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SUPPLEMENTARY INFORMATION

Supplementary Information:

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Organoamine Silver(I) Decatungstate Structures: Remarkable Chemoselectivity and the Exploration of the Intramolecular Redox Reaction upon Thermolysis

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IR and UV/Vis-measurements

$(NBu_4)_2[Ag(PhCN)_3]_2[W_{10}O_{32}]$ (1): IR bands (KBr): ν (cm^{-1}) = 3581 (w), 3085 (w, C-H, PhCN, υ_{as}), 3037(w, C-H, PhCN, υ_s), 2960 (s, C-H, NBu_4), 2933(s, C-H, NBu_4), 2875(s, C-H, NBu_4), 2246 (sh, C≡N, υ_{as}), 2233 (s, C≡N, υ_{as}), 1984 (w, C-H, PhCN, γ), 1915 (w, C-H, PhCN, γ), 1828 (w, C-H, PhCN, γ), 1789 (w, C-H, PhCN, γ), 1699 (w, C-H, PhCN, γ), 1617 (m, C=C, PhCN, υ), 1595 (s, C=C, PhCN, υ), 1486 (s, C=C, PhCN, υ), 1446 (s, C=C, PhCN, υ), 1381 (s, C-H, NBu_4, δ), 1344 (w, C-H, NBu_4, δ), 1292 (m, PhCN, C-H, δ), 1195 (m, PhCN, C-H, δ), 1176 (m, C-H, PhCN, δ), 1153 (m, C-H, NBu_4, δ), 1070 (w, C-H, NBu_4, δ), 1026 (w, C-H, NBu_4, δ), 996 (m, C-H, PhCN, δ), 958 (s, W-$O_{terminal}$, υ_{as}), 889 (s, W-$O_{corner\ shared}$-W, υ_{as}), 800 (br, s, W- $O_{edge\ shared}$-W, υ_{as}), 759 (m, C-H, PhCN, γ), 688 (s, C=C, PhCN, φ), 624 (w, C-C=C, δ), 581 (br, m, W-$O_{edge\ shared}$-W, υs), 552 (s, C-H, PhCN, δ), 434 (s), 401 (s); UV/Vis (KBr): λ (nm) = 210, 223, 272, 329.

$[Ag(PhCN)_2]_4[W_{10}O_{32}]$ (2): IR bands (KBr): ν (cm^{-1}) = 3579 (m), 3064 (w, C-H, υ_{as}), 2281 (m, C≡N, υ_{as}), 2229 (s, C≡N, υ_{as}), 1978 (w, C-H, γ), 1902 (w, C-H, γ), 1772 (w, C-H, γ), 1618 (s, C=C, υ), 1596 (s, C=C, υ), 1487 (s, C=C, υ), 1447 (s, C=C, υ), 1291 (m, C-H, δ), 1195 (m, C-H, δ), 1175 (m, C-H, δ), 1003 (m, C-H, δ), 963 (s, W-$O_{terminal}$, υ_{as}), 893 (s, W-$O_{corner\ shared}$-W, υ_{as}), 793 (s, W- $O_{edge\ shared}$-W, υ_{as}), 758 (sh, C-H, γ), 684 (m, C=C, PhCN, φ), 585 (br, m, W-$O_{edge\ shared}$-W, υ_s), 548 (s, C-H, PhCN, δ), 424 (br, s, C=C, PhCN, φ). UV/Vis (KBr): λ (nm) = 205, 223, 271, 277, 320.

$[Ag(PhCN)_2(thb)]_4[W_{10}O_{32}]$ (PhCN) (3): IR bands (KBr): ν (cm^{-1}) = 3483 (br, s), 3167 (m), 3121 (w, N-H, thb, υ), 3038 (w, C-H, PhCN, υ_s), 2832 (m, CH3, thb, υ), 2242 (s, C≡N, υ_{as}), 2226 (s, C≡N, υ_{as}), 1694 (br, s, C=N, thb, υ_{as}), 1596 (m, C=C, PhCN, υ), 1553 (s, C=O, thb, υ_s); 1504 (m), 1489 (m, C=C, PhCN, υ), 1456 (sh), 1447 (m, C=C, PhCN, υ), 1419 (w), 1367 (s), 1330 (w, C-N, thb, υ), 1291 (m, PhCN, C-H, δ), 1231 (s, C-N, thb, υ), 1204 (m), 1178 (w, C-H, PhCN, δ), 1142 (m, C-N, thb, υ_{as}), 1069 (w, C-N, thb, υ), 1045 (w C-N, thb, υ_s), 998 (w, C-H, PhCN, δ), 960 (br, s, W-Oterminal, υ_{as}), 890 (s, W-Ocorner shared-W, υ_{as}), 799 (br, s, , W- $O_{edge\ shared}$-W), 761 (sh, w, C-H, PhCN, γ), 687 (s, C=C, PhCN, φ), 608 (m, C=C-C, thb, δ), 589(br, m, W-$O_{edge\ shared}$-W, υ_s), 549 (m, C-H, PhCN, δ), 515 (m, N-C-C, thb, δ), 452 (sh, w, C-N-C, thb, δ_{as}), 434 (s), 425 (s, , s, C=C, PhCN, φ). UV/Vis (KBr): λ (nm) = 208, 223, 278, 326.

SUPPLEMENTARY INFORMATION

Powder X-Ray Diffractograms

All measurements accomplished with Cu-Kα-Radiation, λ = 1.5406 Å, at room temperature on a STOE STADI transmission powder diffractometer.

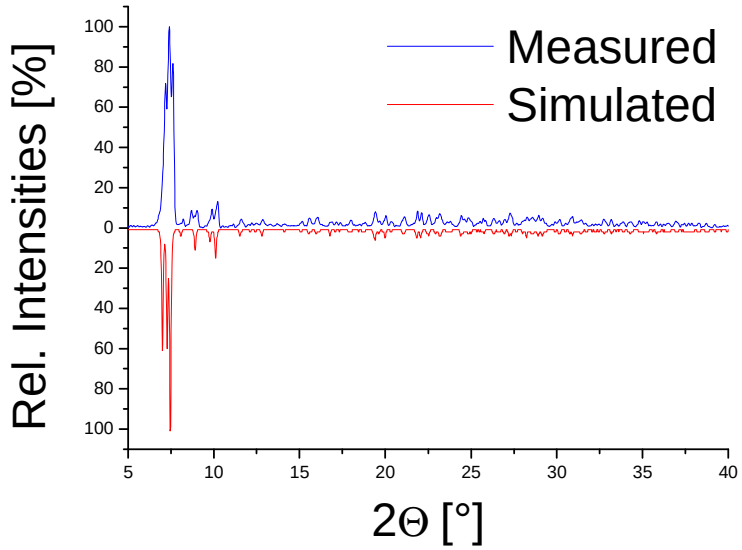

Figure S1. Powder X-ray diffractogram of $(NBu_4)_2[Ag(PhCN)_3]_2[W_{10}O_{32}]$ (**1**).

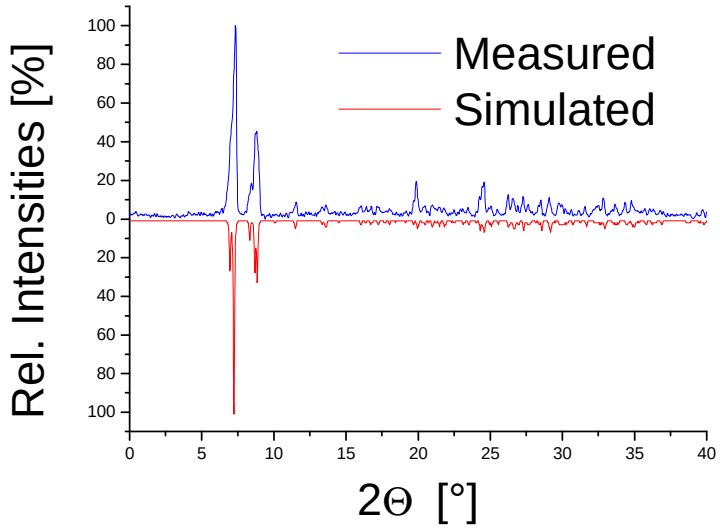

Figure S2. Powder X-ray diffractogram of $[Ag(PhCN)_2]_4[W_{10}O_{32}]$ (**2**).

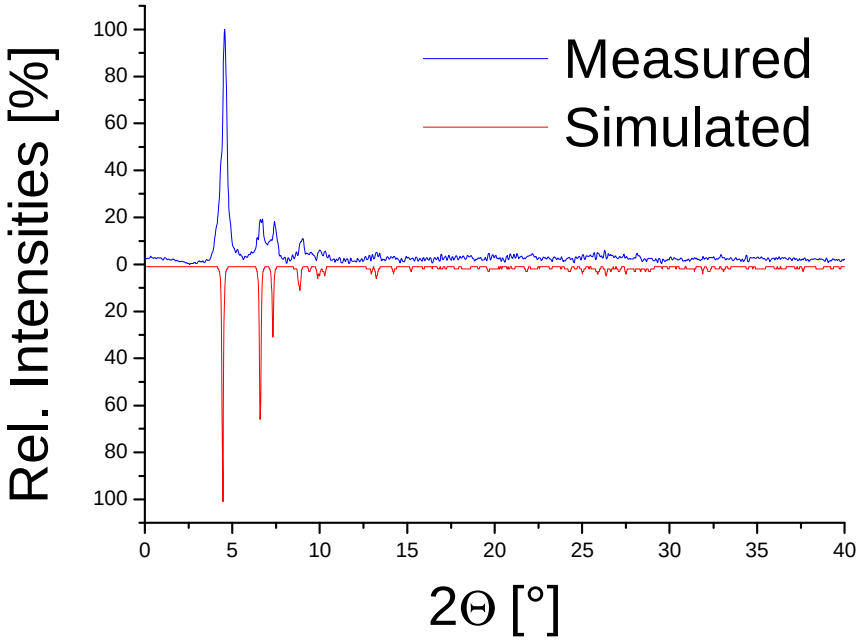

Figure S3. Powder X-ray diffractogram of $[Ag(PhCN)_2(thb)]_4[W_{10}O_{32}](PhCN)$ (**3**). The simulated diffractogram is based on the crystal structure at 170(2) K.

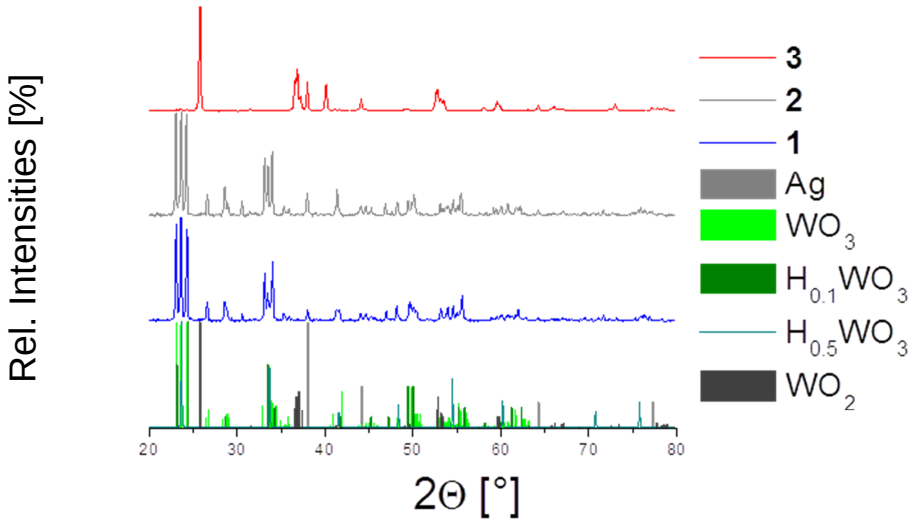

Figure S4 Powder X-ray diffraction patters of the DTA residues of **1**, **2** and **3** and simulations for respective matching species.[1]

DTA/TG Measurements

The DTA/TG measurements were accomplished on a Netzsch STA 409 thermal analyzer with a heating rate of 20°C/min under nitrogen atmosphere. The organic moieties, to which the approximate weight loss corresponds, are shown above the blue lines. The respective figures are only approximations, due to the fast exothermic reactions.

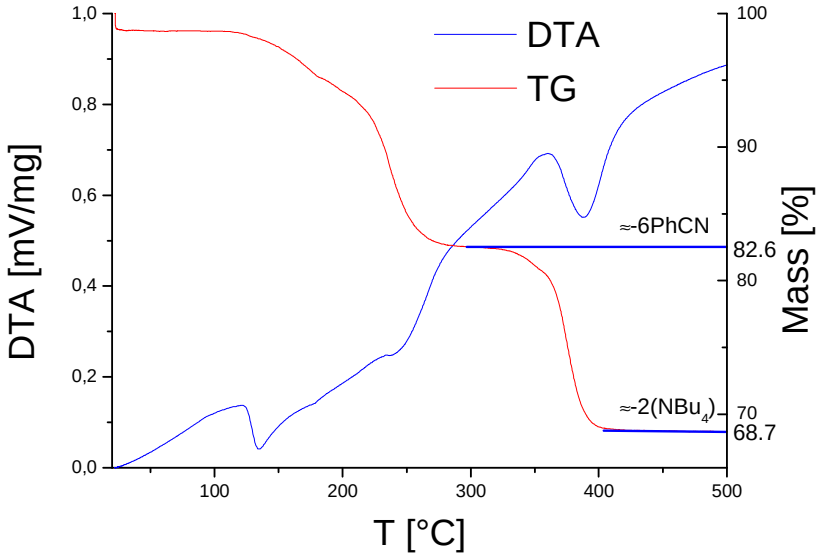

Figure S5. DTA/TG of $(NBu_4)_2[Ag(PhCN)_3]_2[W_{10}O_{32}]$ (**1**).

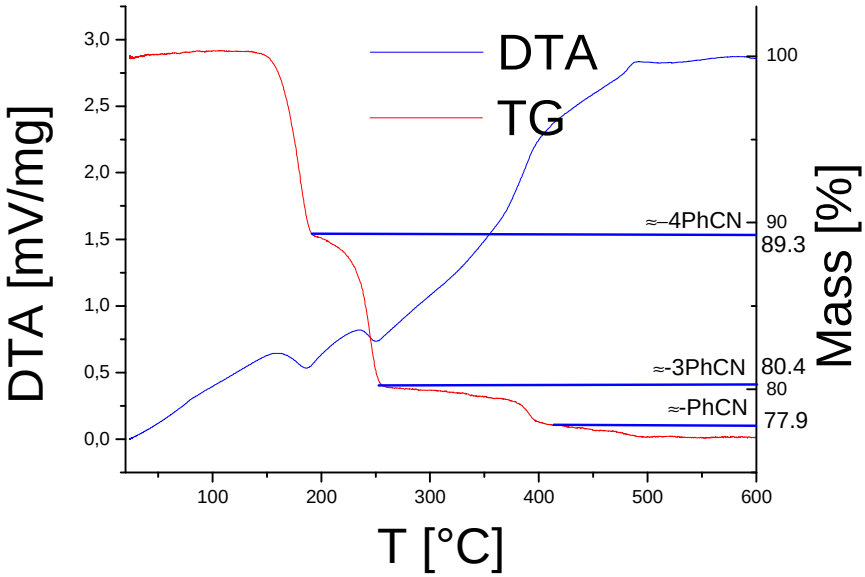

Figure S6. DTA/TG of $[Ag(PhCN)_2]_4[W_{10}O_{32}]$ (**2**).

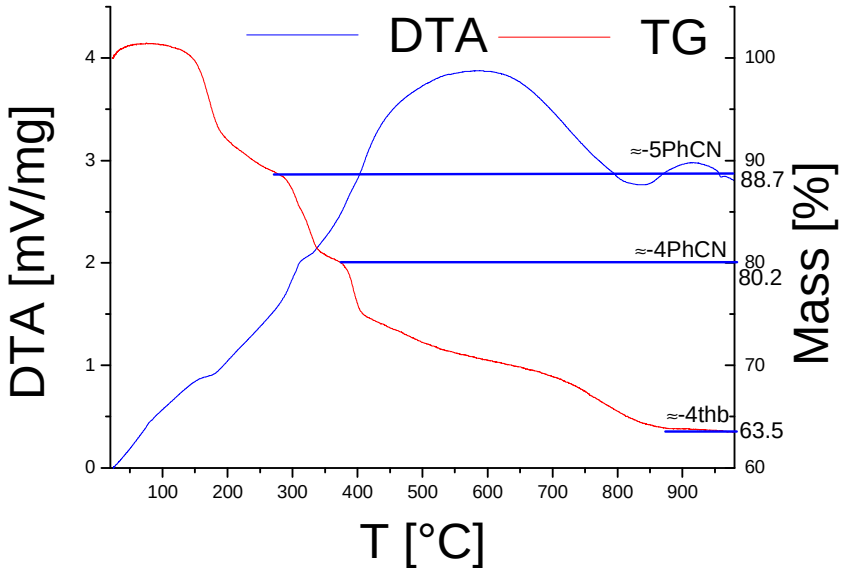

Figure S7. DTA/TG of $[Ag(PhCN)_2(thb)]_4[W_{10}O_{32}](PhCN)$ (**3**).

References

1. O. Glemser and C. Naumann, *Z. Anorg. Allg. Chem.*, 1951, **265**, 288; *Natl. Bur. Stand. (U.S.), Circ. 539*, 1953, **I**; *Natl. Bur. Stand. (U. S.), Monogr. 25*, 1981, **18**; P. M. Woodward, A. W. Sleight and T. Vogt, *J. Phys. Chem. Solids*, 1995, **56**, 1305.