Electronic supplementary information for

$Ag_{44}(SR)_{30}^{4-}$: a silver-thiolate superatom complex

Kellen M. Harkness,[‡] Yun Tang,[‡] Amala Dass, Jun Pan, Nuwan Kothawala, Vijay Reddy, David E. Cliffel, Borries Demeler, Francesco Stellacci, Osman Bakr,[*] John A. McLean*

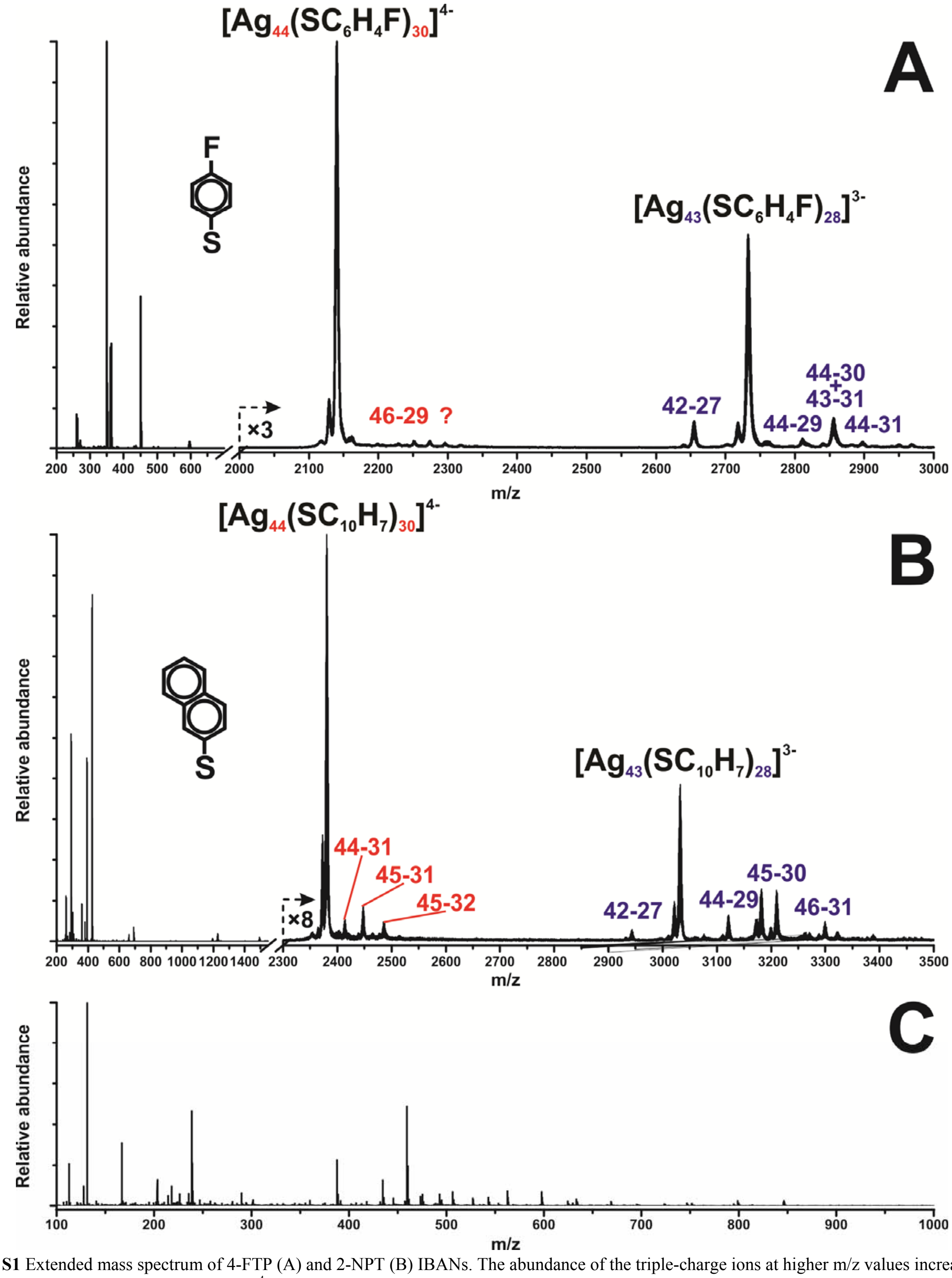

Figure S1 Extended mass spectrum of 4-FTP (A) and 2-NPT (B) IBANs. The abundance of the triple-charge ions at higher m/z values increases with higher voltage settings, while $[Ag_{44}(SR)_{30}]^{4-}$ decreases in abundance. Thus the ion species shown in this figure are likely to be products of in-source fragmentation of $[Ag_{44}(SR)_{30}]^{4-}$ and gas-phase interactions between $[Ag_{44}(SR)_{30}]^{4-}$ and free Ag^{+} and SR^{-}. Notably, any ions with an electron number other than 18 (Equation 1) are among the lowest abundance ions. The most abundant fragment ion, $[Ag_{43}(SR)_{28}]^{3-}$, is a product of the loss of $[Ag(SR)_2]^{-}$. Ions observed in positive ion mode (panel C) consist of low molecular weight silver-thiolate ions and impurities.

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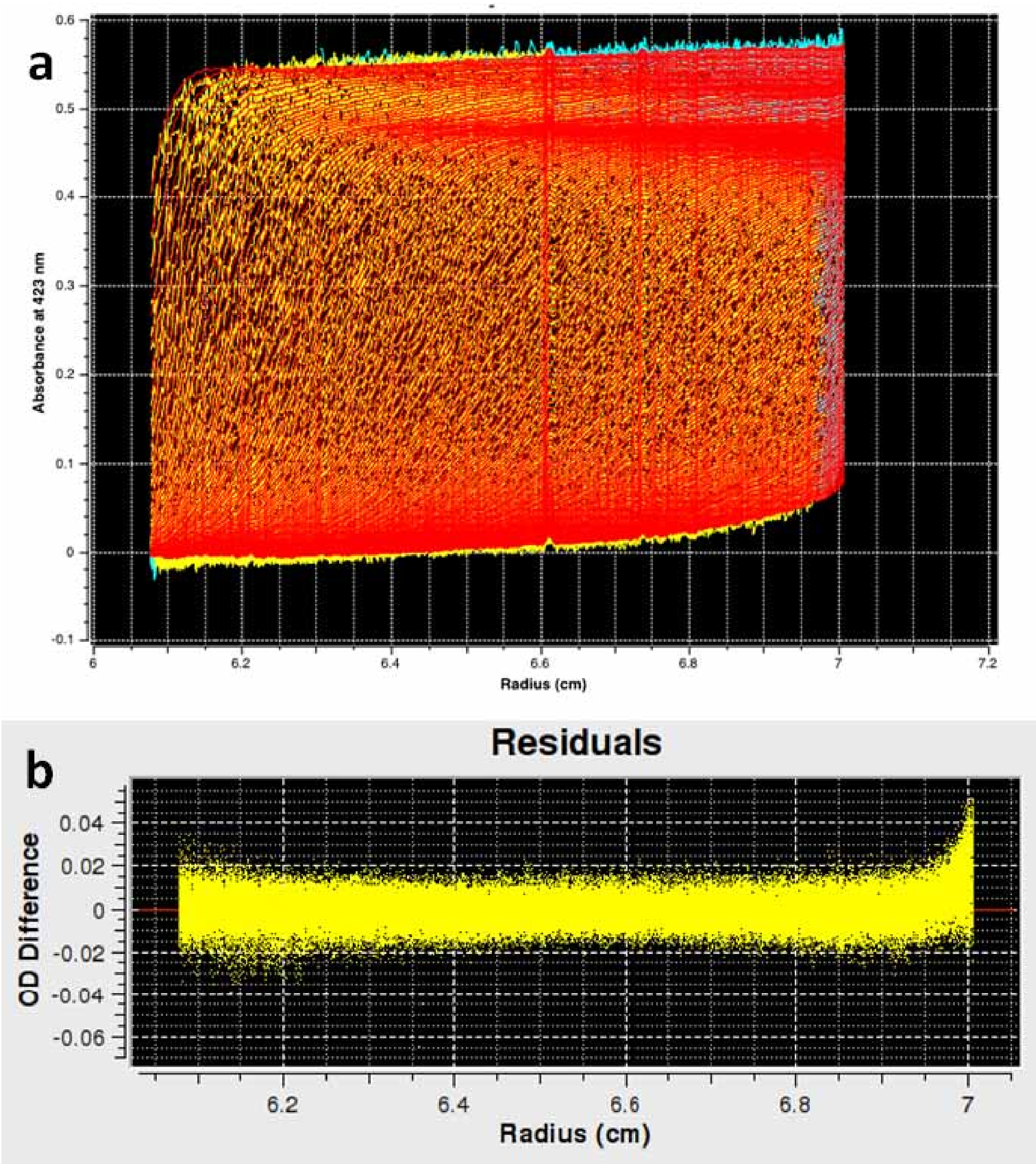

Figure S2 (a) Experimental (yellow) sedimentation profiles of 2NPT-IBANs in DMF overlaid with the simulated (red) model profile, which were obtained by analyzing 189 experimental profiles from the start to the end of the sedimentation process by 2DSA. (b) The small residual difference (RMSD=0.006897) between the model and experimental data attests to the wellness of the fit.

Table S1 SV-AUC data and calculated properties of 2-NPT IBANs. Data and calculated properties for gold-thiolate SCs (from R. P. Carney, J. Y. Kim, H. Qian, R. Jin, H. Mehenni, F. Stellacci and O. M. Bakr, *Nat. Commun.*, **2011**, *2*, 335) are included for comparison.

Nanoparticle	*s* (S)	*D* ($cm^2 \cdot s^{-1}$) × 10^{-6}	Molecular weight (g/mol)	Diameter (nm)	Density (g/cm^3)
$[Au_{25}(SCH_2CH_2Ph)_{18}]^-TOA^+$	6.8	2.8	8000	2.41	1.95
$Au_{38}(SCH_2CH_2Ph)_{24}$	9.6	2.7	11030	2.58	2.43
$[Ag_{44}(SC_{10}H_{17})_{30}]^{4-}$ (observed)	3.7	1.7	11250	2.72	1.77
$[Ag_{44}(SC_{10}H_{17})_{30}]^{4-}$ (expected)	-	-	9520	2.48	1.99
$Au_{144}(SCH_2CH_2Ph)_{60}$	27.1	2.5	35260	2.83	4.51