Electronic Supporting Information

Four [Tp*W(μ_3-S)$_3$Cu$_3$(μ_3-Br)]-based clusters: synthesis, structural characterization and third-order NLO properties

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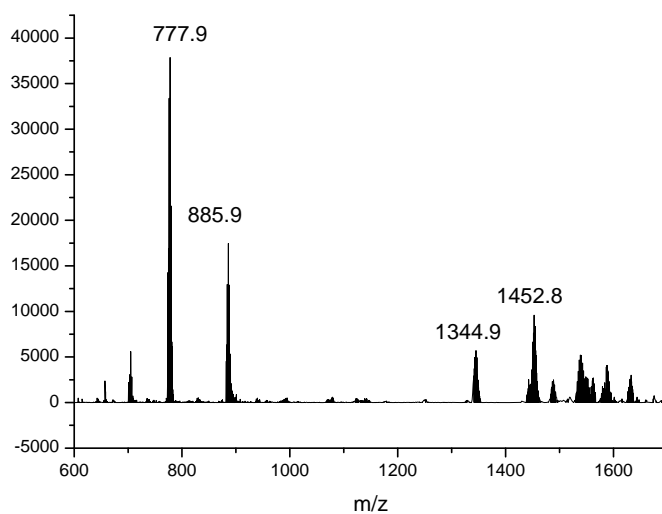
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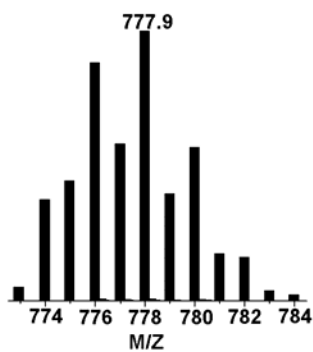
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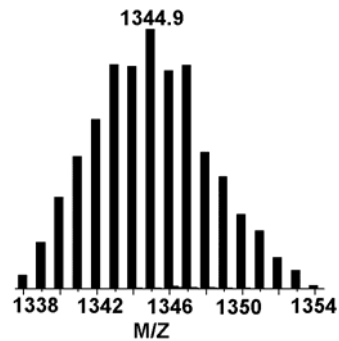
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(a)

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Figure S1. (a) The positive-ion ESI mass spectrum of **2**. (b) View of the observed (dark) and the

calculated (gray) isotopic patterns for the [{Tp*WS$_3$Cu$_2$}+DMF]$^+$ cation. (c) View of the observed

(dark) and the calculated (gray) isotopic patterns for the [(Tp*WS$_3$)$_2$Cu$_3$]$^+$ cation (c).
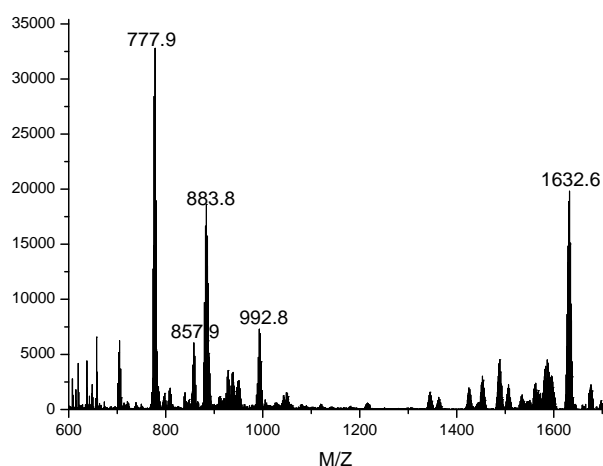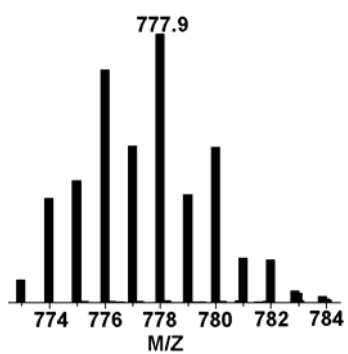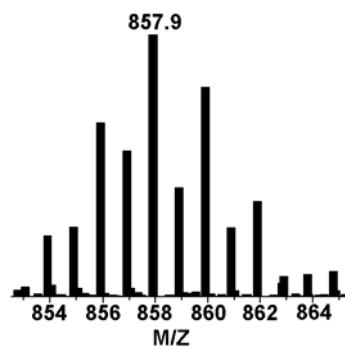
(a)

(b)

(c)

Figure S2. (a) The positive-ion ESI mass spectrum of **3** in DMF. (b) View of the observed (dark) and the calculated (gray) isotopic patterns for the $[\{Tp^*WS_3Cu_2\}+DMF]^+$ cation. (c) View of the observed (dark) and the calculated (gray) isotopic patterns for the $[\{Tp^*WS_3Cu_2Br\}+DMF+H]^+$ cation.
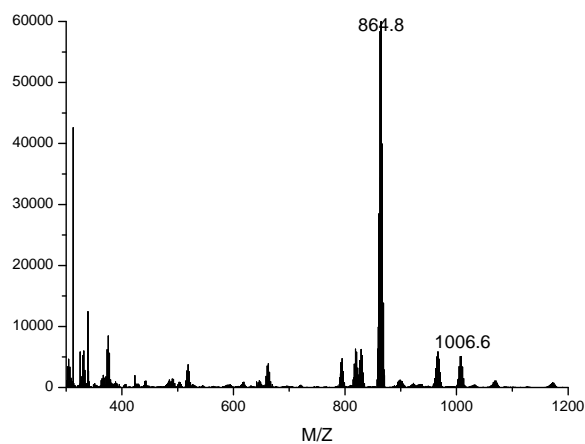
(a)

(b)

(c)

Figure S3. (a) The negative-ion ESI mass spectrum of **3** in DMF. (b) View of the observed (dark) and the calculated (gray) isotopic patterns for the $[Tp*WS_3Cu_2Br_2]^-$ anion. (c) View of the observed (dark) and the calculated (gray) isotopic patterns for the $[Tp*WS_3Cu_3Br_3]^-$ anion.
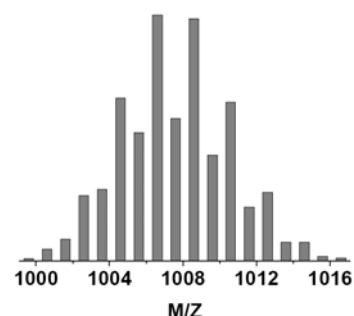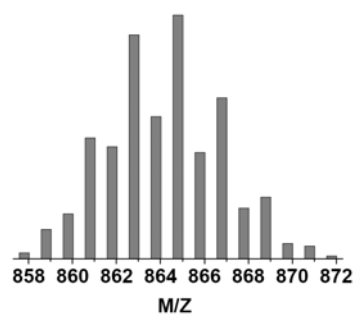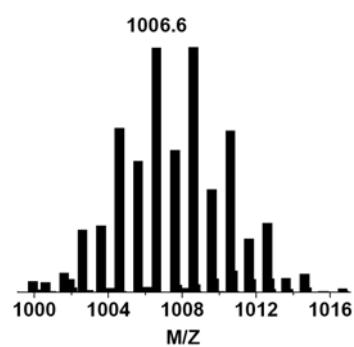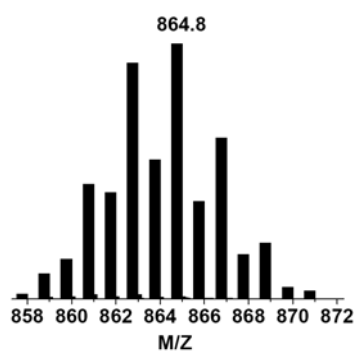
(a)

(b)

(c)

Figure S4. (a) The positive-ion ESI mass spectrum of **4** in DMF. (b) View of the observed (dark)

and the calculated (gray) isotopic patterns for the $[\{Tp^*WS_3Cu_2\}+DMF]^+$ cation. (c) View of the

observed (dark) and the calculated (gray) isotopic patterns for the $[\{Tp^*WS_3Cu_2(MA)_2\}]^+$ cation.
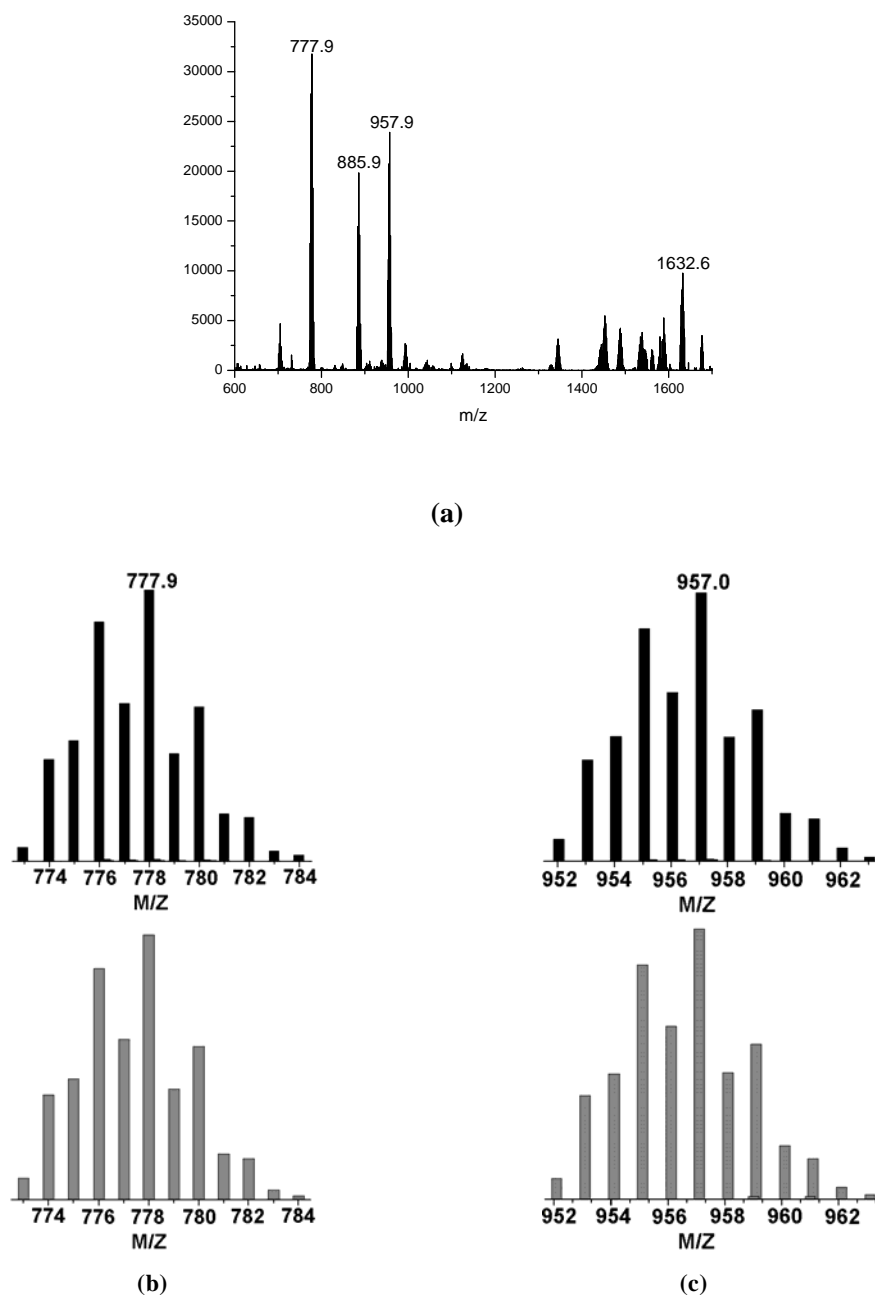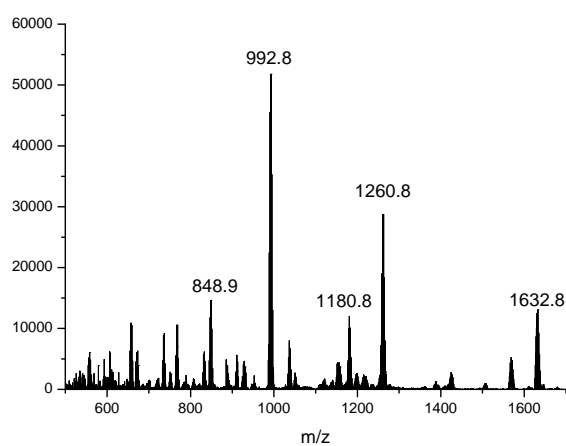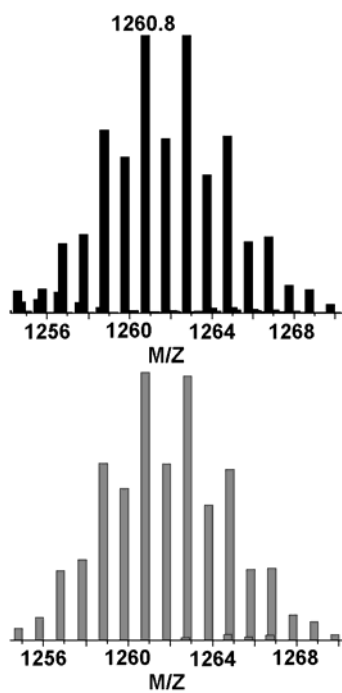
S6

(a)

(b)

Figure S5. (a) The positive-ion ESI mass spectrum of **5** in DMF. (b) View of the observed (dark)

and the calculated (gray) isotopic patterns for the $[\{Tp^*WS_3Cu_3Br_3(MA)_2\}+2H]^+$ cation.
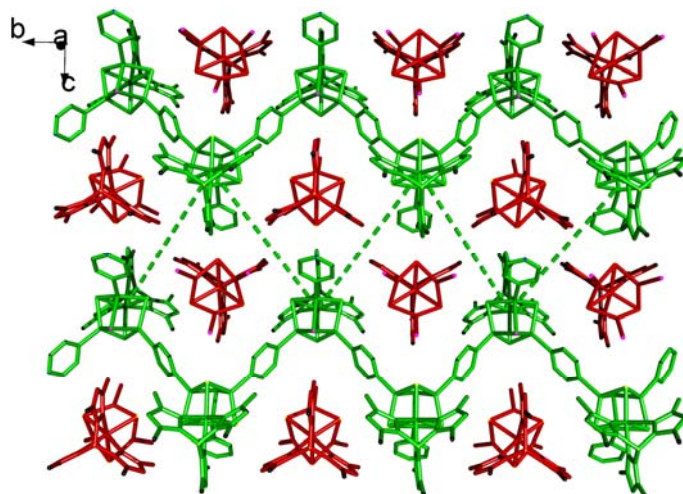
Figure S6. View of the arrangement of the cationic chain and the cluster anion of **3**·H_2O along the
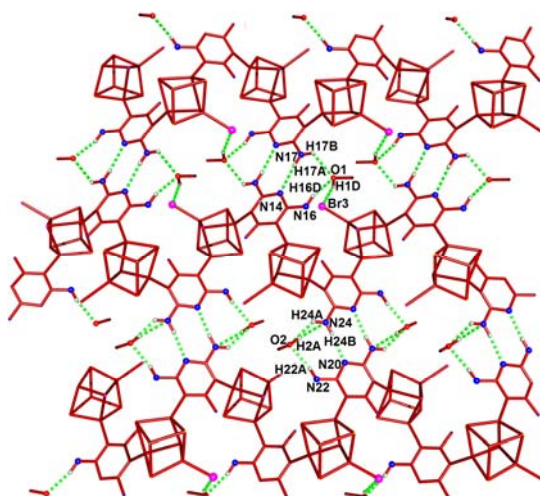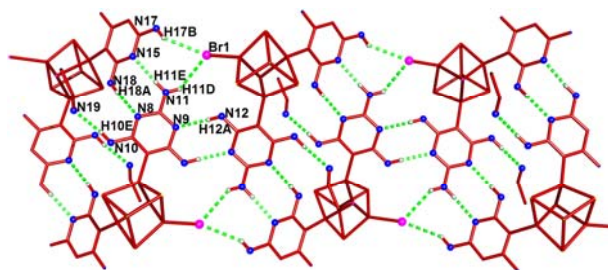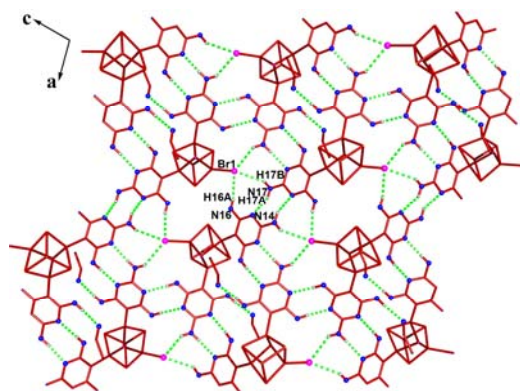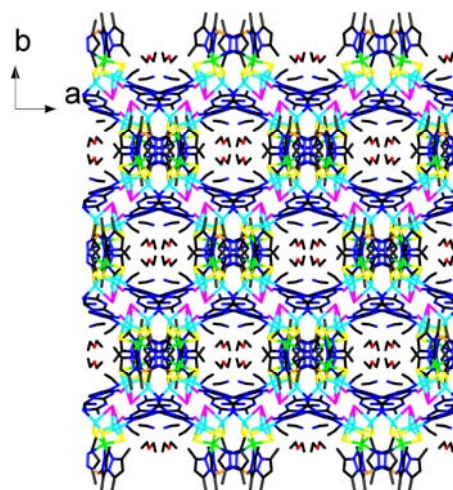
bc plane.

Figure S7.   View of the 2D network derived from the hydrogen bonding interactions among the

MA ligands and MeOH solvent molecules in **4**·2MeOH.

(a)

(b)

(c)

Figure S8. (a) The H-bonding 1D chain in **5**·MeCN·0.5Et$_2$O extended along the c axis. (b) The H-bonding 2D network in **5**·MeCN·0.5Et$_2$O viewed along the ac plane. (c) The 3D H-bound structure in **5**·MeCN·0.5Et$_2$O looking down the c axis.
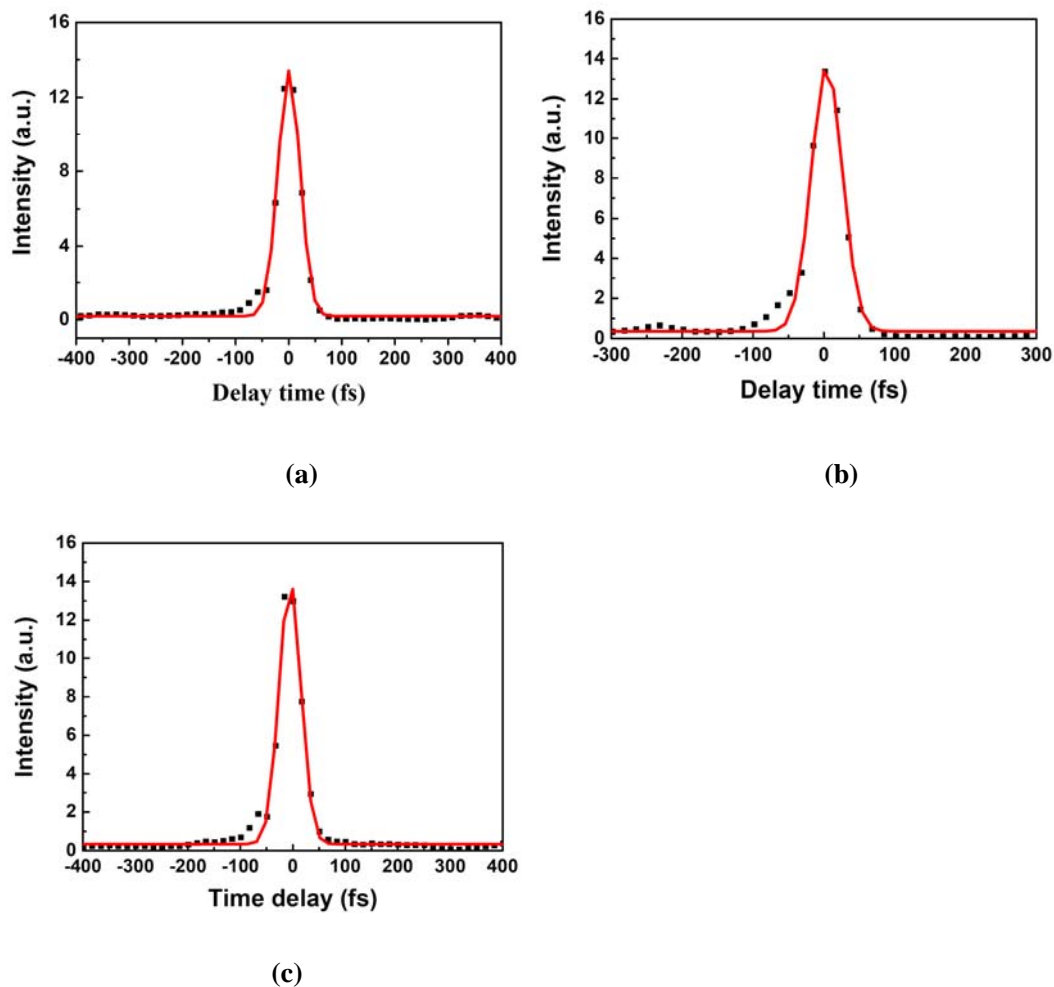
(a)

(b)

(c)

Figure S9. DFWM signal for the DMF solutions of **2** (a), **4 (b)** and **5 (c)** with concentrations

5.56×10^{-4} M for **2**, 2.75×10^{-4} M for **4** and 5.54×10^{-4} M for **5**. The black solid squares are

experimental data, and the red solid curves are the theoretical fit.