## **Electronic Supplementary Information**

Six [Tp\*WS<sub>3</sub>Cu<sub>2</sub>]-based clusters derived from [Et<sub>4</sub>N][Tp\*WS<sub>3</sub>], Cu(I) salts and phosphine ligands: syntheses, structures and enhanced third-order NLO properties

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**(a)** 



**(b)** 



(c)



(**d**)



Figure S1. (a) The positive-ion ESI mass spectrum of 2. (b) The positive-ion ESI mass spectrum of 3.
(c) The positive-ion ESI mass spectrum of 4. (d) The positive-ion ESI mass spectrum of 5. (e) The positive-ion ESI mass spectrum of 6. (f) The positive-ion ESI mass spectrum of 7.



**Figure S2.** (a) The calculated isotope pattern (top) and the positive-ion ESI mass spectrum (bellow) of the  $[Tp*WS_3Cu_2(dppm)]^+$  cation of **3**. (b) The calculated isotope pattern (top) and the positive-ion ESI mass spectrum (bellow) of the  $[Tp*WS_3Cu_2(dpppds)]^+$  cation of **4**. (c) The calculated isotope pattern (top) and the positive-ion ESI mass spectrum (bellow) of the  $[Tp*WS_3Cu_2(dpppds)]^+$  cation of **4**. (c) The calculated isotope pattern (top) and the positive-ion ESI mass spectrum (bellow) of the  $[Tp*WS_3Cu_2(bdppmapy)]^+$  cation of **5**. (d) The calculated isotope pattern (top) and the positive-ion ESI mass spectrum (bellow) of the  $[Tp*WS_3Cu_2(dpppda)]^+$  dication of **7**.



**Figure S3.** View of the cluster dication of **6** with a labelling scheme and 50% thermal ellipsoids. All H atoms were omitted for clarity.



**Figure S4.** (a) The DFWM signal for the DMF solutions of  $6 \times 10^{-5}$  M for **3**. (b) The DFWM signal for the DMF solutions of  $6 \times 10^{-5}$  M for **4**. (c) The DFWM signal for the DMF solutions of  $6 \times 10^{-5}$  M for **5**. (d) The DFWM signal for the DMF solutions of  $6 \times 10^{-5}$  M for **6**. (e) The DFWM signal for the DMF solutions of  $6 \times 10^{-5}$  M for **7** with 80 fs and 1.5 mm cell. The black solid squares are experimental data, and the red solid curves are the theoretical fit.