## **Supporting Information**

## Stepwise Addition of CuNCS onto [Et<sub>4</sub>N][Tp\*WS<sub>3</sub>]: Design, Syntheses, Structures and Third-Order Nonlinear Optical Properties

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## **Table of Contents**



**Figure S1.** View of the 2D network of **5** viewed along the *c* axis. The red and lake blue balls represent the  $[Tp*WS_4Cu_3]$  cores and the  $[Cu(NCS)_4]$  units. The yellow sticks represent the connections provided by the NCS groups.**5** looking down the *c* axis. All the hydrogen atoms were omitted.



**Figure S2**. *Z*-scan data of a  $2.33 \times 10^{-3}$  M DMF of **2** at 800 nm. (a) The data were evaluated under the open aperture configuration. (b) The data were assessed by dividing the normalized *Z*-scan data obtained under the closed aperture by the normalized *Z*-scan data in (a). The black squares are the experimental data, and the solid curve is the theoretical fit.



**Figure S3**. *Z*-scan data of  $1.12 \times 10^{-3}$  M DMF of **4** at 800 nm. (a) The data were evaluated under the open aperture configuration. (b) The data were assessed by dividing the normalized *Z*-scan data obtained under the closed aperture by the normalized *Z*-scan data in (a). The black dots are the experimental data, and the solid curve is the theoretical fit.



**Figure S4**. *Z*-scan data of  $1.03 \times 10^{-3}$  M MeCN of **5** at 532 nm. (a) The data were evaluated under the open aperture configuration. (b) The data were assessed by dividing the normalized *Z*-scan data obtained under the closed aperture by the normalized *Z*-scan data in (a). The black dots are the experimental data, and the solid curve is the theoretical fit.