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Electronic Supplementary Information

Rectangle and [2] catenane from cluster modular construction

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Experiment section

General procedures

[Et₄N][Tp*WS₃] (1), [Et₄N][Tp*WS₃(CuCl)₃] (2), and [Et₄N][{Tp*W(μ_3 -S)₃Cu₃Cl}₂(μ -Cl)₂(μ_4 -Cl)] (3) were synthesized according to the literature.^{S1-S3} All the solvents used were pretreated with activated molecular sieves and refluxed over CaH₂ under N₂. Other chemical reagents were directly available from commercial sources and used without further purification. Elemental analyses for N, C and H were conducted by Carlo-Erba CHNO-S microanalyzer. Infrared (IR) spectra were conducted by Varian 1000 spectrometer (400–4000 cm⁻¹) with KBr discs. UV–Vis spectra were conducted by Varian Cary-50 UV–Vis spectrophotometer.

Synthesis of [Et₄N]₂[{Tp*WS₃Cu₃(CN)_{0.5}}₂(µ-Cl)₂(µ₄-Cl)]₂(PF₆)₂ (4)

A CH₂Cl₂/CHCl₃ (2.5 mL/2.5 mL) solution of **1** (22.6 mg, 0.032 mmol), [Cu(MeCN)₄]PF₆ (35.6 mg, 0.096 mmol), CsCl (8.1 mg, 0.048 mmol) and isonicotinic acid (5.9 mg, 0.048 mmol) was stirred for 30 minutes under ambient temperature and then CuCN (4.3 mg, 0.048 mmol) was added. The solution was filtered again after 12 hours of stirring. Hexane was carefully layered onto the filtrate to generate black crystals of **4** in about 15 days. The crystals were isolated and washed with hexane. Yield: 8.7 mg (28 % based on W). Anal. Calcd for $C_{78}H_{128}B_4Cl_6Cu_{12}F_{12}N_{28}P_2S_{12}W_4$: C 24.10, H 3.33, N 10.09; found: C 23.55, H 3.28, N 9.62. UV-Vis (MeCN, λ_{max} (nm (ϵ M⁻¹cm⁻¹))): 315 (29930). IR (KBr disc): 3734 (w), 2971 (m), 2922 (m), 2852 (w), 2565 (m), 2168 (m), 1635 (m), 1547 (s), 1453 (s), 1439 (s), 1415 (s), 1385 (m), 1347 (s), 1221 (s), 1071 (m), 1034 (s), 984 (w), 859 (s), 849 (s), 790 (w), 692 (w), 651 (w), 558 (m), 481 (w), 415 (w) cm⁻¹.

Synthesis of [(Tp*WS₃Cu₃)₂(µ₃-Cl)₂(dpp)₃]₂(OTf)₄·2CHCl₃ (5·2CHCl₃)

Method 1: A CH₂Cl₂/CHCl₃ (2.0 mL/2.0 mL) solution of **2** (40.2 mg, 0.04 mmol) and AgOTf (30.8 mg, 0.12 mmol) was stirred for 30 minutes under ambient temperature and then filtrated. Ligand

bpp (23.8 mg, 0.12 mmol) was subsequently introduced to the purple filtrate and the mixture was further stirred for 2 hours before filtration. Et₂O was carefully layered onto the filtrate to generate black crystals of **5**·2CHCl₃ in about 4 days. The crystals were isolated by filtration and washed with Et₂O. Yield: 18.3 mg (35 % based on W). **Method 2**: A CH₂Cl₂/CHCl₃ (2.5 mL/2.5 mL) solution of **3** (47.9 mg, 0.025 mmol) and AgOTf (2.8 mg, 0.05 mmol) was stirred for 30 minutes under ambient temperature and then filtrated. Ligand bpp (14.8 mg, 0.075 mmol) was subsequently introduced to the purple filtrate and the mixture was further stirred for 2 hours before filtration. Et₂O was carefully layered onto the filtrate to generate black crystals of **5**·2CHCl₃ in about 4 days. The crystals were isolated by filtration and washed with Et₂O. Yield: 26.0 mg (40 % based on W). Anal. Calcd for C₁₄₄H₁₇₄B₄Cl₁₀Cu₁₂F₁₂N₃₆O₁₂S₁₆W₄: C 33.02, H 3.36, N 9.63; found: C 33.26, H 3.62, N 9.90. UV-Vis (MeCN, λ_{max} (nm (ε M⁻¹cm⁻¹))): 315 (19260). IR (KBr disc): 3735 (vw), 2925 (w), 2567 (m), 1617 (s), 1547 (m), 1507 (w), 1416 (m), 1384 (w), 1350 (m), 1276 (m), 1223 (m), 1155 (m), 1070 (w), 1031 (s), 860 (w), 819 (w), 689 (w), 668 (m), 638 (m), 518 (w), 480 (vw), 418 (w) cm⁻¹.

X-ray structure determination

All the structures were measured on a Bruker D8-Quest (4) and a Bruker D8-Venture (5·2CHCl₃) CCD X-ray diffractometers with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. Single crystals were mounted on the top of a glass fiber in a stream of nitrogen. The program Bruker SAINT was applied for the refinement of cell parameters and the reduction of collected data of 4 and 5·2CHCl₃, respectively, while absorption corrections (multi-scan) were used.^{S4} By using the full-matrix least-squares method in the *SHELXTL-2016* programs,^{S5} all the crystal structures were solved by direct methods and refined on F^2 . For 4, the NEt₄ cation lies on a special position of higher symmetry than the molecule can possess. It was treated as disorder by applying PART –1 and

PART 0 in the *.ins* file with the site occupation factors changed to 0.50 for the atoms. N1/C1 displayed occupational disorder and the occupancies for these domains were fixed at 0.50 each, followed by applying EXYZ and EADP for these disordered pairs. The H atom on B1 was added by HFIX 13 first and the B–H distances restrained to 1.15Å and thermal parameters constrained to $U_{iso}(H) = 1.2U_{eq}(B)$. For 4 and 5·2CHCl₃, some amount of spatially delocalized electron density in the lattices were found but acceptable refinement results could not be obtained for these electron densities. The solvent contributions were then modeled using SQUEEZE in the Platon program suite.^{S6} Crystallographic data have been uploaded to the Cambridge Crystallographic Data Center (CCDC) as supplementary publication numbers 1814877 and 1814878. These data can be either achieved free of charge from the CCDC *via* www.ccdc.cam.ac.uk/data_request/cif.

Third-order NLO measurements of 1-5

DMF solutions of 1-5 (2.0 × 10⁻⁴ M) were placed in a 2 mm quartz cuvette. Solutions of 1-5 were stable in air and laser under experimental conditions. The pico-second *Z*-scan technique and a linear polarized laser light ($\lambda = 532$ nm; repetition rate = 2 Hz; width = 15ps) generated from a frequency-doubled, mode-locked, Q-switched Nd:YAG laser were applied to investigate absorption and refraction. The test method was the same as that conducted previously.⁸⁷

Third-order NLO properties of 3-5

The nonlinear absorption was measured with open aperture. The transmittance of light (*T*) is a function of the sample's *Z* position. The nonlinear absorption ($\alpha = \beta$ (*I_i*)) and the linear absorption coefficient (α_0) are determined by formula (1) below, where α is the effective third-order NLO absorptive coefficient, τ is the time, and *L* was the sample thickness.

$$T(Z) = \frac{\alpha_0}{\sqrt{\pi}\beta I_i(Z)(1 - e^{-\alpha_0 L})} \int_{-\infty}^{\infty} \ln \left[1 + \beta I_i(Z) \frac{1 - e^{-\alpha_0 L}}{\alpha_0} e^{-\tau^2} \right] d\tau$$
(1)

The nonlinear refractive data was determined by the ratio of the transmittance measured by closed- and open-aperture. The difference between trough and peak positions (ΔZ_{V-P}), and difference between their normalized transmittance values (ΔT_{V-P}) fit the following two formulae originated for a third-order NLO process. Also, the effective third-order NLO refractive index n_2 could be achieved by calculation with formula (3) where *I* is the peak irradiation intensity at focus, and λ is the wavelength of the laser.

$$\Delta Z_{V-P} = 1.72 \pi \omega_0^2 / \lambda \tag{2}$$

$$n_2^{eff} = \lambda \alpha_0 \Delta T_{V-P} / \left[0.812 \pi I \left(1 - e^{\alpha L} \right) \right]$$
(3)

The effective third-order NLO susceptibility $\chi^{(3)}$ and the second hyperpolarizability γ values could be obtained by calculation with the following formulas from β and n_2 . *N* is the density of the molecules in the unit of number of molecules per cubic centimeters, and n_0 is the linear refractive index of DMF ($n_0 = 1.43$).

$$\chi_{I}^{(3)} = 9 \times 10^{8} \varepsilon_{0} n_{0}^{2} c^{2} \beta / (4\omega\pi)$$
(4)

$$\chi_R^{(3)} = c n_0^2 n_2 / (80\pi)$$
⁽⁵⁾

$$\chi^{(3)} = \left[\left(\chi_{I}^{(3)} \right)^{2} + \left(\chi_{R}^{(3)} \right)^{2} \right]^{1/2}$$
(6)

$$\gamma = \chi^{(3)} / [N((n_0^2 + 2)/3)^4]$$
(7)

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	4	5·2CHCl ₃
formula	$C_{78}H_{128}B_4Cl_6Cu_{12}F_{12}N_{28}P_2S_{12}W_4\\$	$C_{144}H_{174}B_4Cl_{10}Cu_{12}F_{12}N_{36}O_{12}S_{16}W_4$
fw	3886.56	5237.76
cryst. syst.	monoclinic	monoclinic
space group	C2/m	C2/c
a/Å	16.850(7)	26.5566(15)
<i>b</i> /Å	35.352(14)	22.6712(15)
c/Å	17.915(7)	36.931(2)
a/deg	90	90
β /deg	116.535(11)	91.034(2)
γ/deg	90	90
$V/\text{\AA}^3$	9547(7)	22232(2)
$D_c/({\rm g~cm^{-3}})$	1.352	1.565
Ζ	4	8
μ (Mo–K α)/mm ⁻¹	3.980	3.515
<i>F</i> (000)	3776	10336
total reflns	209926	250032
unique reflns	11671	27574
no. of observations	7287	17320
no. of param	339	1096
R _{int}	0.0992	0.1403
R_1^a	0.0860	0.0773
wR_2^b	0.2322	0.1938
GOF^{c}	1.062	1.055

 Table S1
 Crystal data and structure refinement parameters for 4 and 5·2CHCl₃.

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. {}^{b}wR_{2} = \{\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}\}^{1/2}. {}^{c} \text{GOF} = \{\Sigma w ((F_{o}^{2} - F_{c}^{2})^{2})] / (n-p)\}^{1/2}, \text{ where } n = \text{number of reflections and } p = \text{total number of parameters refined.}$

W(1)…Cu(1)	2.6412(19)	Cu(2)-Cl(1)	2.226(4)	
W(1)····Cu(2)	2.663(2)	Cu(2)-S(3)	2.228(3)	
W(1)····Cu(3)#1	2.674(2)	Cu(2)-S(2)	2.247(4)	
Cu(1)-C(1)	1.904(12)	Cu(2)-Cl(2)	2.739(3)	
Cu(1)-N(1)	1.904(12)	Cu(2)····Cu(3)#1	2.885(3)	
Cu(1)-S(1)	2.215(4)	Cu(3)-S(3)#1	2.234(4)	
Cu(1)-S(2)	2.218(4)	Cu(3)-Cl(1)	2.237(4)	
Cu(1)···· $Cu(2)$	2.874(3)	Cu(3)-S(1)#1	2.246(4)	
Cu(1)…Cu(3)#1	2.878(3)	Cu(3)-Cl(2)	2.723(3)	

Table S2Selected bond lengths [Å] 4.

Symmetry transformations used to generate equivalent atoms: #1: -x + 1, y, -z + 1; #2: x, -y + 1, z; #3: -x + 1/2, -y + 3/2, -z + 2.

W(1)····Cu(2)	2.6392(13)	Cu(3)-S(3)	2.232(3)
W(1)····Cu(1)	2.6431(13)	Cu(3)-S(1)	2.234(3)
W(1)····Cu(3)	2.6510(13)	Cu(3)-Cl(1)	2.635(3)
W(2)····Cu(5)	2.6186(13)	Cu(4)-S(5)	2.219(3)
W(2)····Cu(4)	2.6473(13)	Cu(4)-S(4)	2.234(3)
W(2)····Cu(6)	2.6660(14)	Cu(4)-Cl(2)	2.572(3)
Cu(1)-S(2)	2.228(3)	Cu(4)····Cu(5)	2.8279(19)
Cu(1)-S(3)	2.245(3)	$Cu(4)\cdots Cu(6)$	2.868(2)
Cu(1)-Cl(1)	2.602(3)	Cu(5)-S(6)	2.217(3)
$Cu(1)\cdots Cu(2)$	2.7964(19)	Cu(5)-S(5)	2.222(3)
$Cu(1)\cdots Cu(3)$	2.8452(18)	Cu(5)-Cl(2)	2.701(3)
Cu(2)-S(2)	2.219(3)	Cu(5)····Cu(6)	2.8105(19)
Cu(2)-S(1)	2.228(3)	Cu(6)-S(6)	2.226(3)
Cu(2)-Cl(1)	2.652(3)	Cu(6)-S(4)	2.259(3)
$Cu(2)\cdots Cu(3)$	2.8737(18)	Cu(6)-Cl(2)	2.595(3)

Table S3Selected bond lengths [Å] for 5·2CHCl3.



Scheme S1 Hypothesis that the Cu(I) salt introduced at the later stage becomes the terminal Cu-X of the cluster in the synthesis procedure of **4**.



Scheme S2 Proposed Lego-like bricks for the basic structural components of 1-5



Fig. S1 Z-scan data for **3** $(2.0 \times 10^{-4} \text{ M})$ in DMF solution at 532 nm which displayed a reversed absorption (upper) and nonlinear refraction (bottom). The black solid spheres are experimental data, and the red curve is the theoretical fit.



Fig. S2 Z-scan data for **5** $(2.0 \times 10^{-4} \text{ M})$ in DMF solution at 532 nm which displayed a reversed absorption. The black solid spheres are experimental data, and the red curve is the theoretical fit.



Fig. S3 Electronic spectra of **4** and **5** $(1.0 \times 10^{-4} \text{ M})$ in MeCN solution.