Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Charge Transfer Interactions of Pyrazine with Ag_{12} Clusters—— Towards Precise SERS Chemical Mechanism

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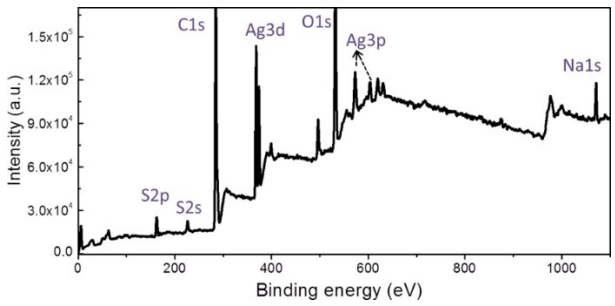


Fig. S1 A typical X-ray photoelectron surveys spectrum of the as-prepared Ag_{12} NCs.

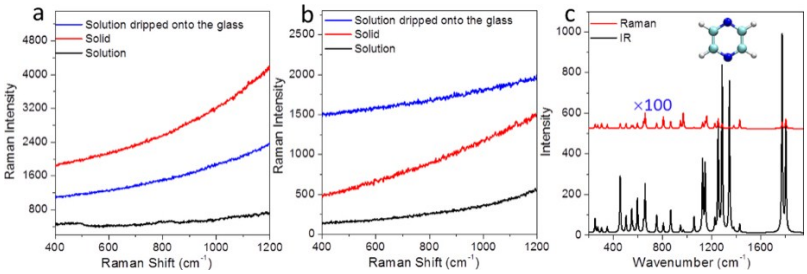


Fig. S2 Exclusion experiments showing no Raman interference of Ag_{12} NCs (a), and the ligand H_2SMA (b). Also, the DFT-calculated Raman activity display rather weak signal in the region lower than 2000 cm^{-1} (c), which is in sharp contrast to its IR activity.

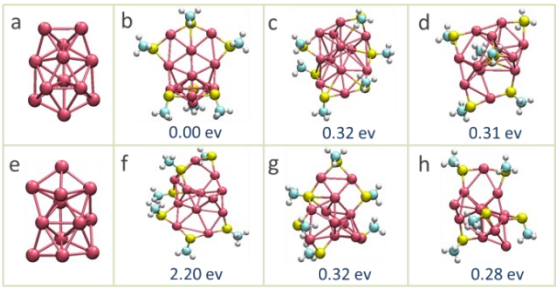


Fig. S3 Optimized isomers geometries of bare Ag_{12} (a) Ag_{12}^{Cs}, (e) Ag_{12}^{C1}, (b/c/d) $Ag_{12}^{Cs}(SCH_3)_6$ and (f/g/h) $Ag_{12}^{C1}(SCH_3)_6$. The energy of Ag_{12}^{Cs} is set as zero reference (energy = 0.00 eV).

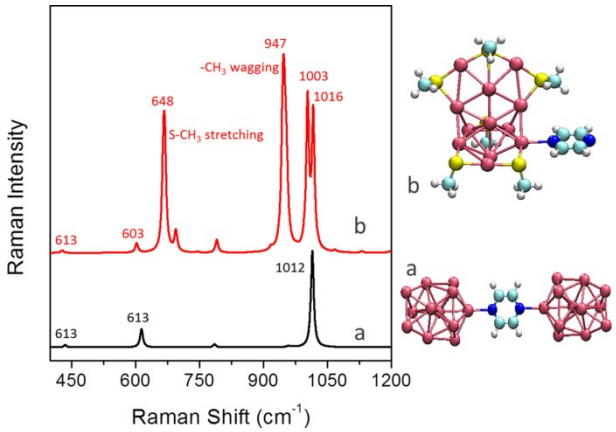
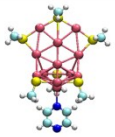
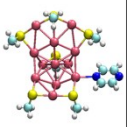


Fig. S4 Calculated Raman spectra of the other models: (a) Ag_{12}-pyrazine-Ag_{12}, (b) edge-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine.

Table S1 Natural population analysis (NPA) charge distribution of $Ag_{12}(SCH_3)_6$, pyrazine, bottom- and edge- adsorbed pyrazine on the cluster.

	$Ag_{12}(SCH_3)_6$	Pyrazine	bottom-adsorbed	edge-adsorbed
Structure				
Surface charge distributions	1 Ag 0.48953 2 Ag 0.48953 3 Ag -0.97812 4 Ag 0.22044 5 Ag 0.28568 6 Ag 0.28579 7 Ag 0.49558 8 Ag 0.28294 9 Ag 0.21734 10 Ag 0.2459 11 Ag 0.283 12 Ag 0.24596 13 S -0.37201 14 S -0.38731 15 S -0.3628 16 S -0.36278 17 S -0.38778 18 S -0.38729 19 H 0.24914 20 H 0.23992 21 H 0.24914 22 H 0.24188 23 H 0.24179 24 H 0.2307 25 H 0.24236 26 H 0.2344 27 H 0.24615 28 H 0.23439 29 H 0.24236 30 H 0.24615 31 H 0.24007 32 H 0.24007 33 H 0.22814 34 H 0.2307 35 H 0.24188 36 H 0.24179 37 C -0.77336 38 C -0.77022 39 C -0.77335 40 C -0.7723 41 C -0.76517 42 C -0.77022	43 C -0.01934 44 C -0.01934 45 N -0.41842 46 N -0.41842 47 C -0.01934 48 C -0.01934 49 H 0.22855 50 H 0.22855 51 H 0.22855 52 H 0.22855	1 Ag 0.4754 2 Ag 0.47528 3 Ag -1.01482 4 Ag 0.18887 5 Ag 0.27661 6 Ag 0.27471 7 Ag 0.515 8 Ag 0.2945 9 Ag 0.21081 10 Ag 0.26455 11 Ag 0.29177 12 Ag 0.2649 13 S -0.3655 14 S -0.3929 15 S -0.36598 16 S -0.36616 17 S -0.39592 18 S -0.39306 19 H 0.24652 20 H 0.23723 21 H 0.24653 22 H 0.24188 23 H 0.24085 24 H 0.22223 25 H 0.24122 26 H 0.23391 27 H 0.24366 28 H 0.23395 29 H 0.24122 30 H 0.24371 31 H 0.23889 32 H 0.23872 33 H 0.22369 34 H 0.2226 35 H 0.24192 36 H 0.2407 37 C -0.7735 38 C -0.76932 39 C -0.77358 40 C -0.77087 41 C -0.76721 42 C -0.76923 43 C 0.01317 44 C -0.00155 45 N -0.48506 46 N -0.40071 47 C -0.00138 48 C 0.01328 49 H 0.24331 50 H 0.24063 51 H 0.24066 52 H 0.24388	1 Ag 0.48136 2 Ag 0.48616 3 Ag -0.93738 4 Ag 0.20533 5 Ag 0.27805 6 Ag 0.27765 7 Ag 0.48652 8 Ag 0.27426 9 Ag 0.21586 10 Ag 0.25015 11 Ag 0.27678 12 Ag 0.22175 13 S -0.36678 14 S -0.38052 15 S -0.36388 16 S -0.37547 17 S -0.39254 18 S -0.40843 19 H 0.24772 20 H 0.23846 21 H 0.24822 22 H 0.24082 23 H 0.2418 24 H 0.23091 25 H 0.24139 26 H 0.23392 27 H 0.24573 28 H 0.23357 29 H 0.24216 30 H 0.24107 31 H 0.23941 32 H 0.23871 33 H 0.22854 34 H 0.22977 35 H 0.24211 36 H 0.23374 37 C -0.77251 38 C -0.77093 39 C -0.77348 40 C -0.77174 41 C -0.76605 42 C -0.76791 43 C 0.00968 44 C -0.00751 45 N -0.46904 46 N -0.40815 47 C -0.0084 48 C 0.01313 49 H 0.24901 50 H 0.23611 51 H 0.23782 52 H 0.24302

We have examined the binding energy on bottom-adsorbed and edge-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine complex, as listed in Table S2. The total binding energy is calculated using the equation $\Delta E = E_{complex} - E_{pyrazine} - E_{Ag}$, where $E_{complex}$, $E_{pyrazine}$, and E_{Ag} denote the total energy of $Ag_{12}(SCH_3)_6$-pyrazine complex, a pyrazine molecule and $Ag_{12}(SCH_3)_6$ cluster, respectively. As results, bottom-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine complex shows a larger binding energy (6.75 kcal mol^{-1}) than the edge-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine complex (4.63 kcal mol^{-1}). Meanwhile, the length Ag-N bond of edge-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine complex is larger (2.52 Å) than that of the bottom-adsorbed complex (2.43 Å).

Table S2 Binding interactions between pyrazine and metal clusters. Bond length between Ag and N atoms, R(Ag-N) in Å; Mulliken charge q(pyrazine → cluster) in units of electron charge; and total binding energy, $\Delta E = E_{complex} - E_{pyrazine} - E_{Ag}$ in kcal mol^{-1}.

Complex	**q(pyrazine→ cluster)**	**R(Ag-N)**	**ΔE（Kcal mol^{-1}）**
Bottom-adsorbed	0.305	2.43	-6.75
Edge-adsorbed	0.177	2.52	-4.63

As supplementary information, we have also calculated the deformation density and Milliken charge distribution of edge-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine, as shown in Fig. S5.

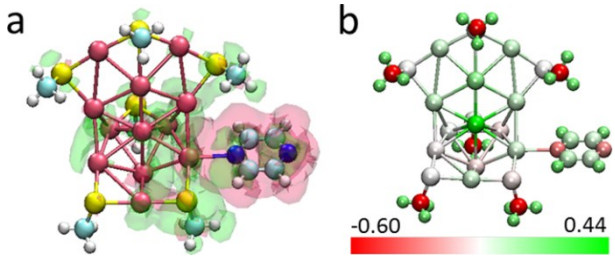


Fig. S5 (a) The calculated deformation density ($\Delta\rho = \rho^{complex} - \rho^{Ag12} - \rho^{pyrazine}$) isosurfaces in the edge-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine, with an isosurface value of 0.0001 a.u. The enhanced density is in green and the depletion density in red. (b) Mulliken charge distribution in the edge-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine.

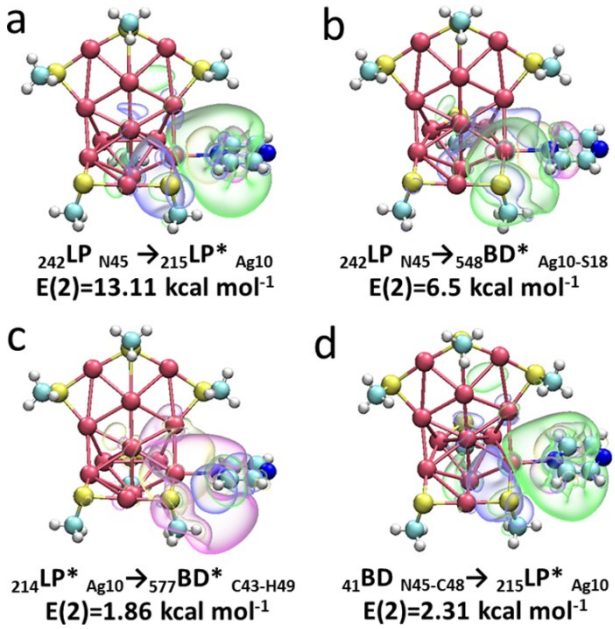


Fig. S6 Natural bond orbital (NBO) donor-acceptor (overlap) interactions in the edge-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine between $Ag_{12}(SCH_3)_6$ and pyrazine. The positive and negative donor orbitals are yellow and purple; the positive and negative acceptor orbitals are green and blue.

Table S3 Second-order perturbation theory analysis of Fock matrix in NBO basis for pyrazine and $Ag_{12}(SCH_3)_6$-pyrazine complex.

Bottom-adsorbed

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
78. CR (1)Ag 9	/500. RY*(1) N 45	0.10	4.54	0.019
78. CR (1)Ag 9	/576. BD*(1) C 43 - N 45	0.09	4.02	0.017
78. CR (1)Ag 9	/580. BD*(1) N 45 - C 48	0.09	4.01	0.017
79. CR (2)Ag 9	/576. BD*(1) C 43 - N 45	0.13	2.73	0.017
79. CR (2)Ag 9	/580. BD*(1) N 45 - C 48	0.13	2.73	0.017
200. LP (1)Ag 9	/575. BD*(1) C 43 - C 44	0.05	0.87	0.006
200. LP (1)Ag 9	/576. BD*(1) C 43 - N 45	0.15	0.83	0.010
200. LP (1)Ag 9	/580. BD*(1) N 45 - C 48	0.15	0.83	0.010
200. LP (1)Ag 9	/582. BD*(1) C 47 - C 48	0.05	0.87	0.006
203. LP (4)Ag 9	/243. LP (2) N 45	1.69	0.09	0.017
204. LP (5)Ag 9	/243. LP (2) N 45	0.09	0.09	0.004
204. LP (5)Ag 9	/500. RY*(1) N 45	0.26	1.35	0.017
204. LP (5)Ag 9	/504. RY*(5) N 45	0.07	2.23	0.011
205. LP*(6)Ag 9	/483. RY*(2) C 43	0.17	0.77	0.020
205. LP*(6)Ag 9	/504. RY*(5) N 45	0.10	1.95	0.024
205. LP*(6)Ag 9	/528. RY*(2) C 48	0.17	0.76	0.020
205. LP*(6)Ag 9	/576. BD*(1) C 43 - N 45	0.62	0.54	0.032
205. LP*(6)Ag 9	/580. BD*(1) N 45 - C 48	0.62	0.54	0.031
206. LP*(7)Ag 9	/482. RY*(1) C 43	0.05	1.05	0.027
206. LP*(7)Ag 9	/501. RY*(2) N 45	0.16	0.96	0.046
206. LP*(7)Ag 9	/527. RY*(1) C 48	0.05	1.05	0.028
206. LP*(7)Ag 9	/575. BD*(1) C 43 - C 44	0.08	0.41	0.019
206. LP*(7)Ag 9	/577. BD*(1) C 43 - H 49	1.32	0.33	0.073
206. LP*(7)Ag 9	/582. BD*(1) C 47 - C 48	0.07	0.41	0.018
206. LP*(7)Ag 9	/584. BD*(1) C 48 - H 52	1.25	0.33	0.071
207. LP*(8)Ag 9	/503. RY*(4) N 45	0.05	0.89	0.026
207. LP*(8)Ag 9	/536. RY*(1) H 49	0.10	0.63	0.030
207. LP*(8)Ag 9	/539. RY*(1) H 52	0.10	0.63	0.031
207. LP*(8)Ag 9	/576. BD*(1) C 43 - N 45	0.12	0.43	0.025
207. LP*(8)Ag 9	/577. BD*(1) C 43 - H 49	0.30	0.39	0.038
207. LP*(8)Ag 9	/579. BD*(1) C 44 - H 50	0.06	0.39	0.016
207. LP*(8)Ag 9	/580. BD*(1) N 45 - C 48	0.11	0.43	0.025
207. LP*(8)Ag 9	/583. BD*(1) C 47 - H 51	0.06	0.39	0.017
207. LP*(8)Ag 9	/584. BD*(1) C 48 - H 52	0.33	0.39	0.040
208. LP*(9)Ag 9	/503. RY*(4) N 45	0.11	0.87	0.038
208. LP*(9)Ag 9	/577. BD*(1) C 43 - H 49	0.19	0.37	0.030
208. LP*(9)Ag 9	/584. BD*(1) C 48 - H 52	0.20	0.37	0.031
36. BD (1) C 43 - C 44	/205. LP*(6)Ag 9	0.58	0.71	0.021
36. BD (1) C 43 - C 44	/207. LP*(8)Ag 9	1.01	0.82	0.026
36. BD (1) C 43 - C 44	/208. LP*(9)Ag 9	0.40	0.84	0.017
36. BD (1) C 43 - C 44	/320. RY*(1)Ag 9	0.08	1.62	0.010
36. BD (1) C 43 - C 44	/323. RY*(4)Ag 9	0.18	3.98	0.024
37. BD (1) C 43 - N 45	/205. LP*(6)Ag 9	0.95	0.82	0.029
37. BD (1) C 43 - N 45	/206. LP*(7)Ag 9	0.17	1.00	0.012
37. BD (1) C 43 - N 45	/207. LP*(8)Ag 9	2.23	0.94	0.042
37. BD (1) C 43 - N 45	/208. LP*(9)Ag 9	1.04	0.96	0.029
38. BD (1) C 43 - H 49	/205. LP*(6)Ag 9	0.18	0.52	0.010
38. BD (1) C 43 - H 49	/207. LP*(8)Ag 9	1.29	0.63	0.026
38. BD (1) C 43 - H 49	/208. LP*(9)Ag 9	0.52	0.65	0.017
39. BD (1) C 44 - N 46	/207. LP*(8)Ag 9	0.18	0.92	0.012
39. BD (1) C 44 - N 46	/208. LP*(9)Ag 9	0.09	0.94	0.008
40. BD (1) C 44 - H 50	/207. LP*(8)Ag 9	0.22	0.63	0.011
40. BD (1) C 44 - H 50	/208. LP*(9)Ag 9	0.10	0.65	0.007
41. BD (1) N 45 - C 48	/205. LP*(6)Ag 9	0.94	0.82	0.029
41. BD (1) N 45 - C 48	/206. LP*(7)Ag 9	0.24	1.00	0.014
41. BD (1) N 45 - C 48	/207. LP*(8)Ag 9	2.20	0.94	0.042
41. BD (1) N 45 - C 48	/208. LP*(9)Ag 9	1.02	0.96	0.029
42. BD (1) N 46 - C 47	/207. LP*(8)Ag 9	0.18	0.92	0.012
42. BD (1) N 46 - C 47	/208. LP*(9)Ag 9	0.09	0.94	0.008
43. BD (1) C 47 - C 48	/205. LP*(6)Ag 9	0.58	0.71	0.021
43. BD (1) C 47 - C 48	/207. LP*(8)Ag 9	1.02	0.82	0.026
43. BD (1) C 47 - C 48	/208. LP*(9)Ag 9	0.41	0.84	0.017
43. BD (1) C 47 - C 48	/320. RY*(1)Ag 9	0.08	1.62	0.010
43. BD (1) C 47 - C 48	/323. RY*(4)Ag 9	0.17	3.98	0.023
44. BD (1) C 47 - H 51	/207. LP*(8)Ag 9	0.22	0.63	0.011
44. BD (1) C 47 - H 51	/208. LP*(9)Ag 9	0.10	0.65	0.007
45. BD (1) C 48 - H 52	/205. LP*(6)Ag 9	0.18	0.52	0.010
45. BD (1) C 48 - H 52	/207. LP*(8)Ag 9	1.32	0.63	0.026
45. BD (1) C 48 - H 52	/208. LP*(9)Ag 9	0.52	0.65	0.017
130. CR (1) C 43	/206. LP*(7)Ag 9	0.12	10.26	0.033
130. CR (1) C 43	/207. LP*(8)Ag 9	1.16	10.20	0.100
130. CR (1) C 43	/208. LP*(9)Ag 9	0.52	10.22	0.067
131. CR (1) C 44	/207. LP*(8)Ag 9	0.34	10.19	0.054
131. CR (1) C 44	/208. LP*(9)Ag 9	0.16	10.21	0.037
132. CR (1) N 45	/205. LP*(6)Ag 9	0.37	14.17	0.075
132. CR (1) N 45	/207. LP*(8)Ag 9	1.80	14.28	0.147
132. CR (1) N 45	/208. LP*(9)Ag 9	0.77	14.30	0.096
133. CR (1) N 46	/207. LP*(8)Ag 9	0.11	14.25	0.037
133. CR (1) N 46	/208. LP*(9)Ag 9	0.05	14.27	0.025
134. CR (1) C 47	/207. LP*(8)Ag 9	0.35	10.19	0.055
134. CR (1) C 47	/208. LP*(9)Ag 9	0.16	10.21	0.037
135. CR (1) C 48	/206. LP*(7)Ag 9	0.10	10.26	0.029
135. CR (1) C 48	/207. LP*(8)Ag 9	1.19	10.19	0.101
135. CR (1) C 48	/208. LP*(9)Ag 9	0.53	10.22	0.067
242. LP (1) N 45	/205. LP*(6)Ag 9	11.65	0.36	0.064
242. LP (1) N 45	/207. LP*(8)Ag 9	10.25	0.47	0.063
242. LP (1) N 45	/208. LP*(9)Ag 9	3.70	0.50	0.039
242. LP (1) N 45	/320. RY*(1)Ag 9	0.28	1.28	0.017
244. LP (1) N 46	/207. LP*(8)Ag 9	0.36	0.44	0.011
244. LP (1) N 46	/208. LP*(9)Ag 9	0.16	0.47	0.008

Edge-adsorbed

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
9. BD (1)Ag 10 - S 18	/500. RY*(1) N 45	0.13	1.40	0.012
9. BD (1)Ag 10 - S 18	/501. RY*(2) N 45	0.12	1.44	0.012
9. BD (1)Ag 10 - S 18	/528. RY*(2) C 48	0.10	1.00	0.009
9. BD (1)Ag 10 - S 18	/536. RY*(1) H 49	0.15	1.07	0.011
9. BD (1)Ag 10 - S 18	/575. BD*(1) C 43 - C 44	0.09	0.90	0.008
9. BD (1)Ag 10 - S 18	/577. BD*(1) C 43 - H 49	0.54	0.83	0.019
9. BD (1)Ag 10 - S 18	/580. BD*(1) N 45 - C 48	0.09	0.86	0.008
82. CR (1)Ag 10	/500. RY*(1) N 45	0.09	4.58	0.019
82. CR (1)Ag 10	/580. BD*(1) N 45 - C 48	0.05	4.03	0.013
84. CR (3)Ag 10	/576. BD*(1) C 43 - N 45	0.07	2.74	0.012
84. CR (3)Ag 10	/580. BD*(1) N 45 - C 48	0.08	2.74	0.013
209. LP (1)Ag 10	/500. RY*(1) N 45	0.07	1.37	0.009
209. LP (1)Ag 10	/528. RY*(2) C 48	0.05	0.97	0.006
209. LP (1)Ag 10	/576. BD*(1) C 43 - N 45	0.11	0.83	0.008
210. LP (2)Ag 10	/243. LP (2) N 45	0.18	0.10	0.006
210. LP (2)Ag 10	/500. RY*(1) N 45	0.07	1.37	0.009
211. LP (3)Ag 10	/243. LP (2) N 45	0.79	0.10	0.013
212. LP (4)Ag 10	/243. LP (2) N 45	0.11	0.10	0.005
213. LP (5)Ag 10	/500. RY*(1) N 45	0.09	1.37	0.010
213. LP (5)Ag 10	/577. BD*(1) C 43 - H 49	0.05	0.79	0.006
213. LP (5)Ag 10	/580. BD*(1) N 45 - C 48	0.05	0.83	0.006
214. LP*(6)Ag 10	/482. RY*(1) C 43	0.21	0.95	0.029
214. LP*(6)Ag 10	/483. RY*(2) C 43	0.14	0.75	0.021
214. LP*(6)Ag 10	/485. RY*(4) C 43	0.07	0.94	0.017
214. LP*(6)Ag 10	/500. RY*(1) N 45	0.08	0.96	0.017
214. LP*(6)Ag 10	/501. RY*(2) N 45	0.18	1.00	0.027
214. LP*(6)Ag 10	/503. RY*(4) N 45	0.06	0.87	0.014
214. LP*(6)Ag 10	/536. RY*(1) H 49	0.11	0.63	0.017
214. LP*(6)Ag 10	/537. RY*(1) H 50	0.05	0.46	0.010
214. LP*(6)Ag 10	/575. BD*(1) C 43 - C 44	0.08	0.46	0.012
214. LP*(6)Ag 10	/576. BD*(1) C 43 - N 45	0.26	0.42	0.021
214. LP*(6)Ag 10	/577. BD*(1) C 43 - H 49	1.86	0.39	0.053
214. LP*(6)Ag 10	/579. BD*(1) C 44 - H 50	0.14	0.37	0.014
214. LP*(6)Ag 10	/582. BD*(1) C 47 - C 48	0.07	0.46	0.011
214. LP*(6)Ag 10	/584. BD*(1) C 48 - H 52	0.10	0.39	0.012
215. LP*(7)Ag 10	/536. RY*(1) H 49	0.09	0.61	0.029
215. LP*(7)Ag 10	/576. BD*(1) C 43 - N 45	0.25	0.40	0.037
215. LP*(7)Ag 10	/577. BD*(1) C 43 - H 49	0.37	0.36	0.042
215. LP*(7)Ag 10	/580. BD*(1) N 45 - C 48	0.21	0.39	0.033
215. LP*(7)Ag 10	/584. BD*(1) C 48 - H 52	0.26	0.36	0.035
238. LP (1) S 18	/577. BD*(1) C 43 - H 49	0.21	0.97	0.013
239. LP (2) S 18	/536. RY*(1) H 49	0.09	1.03	0.010
239. LP (2) S 18	/575. BD*(1) C 43 - C 44	0.05	0.86	0.007
239. LP (2) S 18	/577. BD*(1) C 43 - H 49	1.04	0.79	0.028
548. BD*(1)Ag 10 - S 18	/500. RY*(1) N 45	0.08	0.96	0.027
548. BD*(1)Ag 10 - S 18	/501. RY*(2) N 45	0.10	1.00	0.032
548. BD*(1)Ag 10 - S 18	/528. RY*(2) C 48	0.25	0.56	0.037
548. BD*(1)Ag 10 - S 18	/536. RY*(1) H 49	0.16	0.63	0.031
548. BD*(1)Ag 10 - S 18	/577. BD*(1) C 43 - H 49	0.43	0.38	0.038
548. BD*(1)Ag 10 - S 18	/580. BD*(1) N 45 - C 48	0.15	0.42	0.023
548. BD*(1)Ag 10 - S 18	/584. BD*(1) C 48 - H 52	0.06	0.38	0.015
36. BD (1) C 43 - C 44	/215. LP*(7)Ag 10	1.26	0.85	0.030
36. BD (1) C 43 - C 44	/331. RY*(3)Ag 10	0.08	2.10	0.012
36. BD (1) C 43 - C 44	/332. RY*(4)Ag 10	0.05	1.54	0.008
36. BD (1) C 43 - C 44	/548. BD*(1)Ag 10 - S 18	0.49	0.83	0.019
37. BD (1) C 43 - N 45	/214. LP*(6)Ag 10	0.25	0.95	0.015
37. BD (1) C 43 - N 45	/215. LP*(7)Ag 10	2.77	0.97	0.047
37. BD (1) C 43 - N 45	/216. LP*(8)Ag 10	0.21	0.93	0.013
37. BD (1) C 43 - N 45	/548. BD*(1)Ag 10 - S 18	0.73	0.95	0.024
38. BD (1) C 43 - H 49	/215. LP*(7)Ag 10	0.70	0.66	0.020
38. BD (1) C 43 - H 49	/548. BD*(1)Ag 10 - S 18	0.47	0.64	0.016
39. BD (1) C 44 - N 46	/215. LP*(7)Ag 10	0.13	0.96	0.010
40. BD (1) C 44 - H 50	/215. LP*(7)Ag 10	0.17	0.66	0.010
41. BD (1) N 45 - C 48	/215. LP*(7)Ag 10	2.31	0.97	0.043
41. BD (1) N 45 - C 48	/216. LP*(8)Ag 10	0.09	0.93	0.008
41. BD (1) N 45 - C 48	/331. RY*(3)Ag 10	0.07	2.22	0.011
41. BD (1) N 45 - C 48	/548. BD*(1)Ag 10 - S 18	1.89	0.95	0.039
42. BD (1) N 46 - C 47	/215. LP*(7)Ag 10	0.14	0.96	0.011
43. BD (1) C 47 - C 48	/214. LP*(6)Ag 10	0.07	0.83	0.007
43. BD (1) C 47 - C 48	/215. LP*(7)Ag 10	1.75	0.85	0.035
43. BD (1) C 47 - C 48	/216. LP*(8)Ag 10	0.10	0.81	0.008
43. BD (1) C 47 - C 48	/330. RY*(2)Ag 10	0.05	1.67	0.009
43. BD (1) C 47 - C 48	/331. RY*(3)Ag 10	0.08	2.10	0.011
43. BD (1) C 47 - C 48	/332. RY*(4)Ag 10	0.06	1.55	0.009
43. BD (1) C 47 - C 48	/548. BD*(1)Ag 10 - S 18	0.17	0.83	0.011
44. BD (1) C 47 - H 51	/215. LP*(7)Ag 10	0.25	0.66	0.012
45. BD (1) C 48 - H 52	/215. LP*(7)Ag 10	1.12	0.66	0.025
45. BD (1) C 48 - H 52	/216. LP*(8)Ag 10	0.16	0.62	0.009
45. BD (1) C 48 - H 52	/548. BD*(1)Ag 10 - S 18	0.14	0.64	0.009
130. CR (1) C 43	/214. LP*(6)Ag 10	0.06	10.20	0.025
130. CR (1) C 43	/215. LP*(7)Ag 10	0.99	10.22	0.092
130. CR (1) C 43	/216. LP*(8)Ag 10	0.06	10.18	0.022
130. CR (1) C 43	/548. BD*(1)Ag 10 - S 18	0.24	10.20	0.046
131. CR (1) C 44	/215. LP*(7)Ag 10	0.25	10.23	0.046
132. CR (1) N 45	/215. LP*(7)Ag 10	2.14	14.31	0.160
132. CR (1) N 45	/216. LP*(8)Ag 10	0.16	14.26	0.043
132. CR (1) N 45	/548. BD*(1)Ag 10 - S 18	0.42	14.28	0.072
133. CR (1) N 46	/215. LP*(7)Ag 10	0.08	14.29	0.031
134. CR (1) C 47	/215. LP*(7)Ag 10	0.26	10.23	0.047
135. CR (1) C 48	/215. LP*(7)Ag 10	1.01	10.23	0.093
135. CR (1) C 48	/216. LP*(8)Ag 10	0.12	10.18	0.031
242. LP (1) N 45	/214. LP*(6)Ag 10	0.67	0.46	0.017
242. LP (1) N 45	/215. LP*(7)Ag 10	13.11	0.48	0.072
242. LP (1) N 45	/216. LP*(8)Ag 10	0.93	0.44	0.018
242. LP (1) N 45	/330. RY*(2)Ag 10	0.15	1.30	0.013
242. LP (1) N 45	/548. BD*(1)Ag 10 - S 18	6.50	0.46	0.049
243. LP (2) N 45	/215. LP*(7)Ag 10	0.11	0.33	0.007
243. LP (2) N 45	/216. LP*(8)Ag 10	0.33	0.29	0.011
244. LP (1) N 46	/215. LP*(7)Ag 10	0.25	0.48	0.010

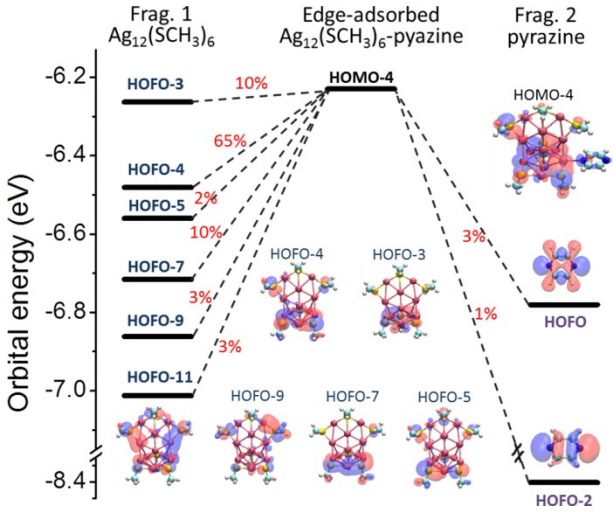


Fig. S7 Orbital interaction diagram for edge-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine formed upon interaction of the $Ag_{12}(SCH_3)_6$ (frag. 1) and pyrazine (frag. 2).

Table S4 Charge decomposition analysis (CDA) of the $Ag_{12}(SCH_3)_6$-pyrazine complex.

Bottom-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine

```
=====  ======== Charge decomposition analysis (CDA) result ============
d = The number of electrons donated from fragment  1 to fragment 2
b = The number of electrons back donated from fragment 2 to fragment 1
r = The number of electrons involved in repulsive polarization
Orb.    Occ.        d             b             d - b          r
196     2       0.001542      0.027027      -0.025485      -0.084262
112     2       0.000016      0.018257      -0.018241       0.008047
210     2       0.003818      0.01795       -0.014132      -0.084547
126     2      -0.001938      0.016469      -0.018407       0.128235
108     2      -0.000074      0.014087      -0.01416        0.014832
134     2       0.000008      0.00988       -0.009872       0.0108
111     2      -0.000051      0.007203      -0.007253       0.002853
187     2      -0.000003      0.005555      -0.005558      -0.002408
144     2      -0.000067      0.00378       -0.003847      -0.004711
137     2      -0.000013      0.003492      -0.003504      -0.004184
197     2       0.000523      0.003135      -0.002612      -0.014567
136     2       0.000062      0.002273      -0.002211       0.001305
183     2      -0.00014       0.002125      -0.002265      -0.012079
92      2      -0.000001      0.002103      -0.002104       0.001848
132     2       0.000817      0.002027      -0.00121        0.024603
101     2       0.000005      0.001681      -0.001677       0.001327
93      2       0.000001      0.001611      -0.00161        0.000374
180     2      -0.000032      0.001586      -0.001619      -0.011449
109     2       0.000016      0.001585      -0.001569       0.001568
100     2       0.000014      0.001372      -0.001358       0.001462
148     2      -0.000005      0.001346      -0.001351      -0.004089
138     2      -0.000039      0.001308      -0.001347      -0.001826
......
-------------------------------------------------------------------
Sum:    420     0.011101      0.152948      -0.141847      -0.117596


========== Extended Charge decomposition analysis (ECDA) ==========
Contribution to all occupied complex orbital:
"Occupied " virtual orbitals of fragment  1:    18896.21%   13.60%
"Occupied " virtual orbitals of fragment  2:    2089.24%    0.95%
Contribution to all virtual complex orbital:
"Occupied " virtual orbitals of fragment  1:    3.79%    30286.40%
"Occupied " virtual orbitals of fragment  2:    10.76%   7099.05%
PL( 1) + CT( 1-> 2)=0.0757      PL( 1) + CT( 2-> 1)=0.2721
PL( 2) + CT( 1-> 2)=0.0189      PL( 2) + CT( 2-> 1)=0.2153
The net electrons obtained by frag.  2 = CT( 1-> 2) - CT( 2-> 1) = -0.1963
```

Edge-adsorbed $Ag_{12}(SCH_3)_6$-pyrazine

```
============ Charge decomposition analysis (CDA) result ============
d = The number of electrons donated from fragment 1 to fragment 2
b = The number of electrons back donated from fragment 2to fragment 1
r = The number of electrons involved in repulsive polarization
Orb.    Occ.        d             b             d - b          r
112     2      -0.000023      0.014677      -0.0147         0.007569
108     2      -0.000146      0.01377       -0.013917       0.014307
206     2       0.001116      0.011263      -0.010147      -0.060818
197     2      -0.000415      0.008675      -0.00909       -0.01316
195     2      -0.000113      0.007632      -0.007745      -0.002701
111     2      -0.000202      0.006444      -0.006646       0.008073
196     2      -0.00051       0.005722      -0.006231      -0.004576
162     2      -0.000123      0.004994      -0.005117      -0.004092
203     2       0.005023      0.004775       0.000248      -0.034563
135     2      -0.000766      0.004738      -0.005504       0.034519
207     2       0.000474      0.004347      -0.003873      -0.023046
209     2       0.002223      0.004182      -0.001959      -0.022052
141     2      -0.000278      0.003988      -0.004265       0.021909
194     2       0.000216      0.003458      -0.003243      -0.001598
192     2      -0.000205      0.003396      -0.003602      -0.022596
143     2      -0.000209      0.003333      -0.003543       0.012995
149     2       0.000255      0.002718      -0.002463       0.012931
136     2      -0.00017       0.002506      -0.002676       0.015192
145     2       0.000026      0.002279      -0.002253       0.009353
198     2       0.000225      0.002273      -0.002048      -0.005929
146     2      -0.000043      0.00208       -0.002123       0.005594
92      2      -0.000007      0.001848      -0.001854       0.00175
200     2       0.001221      0.001822      -0.000601      -0.010554
......
-------------------------------------------------------------------
Sum:    420     0.018703      0.146677      -0.127974      -0.123013


========== Extended Charge decomposition analysis (ECDA) ==========
Contrib ution to all occupied complex orbital:
"Occupied" virtual orbitals of fragment 1: 18897.14%     11.77%
"Occupied" virtual orbitals of fragment 2: 2089.82%      1.27%
Contribution to all virtual complex orbital :
"Occupied" virtual orbitals of fragment 1: 2.86%        30288.23%
"Occupied" virtual orbitals of fragment 2: 10.18%       7098.74%
PL( 1) + CT( 1-> 2) = 0.0571     PL( 1) + CT( 2-> 1) =0.2354
PL( 2) + CT( 1-> 2) = 0.0253     PL( 2) + CT( 2-> 1) =0.2036
The net electrons obtained by frag.  2 = CT( 1-> 2) - CT( 2-> 1) = -0.1783
```