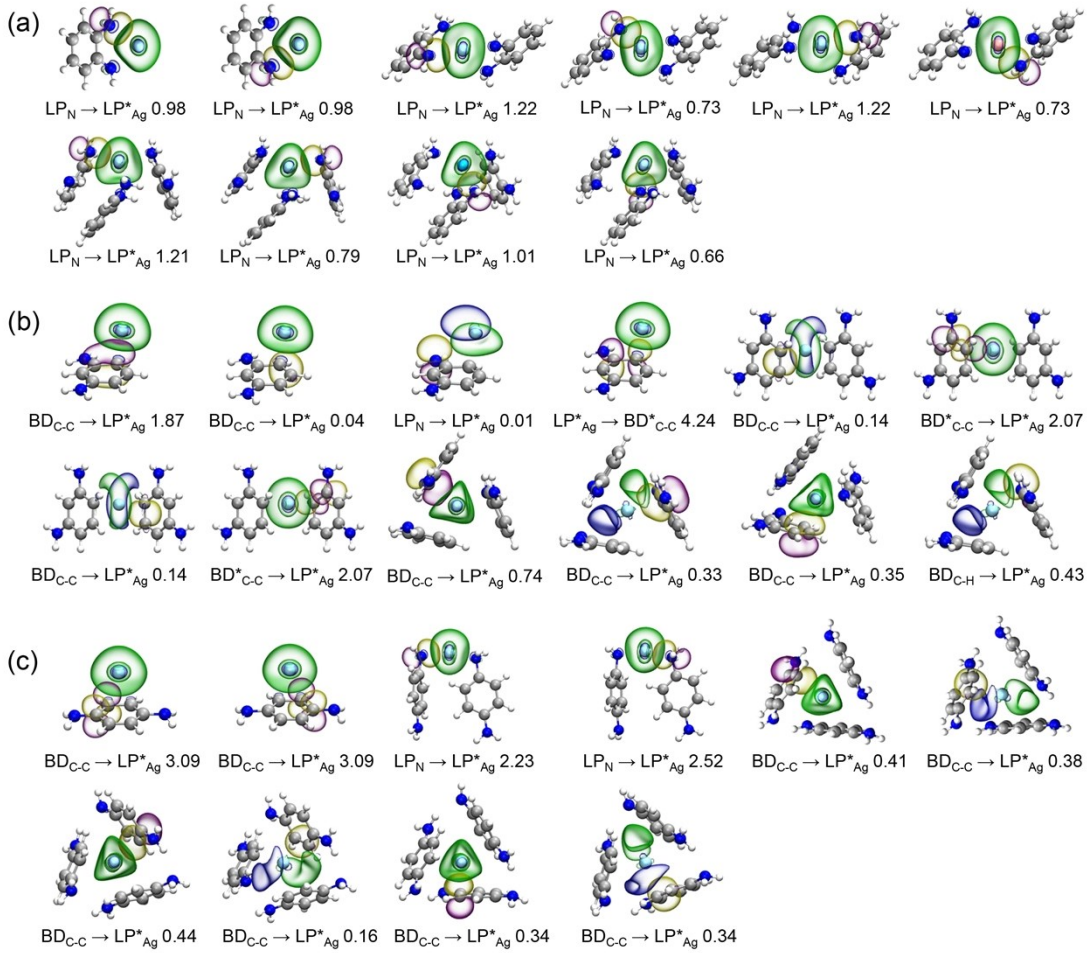


Fig. S6 Details of the NBO analysis for (a) $[Ag\text{-}(OPD)_n]^+$ (b) $[Ag\text{-}(MPD)_n]^+$ (c) $[Ag\text{-}(PPD)_n]^+$ (n=1-3). Donor-accepter charge-transfer interaction energies are in eV.

S6. Energy decomposition analysis

We have conducted detailed energy decomposition analysis (EDA) for all the $[Ag\text{-}(PD)_n]^+$ systems, as shown below. All the energies are given in kJ/mol.

Table S2 Energy decomposition analysis of Ag^+-OPD.

Frag.	Atom	Elec.	Rep.	Disp.	Total
Ag^+	$1Ag^+$	-85.05	31.64	-7.64	-61.04
OPD	2N	-247.41	15.19	-3.15	-235.37
	3C	65.44	0.61	-0.53	65.52
	4C	-46.78	0.01	-0.07	-46.84
	5C	65.44	0.61	-0.53	65.52
	6C	-23.46	0.00	-0.02	-23.47
	7C	-23.46	0.00	-0.02	-23.47
	8C	-46.78	0.01	-0.07	-46.84
	9N	-247.41	15.19	-3.15	-235.37
	10H	84.08	0.00	-0.02	84.07
	11H	84.67	0.00	-0.02	84.65
	12H	24.89	0.00	-0.01	24.88
	13H	16.04	0.00	-0.00	16.04
	14H	16.04	0.00	-0.00	16.04
	15H	24.89	0.00	-0.01	24.88
	16H	84.67	0.00	-0.02	84.65
	17H	84.08	0.00	-0.02	84.07
Ag^+-OPD		-170.09	63.29	-15.28	-122.08

Table S3 Energy decomposition analysis of Ag^+-$(OPD)_2$.

Frag	Atom	Elec	Rep	Disp	Total
OPD1	1N	-212.27	7.59	-3.25	-207.92
	2C	59.13	0.48	-0.82	58.80
	3C	-43.32	0.01	-0.21	-43.51
	4C	60.92	0.58	-0.80	60.70
	5C	-22.35	0.00	-0.09	-22.43
	6C	-22.64	0.00	-0.08	-22.72
	7C	-44.94	0.01	-0.17	-45.10
	8N	-231.82	14.45	-3.70	-221.07
	9H	78.60	0.00	-0.03	78.57
	10H	68.26	0.00	-0.04	68.22
	11H	22.85	0.00	-0.03	22.82
	12H	15.39	0.00	-0.01	15.38
	13H	15.67	0.00	-0.01	15.67
	14H	24.25	0.00	-0.02	24.23
	15H	79.79	0.00	-0.03	79.76
	16H	80.23	0.00	-0.03	80.21

OPD2	17N	-212.27	7.59	-3.25	-207.92
	18C	59.13	0.48	-0.82	58.80
	19C	-43.32	0.01	-0.21	-43.51
	20C	60.92	0.58	-0.80	60.70
	21C	-22.35	0.00	-0.09	-22.43
	22C	-22.64	0.00	-0.08	-22.72
	23C	-44.94	0.01	-0.17	-45.10
	24N	-231.82	14.45	-3.70	-221.07
	25H	78.60	0.00	-0.03	78.57
	26H	68.26	0.00	-0.04	68.22
	27H	22.85	0.00	-0.03	22.82
	28H	15.39	0.00	-0.01	15.38
	29H	15.67	0.00	-0.01	15.67
	30H	24.25	0.00	-0.02	24.23
	31H	79.79	0.00	-0.03	79.76
	32H	80.23	0.00	-0.03	80.21
Ag^+	$33Ag^+$	-157.38	45.67	-12.98	-124.69
OPD1--OPD2		12.92	0.61	-5.63	7.90
OPD1--Ag^+		-157.38	45.67	-12.98	-124.69
OPD2--Ag^+		-157.38	45.67	-12.98	-124.69

Table S4 Energy decomposition analysis of Ag^+-$(OPD)_3$.

Frag	Atom	Elec	Rep	Disp	Total
Ag^+	$1Ag^+$	-170.42	48.90	-14.24	-135.76
OPD1	2N	-206.60	14.19	-7.84	-200.25
	3C	58.06	1.22	-2.95	56.33
	4C	-45.46	0.23	-1.12	-46.34
	5C	54.00	2.30	-4.39	51.91
	6C	-23.48	0.17	-0.85	-24.16
	7C	-22.68	0.40	-1.39	-23.67
	8C	-40.48	1.77	-3.15	-41.85
	9N	-179.99	11.89	-11.54	-179.64
	10H	65.09	0.79	-0.80	65.09
	11H	69.91	0.00	-0.07	69.84
	12H	24.37	0.00	-0.10	24.27
	13H	16.34	0.00	-0.07	16.27
	14H	15.78	0.01	-0.15	15.64
	15H	20.10	0.27	-0.71	19.66
	16H	57.68	0.18	-0.64	57.21
	17H	58.01	0.02	-0.31	57.72
	18N	-216.65	20.42	-5.80	-202.04
	19C	55.51	1.74	-2.75	54.50
	20C	-47.80	0.32	-1.34	-48.81

OPD2	21C	43.39	2.09	-3.40	42.08
	22C	-23.56	0.09	-0.75	-24.23
	23C	-21.43	0.16	-0.92	-22.19
	24C	-35.65	1.14	-2.26	-36.77
	25N	-116.22	2.39	-4.71	-118.55
	26H	77.23	0.00	-0.05	77.19
	27H	71.46	0.00	-0.06	71.40
	28H	28.00	0.01	-0.19	27.82
	29H	16.85	0.00	-0.07	16.78
	30H	14.93	0.00	-0.09	14.84
	31H	17.74	0.14	-0.46	17.42
	32H	53.87	0.09	-0.43	53.52
	33H	38.85	0.01	-0.12	38.74
OPD3	34N	-223.54	10.93	-4.90	-217.51
	35C	62.98	1.79	-2.66	62.11
	36C	-52.50	0.53	-1.47	-53.45
	37C	56.81	1.38	-2.51	55.68
	38C	-26.56	0.20	-0.87	-27.24
	39C	-25.50	0.18	-0.82	-26.14
	40C	-46.46	0.42	-1.31	-47.35
	41N	-168.16	3.98	-4.14	-168.33
	42H	79.43	0.00	-0.04	79.39
	43H	77.81	0.00	-0.06	77.76
	44H	29.37	0.02	-0.20	29.18
	45H	18.41	0.00	-0.08	18.33
	46H	17.26	0.00	-0.07	17.19
	47H	23.49	0.01	-0.14	23.36
	48H	60.73	0.00	-0.04	60.69
	49H	58.85	0.00	-0.05	58.81
Ag^+--OPD1		-142.46	34.55	-11.40	-119.31
Ag^+--OPD2		-88.94	41.55	-9.70	-57.10
Ag^+--OPD3		-109.43	21.70	-7.38	-95.10
OPD1--OPD2		-4.26	15.45	-33.26	-22.08
OPD1—OPD3		-11.99	16.94	-27.51	-22.56
OPD2—OPD3		6.23	0.23	-3.83	2.63

Table S5 Energy decomposition analysis of Ag^+-MPD.

Frag	Atom	Elec	Rep	Disp	Total
MPD	1N	-94.83	0.00	-0.03	-94.86
	2C	58.09	0.03	-0.11	58.00
	3C	-60.76	0.08	-0.20	-60.87
	4C	-81.28	0.07	-0.17	-81.39
	5C	-26.36	1.84	-0.93	-25.44
	6C	-99.01	26.19	-3.49	-76.31
	7C	78.78	1.04	-0.70	79.12
	8N	-136.85	0.10	-0.26	-137.00
	9H	35.70	0.00	-0.00	35.70
	10H	38.08	0.00	-0.00	38.08
	11H	26.56	0.00	-0.01	26.55
	12H	34.75	0.00	-0.01	34.74
	13H	29.12	0.03	-0.08	29.07
	14H	44.67	0.28	-0.23	44.72
	15H	46.17	0.00	-0.00	46.17
	16H	58.36	0.00	-0.00	58.36
Ag^+	$17Ag^+$	-48.81	29.67	-6.22	-25.36
MPD—Ag^+		-97.61	59.34	-12.45	-50.72

Table S6 Energy decomposition analysis of Ag^+-$(MPD)_2$.

Frag	Atom	Elec	Rep	Disp	Total
MPD1	1N	-94.80	0.00	-0.13	-94.93
	2C	57.98	0.05	-0.31	57.72
	3C	-60.46	0.18	-0.56	-60.84
	4C	-80.26	0.10	-0.39	-80.54
	5C	-25.71	3.09	-1.70	-24.32
	6C	-92.05	22.37	-3.79	-73.47
	7C	75.68	1.21	-1.04	75.85
	8N	-129.27	0.10	-0.49	-129.66
	9H	35.42	0.00	-0.00	35.42
	10H	37.79	0.00	-0.00	37.79
	11H	26.39	0.00	-0.05	26.34
	12H	34.32	0.00	-0.03	34.30
	13H	27.61	0.05	-0.20	27.46
	14H	41.08	0.24	-0.31	41.01
	15H	44.01	0.00	-0.00	44.01
	16H	53.46	0.00	-0.01	53.45
	17N	-94.80	0.00	-0.13	-94.93
	18C	57.98	0.05	-0.31	57.72
	19C	-60.46	0.18	-0.56	-60.84

MPD2	20C	-80.26	0.10	-0.39	-80.54
	21C	-25.71	3.09	-1.70	-24.32
	22C	-92.05	22.37	-3.79	-73.47
	23C	75.68	1.21	-1.04	75.85
	24N	-129.27	0.10	-0.49	-129.66
	25H	35.42	0.00	-0.00	35.42
	26H	37.79	0.00	-0.00	37.79
	27H	26.39	0.00	-0.05	26.34
	28H	34.32	0.00	-0.03	34.30
	29H	27.61	0.05	-0.20	27.46
	30H	41.08	0.24	-0.31	41.01
	31H	44.01	0.00	-0.00	44.01
	32H	53.46	0.00	-0.01	53.45
Ag^+	$33Ag^+$	-102.71	54.43	-12.82	-61.10
MPD1-- MPD2		5.13	0.36	-5.23	0.27
MPD1--Ag^+		-102.71	54.43	-12.82	-61.10
MPD2--Ag^+		-102.71	54.43	-12.82	-61.10

Table S7 Energy decomposition analysis of Ag^+-$(MPD)_3$.

Frag	Atom	Elec	Rep	Disp	Total
Ag^+	$1Ag^+$	-138.99	49.21	-16.71	-106.49
MPD1	2N	-123.52	0.43	-2.07	-125.16
	3C	72.27	1.79	-2.39	71.66
	4C	-57.37	0.48	-1.39	-58.28
	5C	-110.26	14.71	-5.33	-100.88
	6C	-18.18	0.54	-1.29	-18.93
	7C	-58.47	0.38	-1.36	-59.46
	8C	72.85	1.91	-2.54	72.21
	9N	-126.47	0.73	-2.64	-128.38
	10H	47.03	0.00	-0.08	46.96
	11H	45.03	0.00	-0.02	45.01
	12H	25.32	0.01	-0.14	25.19
	13H	46.96	1.22	-1.56	46.62
	14H	18.79	0.01	-0.13	18.67
	15H	26.03	0.01	-0.14	25.89
	16H	48.14	0.01	-0.12	48.03
	17H	46.26	0.00	-0.03	46.24
	18N	-117.41	1.91	-3.90	-119.40
	19C	70.77	2.06	-3.11	69.72
	20C	-58.34	0.60	-1.79	-59.53
	21C	-106.61	15.87	-6.74	-97.48
	22C	-18.81	0.84	-1.71	-19.68

MPD2	23C	-58.75	0.76	-2.02	-60.01
	24C	69.71	2.04	-3.23	68.52
	25N	-113.06	1.82	-3.81	-115.04
	26H	41.28	0.15	-0.39	41.05
	27H	44.05	0.00	-0.04	44.01
	28H	26.14	0.02	-0.20	25.96
	29H	44.04	4.58	-2.86	45.75
	30H	19.84	0.02	-0.17	19.69
	31H	26.39	0.04	-0.25	26.17
	32H	41.74	0.21	-0.45	41.50
	33H	44.68	0.00	-0.05	44.63
MPD3	34N	-116.43	1.47	-2.67	-117.63
	35C	66.39	1.76	-2.75	65.40
	36C	-70.64	2.24	-3.01	-71.41
	37C	-83.05	3.70	-2.89	-82.24
	38C	-26.54	9.87	-4.78	-21.46
	39C	-73.96	2.94	-3.28	-74.29
	40C	67.87	1.56	-2.72	66.71
	41N	-119.73	1.52	-2.75	-120.95
	42H	41.40	0.00	-0.03	41.37
	43H	45.42	0.00	-0.03	45.39
	44H	31.29	0.05	-0.40	30.94
	45H	36.08	0.11	-0.33	35.86
	46H	27.31	0.77	-1.27	26.81
	47H	33.01	0.08	-0.49	32.60
	48H	41.93	0.00	-0.03	41.90
	49H	46.93	0.00	-0.03	46.90
Ag^+--MPD1		-98.13	35.53	-11.52	-74.11
Ag^+--MPD2		-79.99	35.05	-11.31	-56.25
Ag^+--MPD3		-99.87	27.85	-10.59	-82.61
MPD1--MPD2		1.87	5.70	-18.36	-10.78
MPD1--MPD3		5.03	3.24	-12.56	-4.29
MPD2--MPD3		-10.58	21.06	-31.77	-21.29

Table S8 Energy decomposition analysis of Ag^+-PPD.

Frag	Atom	Elec	Rep	Disp	Total
Ag^+	$1Ag^+$	-54.26	27.20	-7.14	-34.19
PPD	2C	75.84	0.72	-0.58	75.98
	3C	-57.01	0.14	-0.25	-57.12
	4C	-83.17	12.60	-2.42	-72.99
	5N	-128.57	0.04	-0.15	-128.68
	6C	-57.18	0.14	-0.25	-57.30
	7C	76.36	0.72	-0.58	76.50
	8C	-83.42	12.60	-2.42	-73.25
	9N	-128.42	0.04	-0.15	-128.54
	10H	29.01	0.00	-0.01	29.00
	11H	44.29	0.12	-0.15	44.26
	12H	43.96	0.00	-0.00	43.96
	13H	48.53	0.00	-0.00	48.53
	14H	28.98	0.00	-0.01	28.97
	15H	44.25	0.12	-0.15	44.22
	16H	43.86	0.00	-0.00	43.86
	17H	48.43	0.00	-0.00	48.43
Ag^+-PPD		-108.51	54.40	-14.27	-68.38

Table S9 Energy decomposition analysis of Ag^+-$(PPD)_2$.

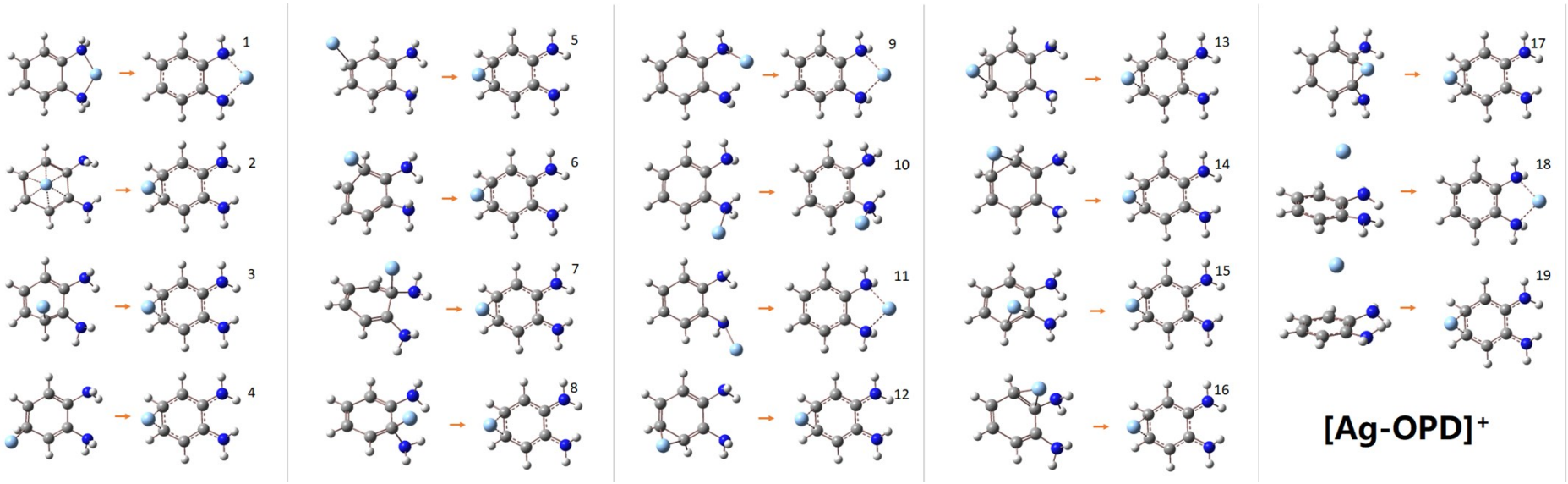
Frag	Atom	Elec	Rep	Disp	Total
PPD1	1C	44.94	0.57	-1.30	44.21
	2C	-42.77	0.45	-1.11	-43.43
	3C	-41.32	0.38	-1.19	-42.14
	4N	-81.36	0.34	-1.05	-82.07
	5C	-55.13	0.77	-1.33	-55.69
	6C	78.04	1.96	-1.96	78.04
	7C	-53.42	0.44	-1.27	-54.25
	8N	-220.15	35.44	-5.64	-190.34
	9H	23.43	0.01	-0.10	23.33
	10H	22.54	0.01	-0.14	22.41
	11H	30.68	0.00	-0.01	30.67
	12H	30.61	0.00	-0.01	30.60
	13H	33.60	0.02	-0.14	33.48
	14H	32.45	0.01	-0.15	32.32
	15H	72.48	0.00	-0.03	72.45
	16H	71.94	0.00	-0.03	71.90
PPD2	17C	69.05	0.79	-1.25	68.59
	18C	-42.48	0.02	-0.27	-42.73
	19C	-53.26	1.23	-2.71	-54.75
	20N	-215.81	38.33	-5.81	-183.29
	21C	-33.88	0.00	-0.18	-34.05
	22C	37.27	0.03	-0.41	36.88
	23C	-36.55	0.54	-1.76	-37.78
	24N	-66.16	0.01	-0.28	-66.43
	25H	25.14	0.00	-0.03	25.11
	26H	38.48	1.50	-1.82	38.15
	27H	71.96	0.00	-0.04	71.92
	28H	72.05	0.00	-0.04	72.02
	29H	18.46	0.00	-0.01	18.45
	30H	18.92	0.51	-0.92	18.50
	31H	25.52	0.00	-0.00	25.51
	32H	25.94	0.00	-0.01	25.92
Ag^+	$33Ag^+$	-101.34	76.56	-12.77	-37.56
PPD1-- PPD2		2.55	6.79	-18.26	-8.92
PPD1-- Ag^+		-109.40	73.99	-12.68	-48.09
PPD2-- Ag^+		-93.28	79.12	-12.87	-27.03

Table S10 Energy decomposition analysis of Ag^+-$(PPD)_3$.

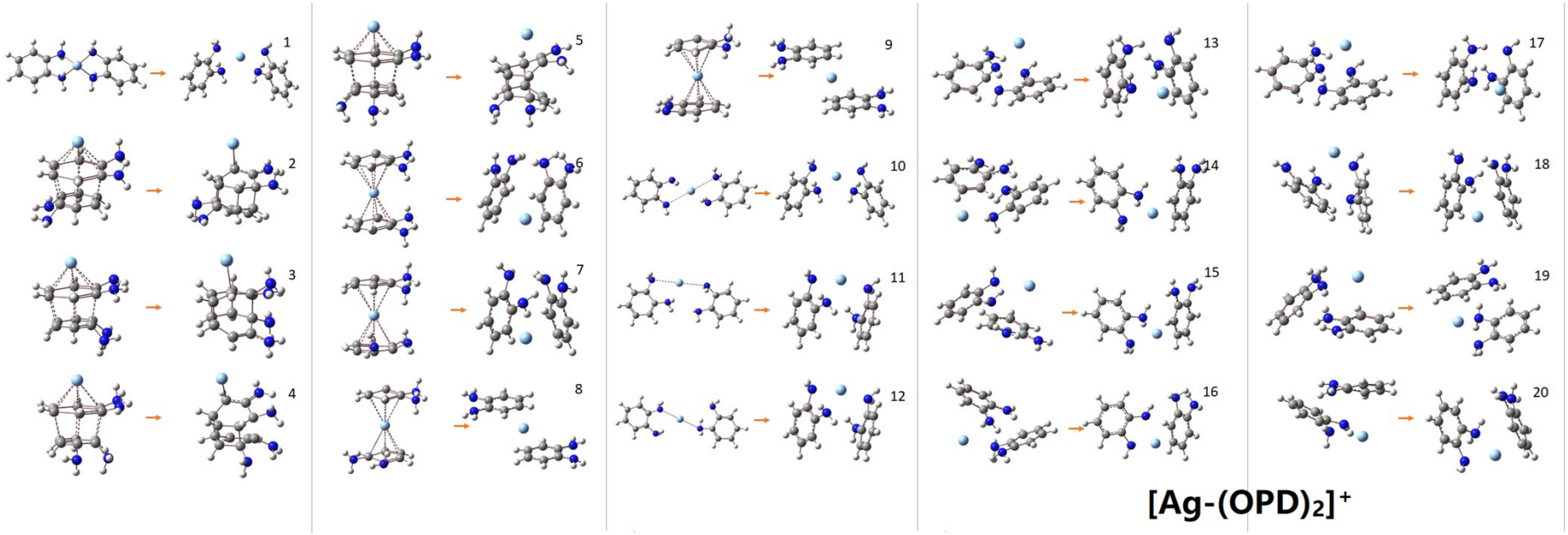
Frag	Atom	Elec	Rep	Disp	Total
Ag^+	$1Ag^+$	-138.68	46.35	-16.19	-108.52
PPD1	2C	61.7	2.04	-2.90	60.89
	3C	-49.87	1.23	-1.81	-50.45
	4C	-61.74	2.82	-3.57	-62.48
	5N	-114.90	3.35	-3.70	-115.24
	6C	-51.89	0.39	-1.39	-52.89
	7C	69.83	1.85	-2.84	68.84
	8C	-69.82	12.10	-5.70	-63.42
	9N	-118.98	3.64	-4.50	-119.85
	10H	26.39	0.03	-0.18	26.24
	11H	33.06	0.12	-0.56	32.62
	12H	40.10	0.00	-0.03	40.07
	13H	41.55	0.00	-0.05	41.50
	14H	27.35	0.01	-0.12	27.23
	15H	36.10	2.14	-2.07	36.17
	16H	41.31	0.00	-0.04	41.28
	17H	38.98	0.46	-0.59	38.85
PPD2	18C	64.49	1.99	-2.87	63.60
	19C	-50.58	1.26	-1.83	-51.16
	20C	-65.50	3.84	-3.61	-65.27
	21N	-120.48	3.42	-3.74	-120.80
	22C	-51.09	0.35	-1.34	-52.08
	23C	67.89	1.20	-2.34	66.75
	24C	-70.27	11.05	-5.09	-64.31
	25N	-116.13	0.85	-2.69	-117.97
	26H	26.73	0.03	-0.19	26.57
	27H	35.59	0.12	-0.53	35.18
	28H	41.61	0.00	-0.03	41.58
	29H	43.81	0.00	-0.05	43.76
	30H	26.65	0.01	-0.12	26.53
	31H	36.29	1.25	-1.61	35.93
	32H	40.15	0.00	-0.03	40.13
	33H	43.71	0.01	-0.13	43.60
	34C	63.73	1.07	-1.97	62.83
	35C	-49.85	0.69	-1.77	-50.93
	36C	-66.21	4.03	-3.18	-65.36
	37N	-113.34	0.41	-1.31	-114.24
	38C	-49.62	0.64	-1.84	-50.82
	39C	66.04	1.62	-2.95	64.72
	40C	-69.96	13.29	-5.79	-62.47
	41N	-109.33	3.69	-4.69	-110.33

PPD3	42H	26.75	0.02	-0.21	26.57
	43H	36.17	0.08	-0.41	35.83
	44H	39.59	0.00	-0.01	39.57
	45H	42.58	0.00	-0.02	42.56
	46H	25.86	0.04	-0.24	25.66
	47H	35.75	2.18	-2.09	35.84
	48H	38.28	0.00	-0.04	38.24
	49H	35.75	0.44	-0.59	35.61
Ag^+--PPD1		-90.15	29.00	-10.45	-71.59
Ag^+--PPD2		-92.91	29.31	-10.56	-74.16
Ag^+--PPD3		-94.29	34.39	-11.38	-71.29
PPD1--PPD2		-5.68	15.39	-24.35	-14.64
PPD1--PPD3		-5.69	15.96	-25.34	-15.07
PPD2--PPD3		4.34	6.05	-17.49	-7.10

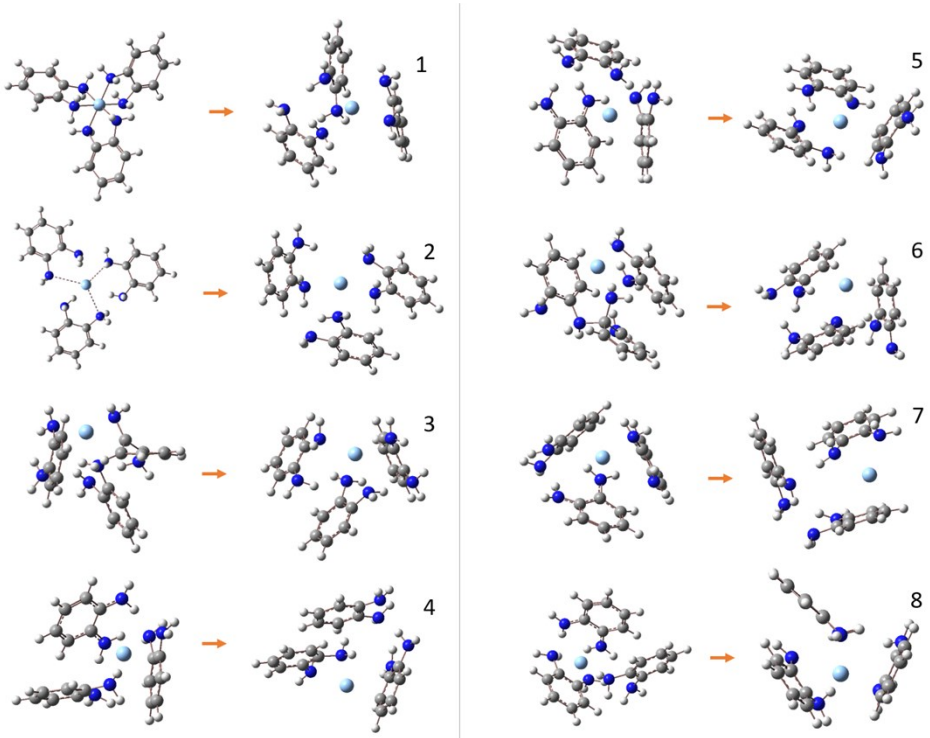
S7. Determination of energy-minima structure



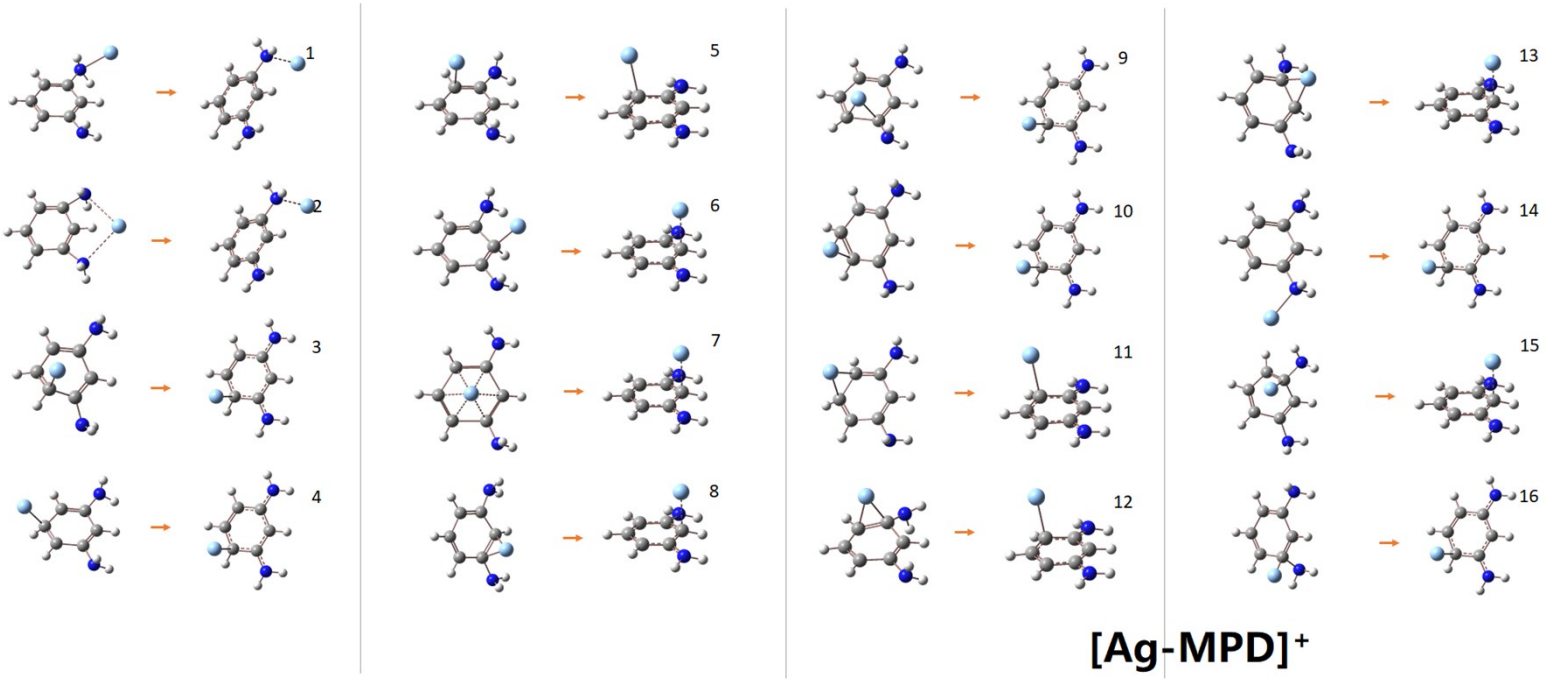
	1	2	3	4	5	6	7	8	9	10
Energy (a.u.)	**-489.277021**	-489.266162	-489.266162	-489.266162	-489.266162	-489.266162	-489.266162	-489.266162	-489.277021	-489.258812
	11	12	13	14	15	16	17	18	19	
Energy (a.u.)	-489.277021	-489.266162	-489.266162	-489.266162	-489.266162	-489.266162	-489.266162	-489.277021	-489.266162	



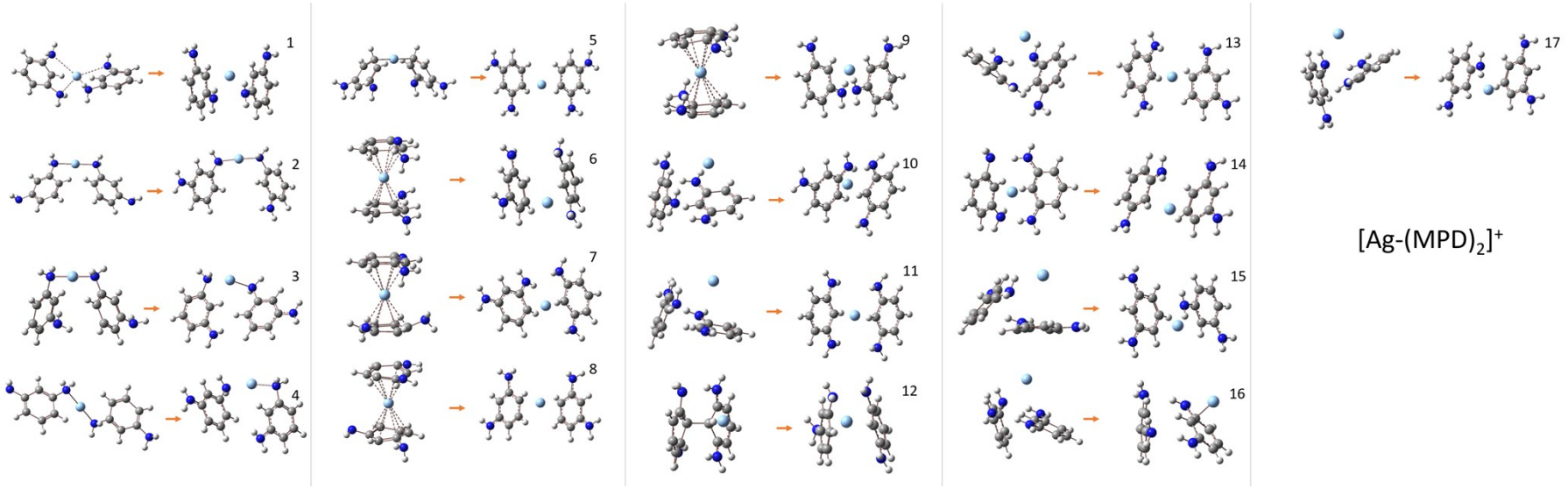
Isomer	1	2	3	4	5	6	7	8	9	10
Energy (a.u.)	**-831.86985**	-831.713535	-831.728	-831.7284	-831.7174	-831.86391	-831.865927	-831.862052	-831.86204	-831.86985
Isomer	11	12	13	14	15	16	17	18	19	20
Energy (a.u.)	-831.865901	-831.865901	-831.862563	-831.866718	-831.8667	-831.866567	-831.862563	-831.865927	-831.86696	-831.866759



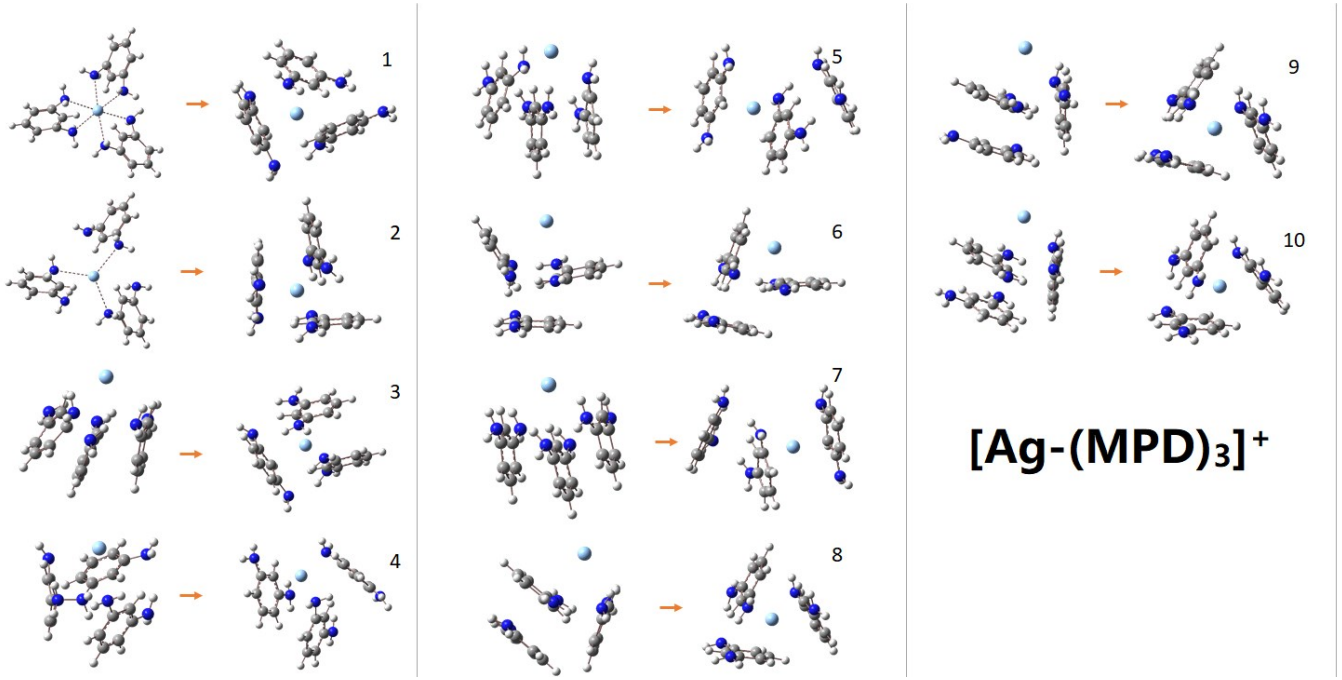
$[Ag\text{-}(OPD)_3]^+$	1	2	**3**	4	5	6	7	8
Energy (a.u.)	-1174.436	-1174.4298	**-1174.437429**	-1174.423917	-1174.431446	-1174.431447	-1174.4279	-1174.4175



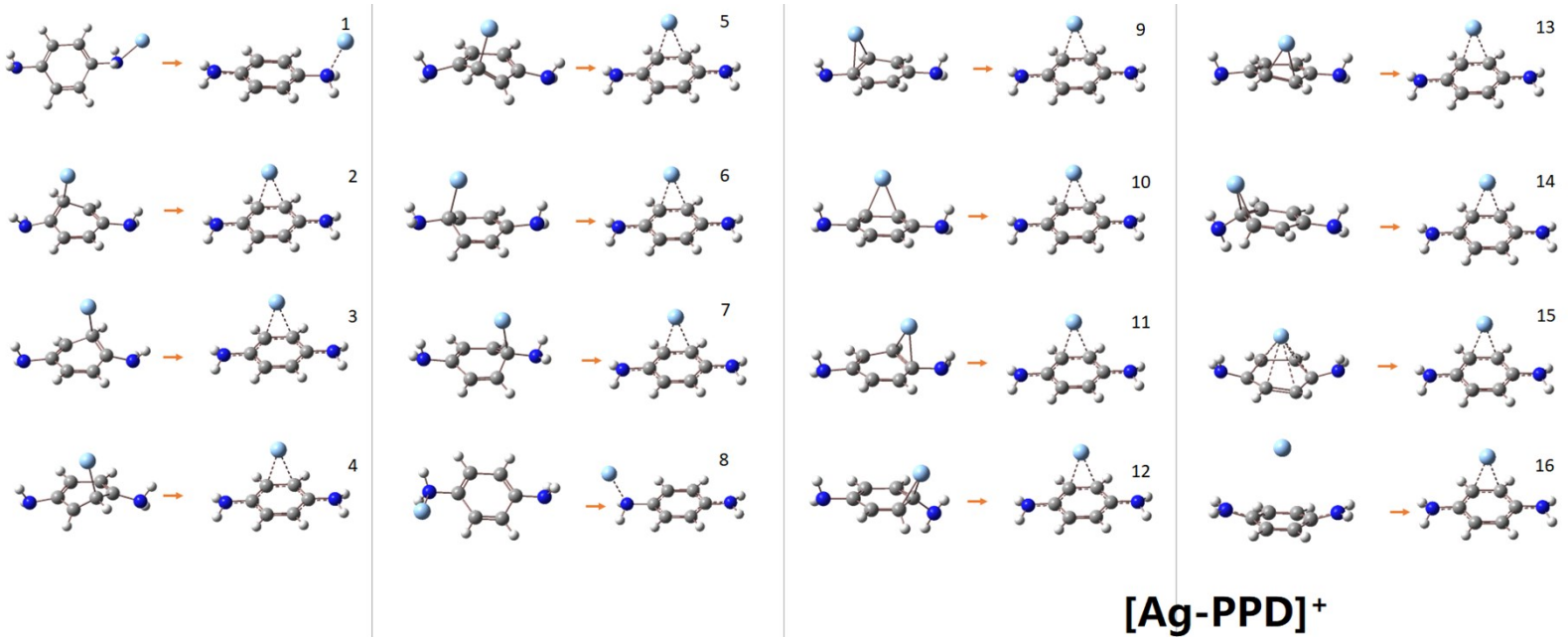
Isomer	1	2	3	4	5	6	7	8
Energy (a.u.)	-489.260923	-489.260923	-489.274054	-489.274054	-489.27405	-489.26904	-489.269039	-489.269039
Isomer	9	10	11	12	13	14	15	**16**
Energy (a.u.)	-489.274054	-489.274054	-489.274054	-489.274054	-489.26904	-489.27405	-489.269039	**-489.274054**



Isomer	1	2	3	4	5	6	7	**8**	9
Energy(a.u.)	-831.8673	-831.864395	-831.864976	-831.865116	-831.873277	-831.872937	-831.869987	**-831.8733**	-831.867254
Isomer	10	11	12	13	14	15	16	17	
Energy(a.u.)	-831.86717	-831.867011	-831.870007	-831.869951	-831.87025	-831.87025	-831.835645	-831.870291	

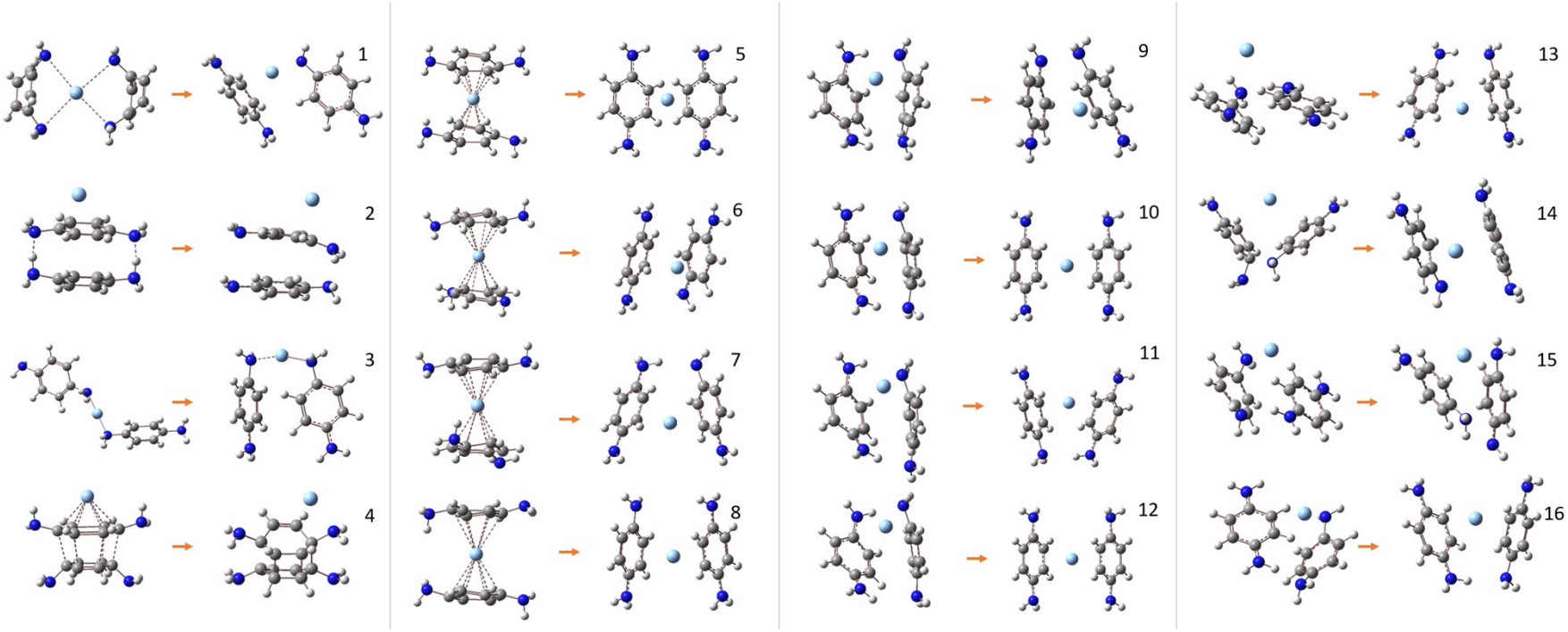


Isomer	1	2	3	4	5	6	7	8	9	**10**
Energy (a.u.)	-1174.43815	-1174.441	-1174.44053	-1174.433012	-1174.428506	-1174.429947	-1174.428543	-1174.4437	-1174.4434	**-1174.4437**

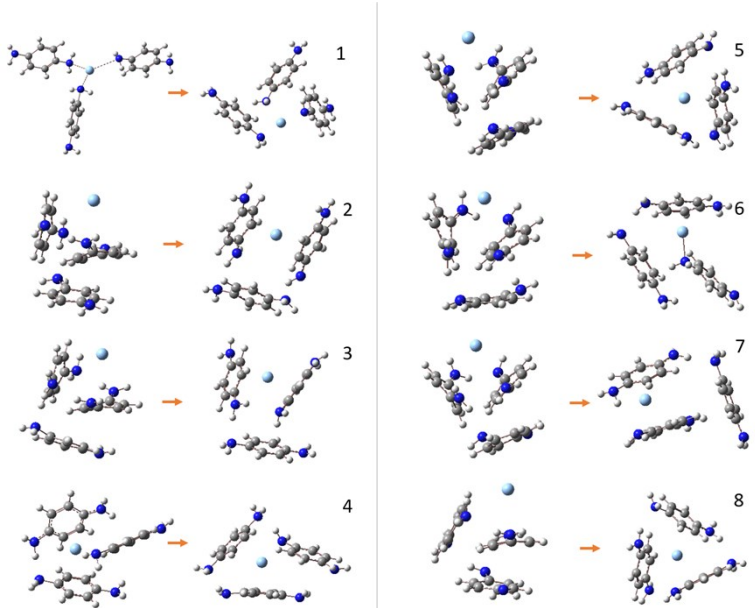


[Ag-PPD]$^{+}$

Isomer	1	2	3	4	5	6	7	8
Energy (a.u.)	-489.261007	-489.261301	-489.261301	-489.261301	-489.261301	-489.261301	-489.261301	-489.261007
Isomer	9	10	11	12	13	14	15	**16**
Energy (a.u.)	-489.261301	-489.261301	-489.261301	-489.261301	-489.261301	-489.261313	-489.261313	**-489.261313**



$[Ag\text{-}(PPD)_2]^+$ Isomer	1	2	**3**	4	5	6	7	8
Energy (a.u.)	-831.858	-831.814	**-831.862**	-831.698	-831.845	-831.855	-831.854	-831.854
$[Ag\text{-}(PPD)_2]^+$ Isomer	9	10	11	12	13	14	15	16
Energy (a.u.)	-831.855	-831.856	-831.854	-831.856	-831.854	-831.856	-831.859	-831.854



$[Ag\text{-}(PPD)_3]^+$ Isomer	Energy (a.u.)	$[Ag\text{-}(PPD)_3]^+$ Isomer	Energy (a.u.)
1	-1174.427447	5	-1174.429365
2	-1174.409722	6	-1174.415520
3	-1174.409878	7	-1174.407315
4	-1174.425637	**8**	**-1174.429365**