Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Mass Spectrometry Guided Surface Modification of the Tellurate Ion Templated 36-Nucleus Silver Alkynl Nanocluster

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Experiment details

Materials and Physical Measurements.

All of the reagents and solvents employed were commercially available and used as received without further purification. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} with a WQF-520A FT-IR spectrometer. The powder X-ray diffraction (PXRD) pattern was recorded with DX-2700 X-ray diffractometer. The solid UV-vis diffuse reflectance spectra were recorded on a Canry-5000 spectrophotometer at room temperature. Luminescence was measured with a Hitachi F-7000 spectrometer. X-ray photoelectron spectroscopy (XPS) data were acquired by using ESCALAB 250Xi. The sample was put under UHV to reach the 10^{-8} Pa range. The non-monochromatized Al Kα source was used at 10 kV and 10 mA. All binding energies were calibrated using the C (1s) carbon peak (284.6 eV), which was applied as an internal standard. ESI-MS was performed on an Agilent Technologies ESI-TOF-MS. Qualitative analysis was carried out using GCMS-QP2010 Plus with EI ion source, EI-MS standard database, and an RTX-5 quartz capillary column.

Characterizations

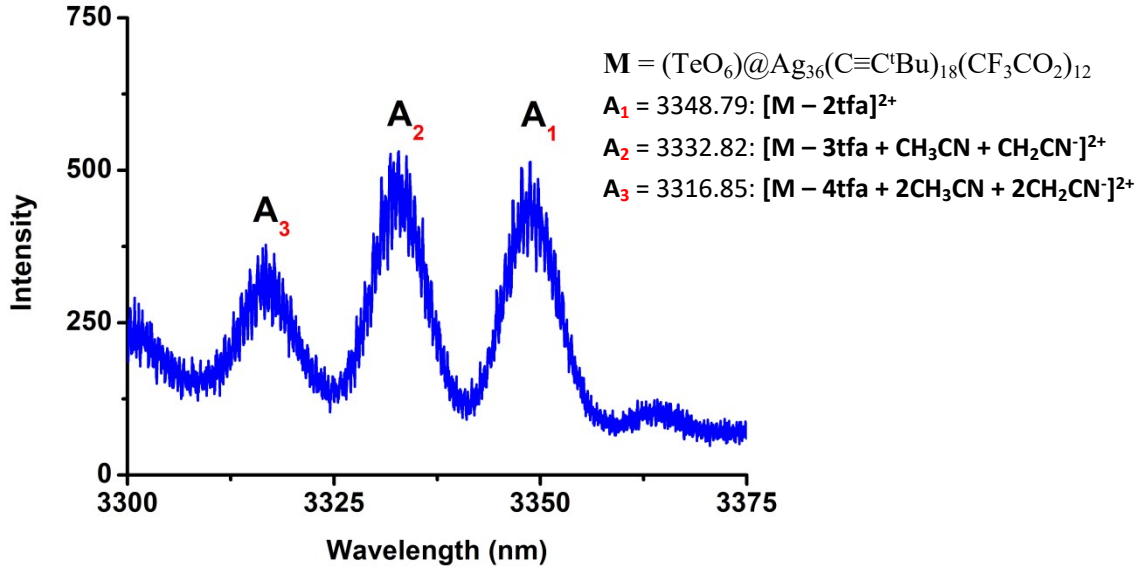


Figure S1. The ESI-MS spectrum of cluster **1** for species A. Note: **M** = $(TeO_6)@Ag_{36}(C{\equiv}C^tBu)_{18}(CF_3CO_2)_{12}$

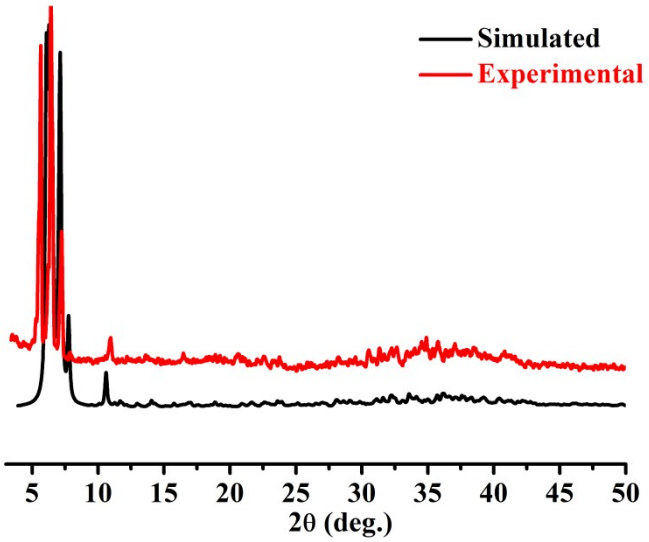


Figure S2. The PXRD pattern of **2.**

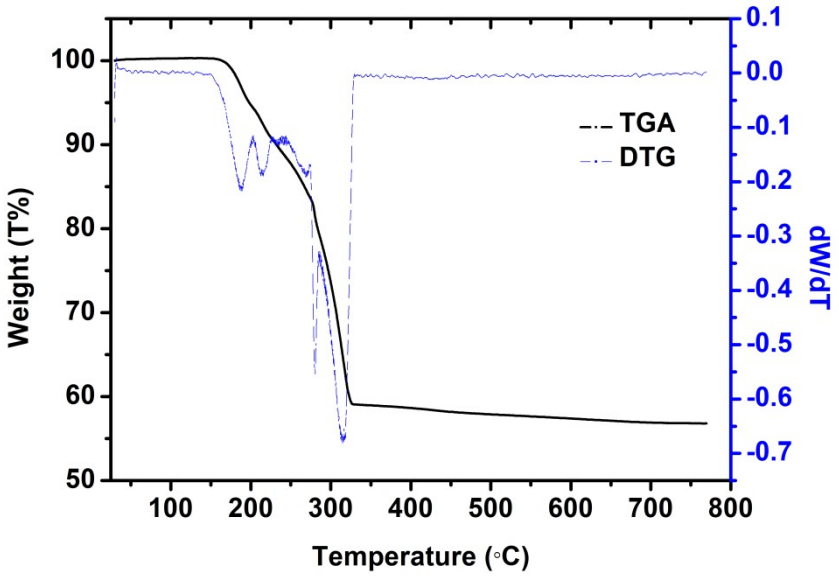


Figure S3. The TGA curve of **2**.

The TGA studies on the as-synthesized powder sample reveal that the sample goes through four decomposed process. The sample begins decomposition at 160 ℃, with the carboxylates (weight loss of 12.3%, calculated 12.4%) lost in the first two steps during 160 ℃ to 245 ℃ with phase inversion temperature 187℃ and 215 ℃ based on the DTG curve, respectively. The last two steps during the decomposition of the whole cluster occur between 245 ℃ and 327 ℃, with phase inversion temperature 279℃ and 312 ℃, respectively. The residue may be Ag_2O with the total weight loss of 43.2 % (the calculated value of 42.9 %).

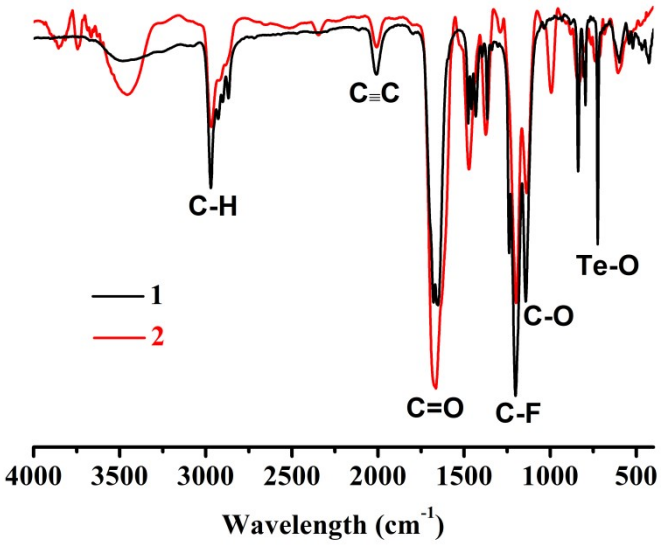
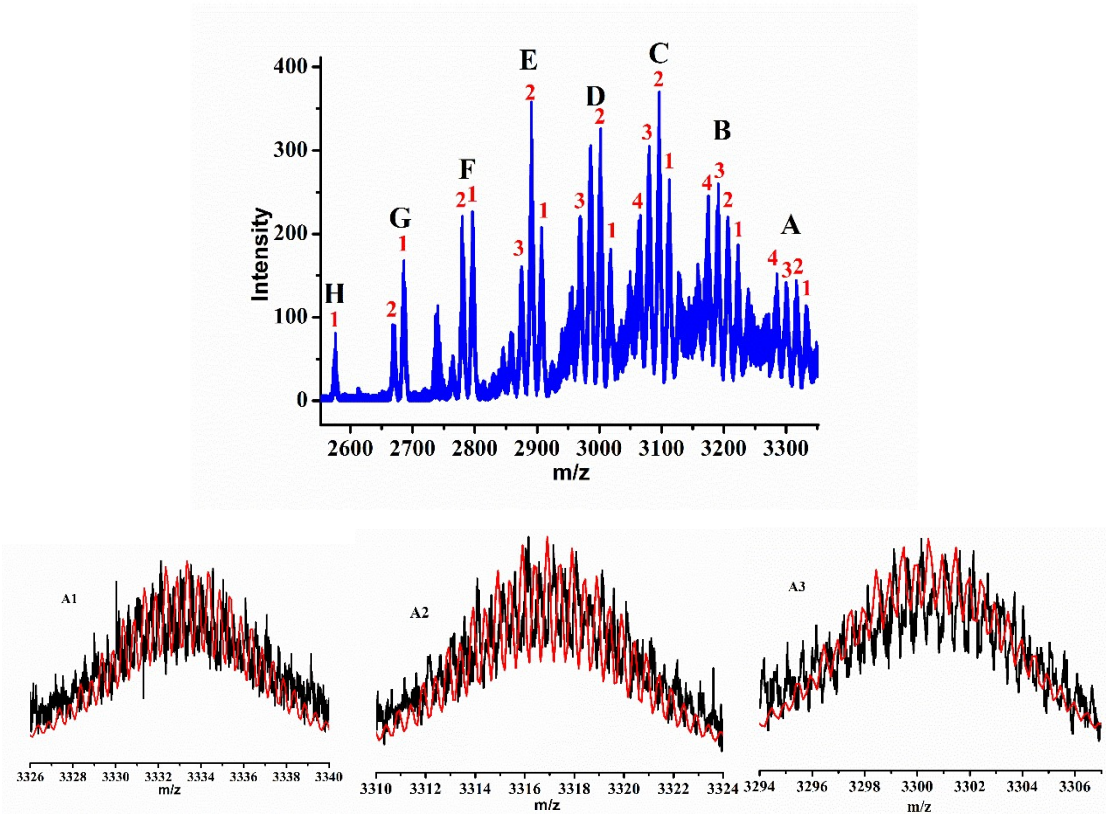
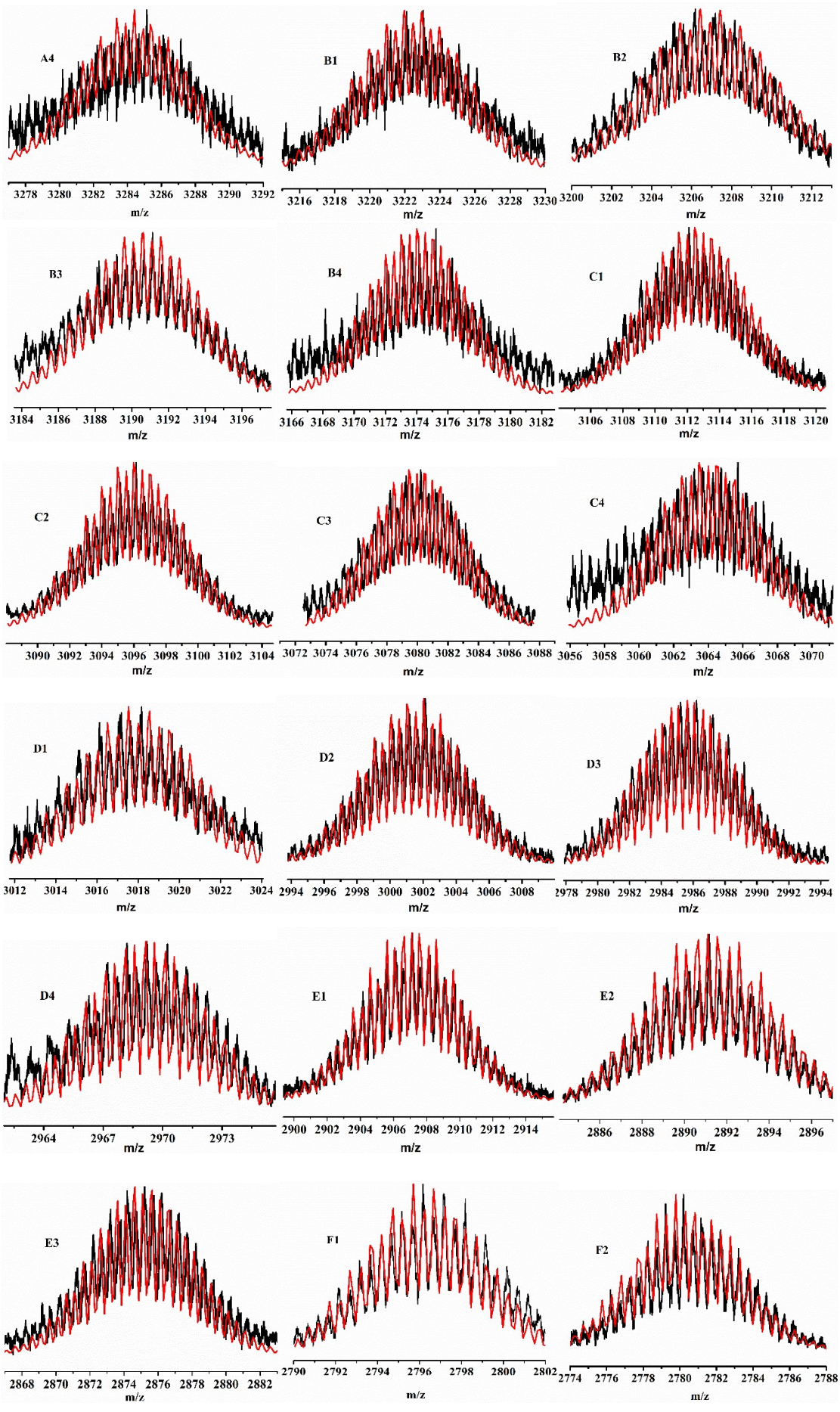


Figure S4. The comparison IR spectra of **1** and **2**.




A4
3278 3280 3282 3284 3286 3288 3290 3292
m/z
B1
3216 3218 3220 3222 3224 3226 3228 3230
m/z
B2
3200 3202 3204 3206 3208 3210 3212
m/z
B3
3184 3186 3188 3190 3192 3194 3196
m/z
B4
3166 3168 3170 3172 3174 3176 3178 3180 3182
m/z
C1
3106 3108 3110 3112 3114 3116 3118 3120
m/z
C2
3090 3092 3094 3096 3098 3100 3102 3104
m/z
C3
3072 3074 3076 3078 3080 3082 3084 3086 3088
m/z
C4
3056 3058 3060 3062 3064 3066 3068 3070
m/z
D1
3012 3014 3016 3018 3020 3022 3024
m/z
D2
2994 2996 2998 3000 3002 3004 3006 3008
m/z
D3
2978 2980 2982 2984 2986 2988 2990 2992 2994
m/z
D4
2964 2967 2970 2973
m/z
E1
2900 2902 2904 2906 2908 2910 2912 2914
m/z
E2
2886 2888 2890 2892 2894 2896
m/z
E3
2868 2870 2872 2874 2876 2878 2880 2882
m/z
F1
2790 2792 2794 2796 2798 2800 2802
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F2
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m/z

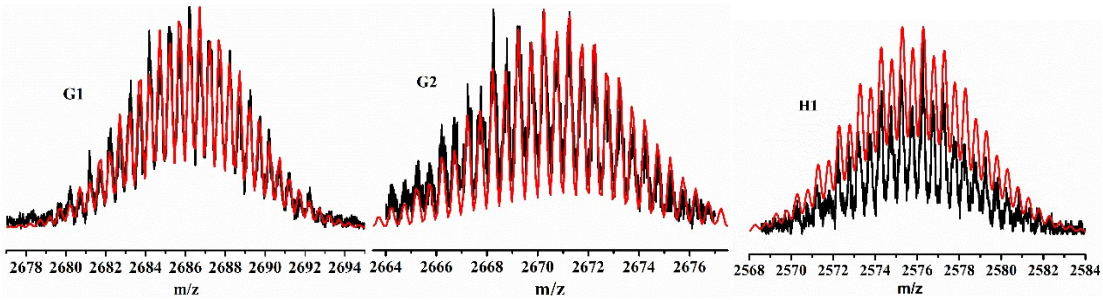

Figure S5. The full ESI-MS spectrum with the experimental (blackline) and simulated (red line) isotopic patterns for species A-H. Note: **M** = $(TeO_6)@Ag_{36}(C{\equiv}C^tBu)_{18}(tfa)_8(F_5PhCO_2)_4$

A_1 = 3333.15: **$[M - 4F_5PhCO_2 + CH_3CN + 2CH_2CN^-]^{2+}$**

A_2 = 3316.50: **$[M - 4F_5PhCO_2 - tfa + CH_3CN + 3CH_2CN^-]^{2+}$**

A_3 = 3300.68: **$[M - 4F_5PhCO_2 - 2tfa + CH_3CN + 4CH_2CN^-]^{2+}$**

A_4 = 3284.66: **$[M - 4F_5PhCO_2 - tfa + 2CH_3CN + 3CH_2CN^-]^{2+}$**

B_1 = 3222.54: **$[M - Ag - 4F_5PhCO_2 - tfa + 2CH_3CN + 2CH_2CN]^{2+}$**

B_2 = 3206.52: **$[M - Ag - 4F_5PhCO_2 - tfa + CH_3CN + 2CH_2CN]^{2+}$**

B_3 = 3190.64: **$[M - Ag - 4F_5PhCO_2 - 2tfa + 2CH_3CN + 3CH_2CN]^{2+}$**

B_4 = 3174.20: **$[M - Ag - 4F_5PhCO_2 - 2tfa + 3CH_2CN]^{2+}$**

C_1 = 3112.10: **$[M - 2Ag - 4F_5PhCO_2 - 3tfa + 3CH_3CN + 3CH_2CN]^{2+}$**

C_2 = 3096.19: **$[M - 2Ag - 4F_5PhCO_2 - 3tfa + 2CH_3CN + 3CH_2CN]^{2+}$**

C_3 = 3080.21: **$[M - 2Ag - 4F_5PhCO_2 - 3tfa + CH_3CN + 3CH_2CN]^{2+}$**

C_4 = 3064.26: **$[M - 2Ag - 4F_5PhCO_2 - 4tfa + 3CH_3CN + 4CH_2CN]^{2+}$**

D_1 = 3017.67: **$[M - 3Ag - 4F_5PhCO_2 - 4tfa + 3CH_3CN + 3CH_2CN]^{2+}$**

D_2 = 3001.67: **$[M - 3Ag - 4F_5PhCO_2 - 4tfa + 3CH_3CN + 3CH_2CN]^{2+}$**

D_3 = 2985.71: **$[M - 3Ag - 4F_5PhCO_2 - 4tfa + 2CH_3CN + 3CH_2CN]^{2+}$**

D_4 = 2969.19: **$[M - 3Ag - 4F_5PhCO_2 - 4tfa + CH_3CN + 3CH_2CN]^{2+}$**

E_1 = 2907.14: **$[M - 4Ag - 4F_5PhCO_2 - 5tfa + 4CH_3CN + 3CH_2CN]^{2+}$**

E_2 = 2891.15: **$[M - 4Ag - 4F_5PhCO_2 - 5tfa + 3CH_3CN + 3CH_2CN]^{2+}$**

E_3 = 2875.12: **$[M - 4Ag - 4F_5PhCO_2 - 5tfa + 2CH_3CN + 3CH_2CN]^{2+}$**

F_1 = 2796.72: **$[M - 5Ag - 4F_5PhCO_2 - 5tfa + 2CH_3CN + 2CH_2CN]^{2+}$**

F_2 = 2780.61: **$[M - 5Ag - 4F_5PhCO_2 - 5tfa + 2CH_3CN + 2CH_2CN]^{2+}$**

G_1 = 2686.23: **$[M - 6Ag - 4F_5PhCO_2 - 6tfa + 2CH_3CN + 2CH_2CN]^{2+}$**

G_2 = 2670.71: **$[M - 6Ag - 4F_5PhCO_2 - 6tfa + CH_3CN + 2CH_2CN]^{2+}$**

H_1 = 2575.76: **$[M - 7Ag - 4F_5PhCO_2 - 7tfa + 2CH_3CN + 2CH_2CN]^{2+}$**

The ESI-MS spectrum is in good agreement with the nanocluster composition. One important molecular ion peaks were observed. The peaks at 3333.15, 3316.50, 3300.68 m/z are assigned to the $[M - 4F_5PhCO_2 + CH_3CN + 2CH_2CN^-]^{2+}$,$[M - 4F_5PhCO_2 - tfa + CH_3CN + 3CH_2CN^-]^{2+}$, $[M - 4F_5PhCO_2 - 2tfa + CH_3CN + 4CH_2CN^-]^{2+}$,(M=$[(TeO_6)@Ag_{36}(C{\equiv}C^tBu)_{18}(tfa)_8(F_5PhCO_2)_4]$), CH_2CN= singly deprotonated acetonitrile (the deprotonated acetonitrile species are produced under the ionization condition and can be also obtained through the C–H activation by coinage metal clusters under mild conditions. Interestingly, other seven groups of fragment peaks (B to H) were significantly observed, and the whole structure was decomposed bit by bit under the ionization condition.

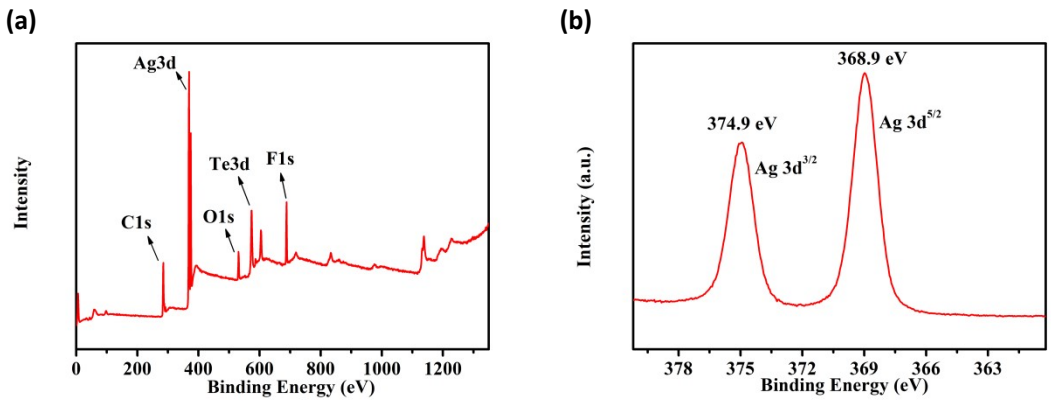

Figure S6. a) XPS spectra of **2**. b) Ag 3d.