Electronic Supplementary Information (ESI)

Activation and amplification of the third-order NLO and luminescent responses of a precursor cluster by a supramolecular approach†

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Table of Contents

Experimental Section······S3

General

Synthesis of **2**·2DMF·MeCN and **3**·4DMF·2MeCN

X-ray Crystallographic Study

The details of the equations used in calculation for third-order NLO properties

Table S1. Summary of crystallographic data for **2**·2DMF·MeCN and **3**·4DMF·2MeCN······S7

Figure S1. The terminal chlorides of the anion of the precursor cluster **1** are replaced by cyanide ligands while DMF molecule fills into the void of the incomplete cubanelike strutcure.······S8

Figure S2. The structure of **2**. a) 1D zigzag chain linked by the Cu$_{\text{cluster}}$-μ-CN-Cu$_{\text{metalloligand}}$ bridges. b) The 2D layer structure of **2** with 4 and 8-membered metallomacrocycles. **c)** Schematic view of the structure.······S9

Figure S3. The structure of **3**. a) The [Tp*WS$_3$Cu$_3$(μ_3-DMF){Cu(CN)$_3$}]$_2$ dicubane-like cluster unit of **3**; the dark green Cu at the top and bottom of the figure belong to two further cubane units; for clarity, methyl groups were omitted. b) 1D chain linked through the Cu$_{\text{cluster}}$-μ-CN-Cu$_{\text{metalloligand}}$ -μ-CN-Cu$_{\text{metalloligand}}$ expanded bridges. c) The 2D layer structure of **3** with 4 and 12-membered metallmacrocycles. d) Schematic view that the 2D layers interconnected in the ABAB mode to the 3D anion network.······S11

Figure S4 3-connected topological network of **3** with unprecedented Schläfli symbol (4.8.10)$_2$(8.8.12) (left) and double-stranded helixes with the opposite handless, right-and left-handed helicates are simplified to green and rose respectively (right).······S12

Figure S5 Coordination environment of the potassium ion in **3**.······S12

Figure S6. Electronic spectra of **1-3**······S13

Figure S7 The DFWM signal for the DMF solutions of **2** and **3**······S13

Figure S8 Excitation (top) and emission (bottom) spectra of **2** and **3** in the solid state at ambient temperature.······S14

Figure S9. IR spectrum of compound **2**.······S15

Figure S10. IR spectrum of compound **3**.······S15

Experimental Section

General. Solvents like DMF and MeCN were dried over CaH_2 and distilled in vacuo. All chemicals and reagents were obtained from commercial sources and used as received. Compound **1** was prepared according to the literature procedures previously reported.[1] The elemental analyses for C, H, N were performed on a Carlo-Erba CHNO-S microanalyzer. The IR spectra were recorded on a Varian 1000 FT-IR spectrometer as KBr disks (4000-400 cm^{-1}). UV-vis spectra were measured on a Varian 50 UV-visible spectrophotometer. The emission and excitation spectra were measured on a Varian Cary Elipse fluorescence spectrophotometer.

Synthesis of 2·2DMF·MeCN. To a Pyrex glass tube (10 cm in length and 0.5 cm in diameter) was loaded **1** (124 mg, 0.1 mmol), CuCN (27mg, 0.3 mmol), 2 mL of MeCN and 1 mL of DMF. The tube was sealed and heated in an oven at 85°C for two days. After being cooled to ambient temperature at a rate of 5°C 100 min^{-1}, black crystals of **2**·2DMF·MeCN were formed. Yield: 84 mg (55% based on W). Anal. Calcd. for $C_{50}H_{75}B_2Cu_8N_{23}O_4S_6W_2$: C, 28.10; H, 3.48; N, 14.96. Found: C, 28.07; H, 3.35; N, 14.93%. IR (KBr): 3442 (br, s), 2964 (w), 2924 (w), 2131 (m), 1647 (s), 1548 (m), 1436 (w), 1413 (m), 1384 (m), 1349 (m), 1221 (m), 1071 (m), 1035 (m), 860 (w), 822 (w), 792 (w), 650 (w), 416 (w) cm^{-1}.

Synthesis of 3·4DMF·2MeCN. Method A: To a Pyrex glass tube (10 cm in length and 0.5 cm in diameter) was loaded **1** (124 mg, 0.1 mmol), 2 mL of MeCN and 1 mL of DMF and $KCu(CN)_2$ (31 mg, 0.3 mmol). The tube was sealed and heated in an oven at 100°C for two days. After being cooled to ambient temperature at a rate of 5°C 100 min^{-1}, black crystals of **3**·4DMF·2MeCN were formed. Yield: 32 mg (17% based on W). Anal. Calcd. for $C_{62}H_{78}B_2Cu_{10}KN_{28}O_6S_6W_2$: C, 29.98; H, 3.04; N, 15.27. Found: C, 30.04; H, 3.09; N, 15.32%. IR (KBr): 3441 (br, s), 2924 (w), 2873 (w), 2125 (s), 1649 (s), 1547 (m), 1439 (m), 1414 (m), 1385 (m), 1348 (s), 1223 (s), 1096 (m), 1070 (s), 860 (w), 1033 (s), 986 (w), 860 (m), 807 (m), 691 (w), 665 (m), 481 (w), 415 (m) cm^{-1}.

Method B: To the 2 mL of MeCN and 1 mL of DMF mixed solution containing **1** (124 mg, 0.1 mmol) was added $KCu(CN)_2$ (31 mg, 0.3 mmol)). After two hours, some dark red precipitate was gradually developed. The resulting mixture was quickly filtered at room temperature, and black crystals of **3**·4DMF·2MeCN were formed by evaporation of solvents from the filtrate a week later. Yield: 69 mg (37% based on W).

X-ray Crystallographic Study

Diffraction intensities of **2**·2DMF·MeCN and **3**·4DMF·2MeCN were collected on a Rigaku Mercury CCD X-ray diffractometer (Mo Kα, $\lambda = 0.71073$ Å). The crystals of **2**·2DMF·MeCN and **3**·4DMF·2MeCN were mounted at the top of a glass fiber with grease at 223 K in a stream of gaseous nitrogen. Cell parameters were refined on all observed reflections by using the program *CrystalClear* (Rigaku and MSc, Ver. 1.3, 2001). The collected data were reduced by the program *CrystalClear*, and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **2**·2DMF·MeCN and **3**·4DMF·2MeCN were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with *SHELXTL-97* program.[2] All the non-hydrogen atoms except the MeCN and DMF solvent molecules in **2**·2DMF·MeCN and **3**·4DMF·2MeCN were refined anisotropically. Hydrogen atoms for the C atoms of MeCN and DMF solvent molecules in **2**·2DMF·MeCN and MeCN solvent molecules in **3**·4DMF·2MeCN were not located. Each H atom at the B atom of **2**·2DMF·MeCN and **3**·4DMF·2MeCN were located from Fourier maps. Other H atoms were placed in geometrically idealized positions (C-H=

0.98 Å, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups; C-H = 0.99 Å, with $U_{iso}(H) = 1.2U_{eq}(C)$ for methylene groups; C-H = 0.95 Å, with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic rings) and constrained to ride on their parent atoms. Crystal data along with data collection and refinement parameters for **2**·2DMF·MeCN and **3**·4DMF·2MeCN are summarized in **Table S1**.

References

[1] Z. H. Wei, H. X. Li, M. L. Cheng, X. Y. Tang, Y. Chen, Y. Zhang and J. P. Lang, *Inorg. Chem.,* 2009, **48**, 2808.

[2] (a) Sheldrick, G. M. *SHELXS-97, Program for Solution of Crystal Structures*, University of Göttingen, Germany, **1997**. (b) Sheldrick, G. M. *SHELXL-97, Program for Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

Details of the equations used in calculations of Third-order NLO properties

The third-order nonlinear optical susceptibility $\chi^{(3)}$ is measured *via* a comparison with that of a reference sample CS_2, calculated from the DFWM signal (*I*), the linear refractive index (*n*), the sample thickness (*L*) and absorption correction factor using eq. 1:[1]

$$\chi_s^{(3)} = \left(\frac{I_s}{I_r}\right)^{1/2} \cdot \frac{L_r}{L_s} \cdot \left(\frac{n_s}{n_r}\right)^2 \cdot \frac{\alpha \cdot L \cdot \exp(\alpha L/2)}{1-\exp(-\alpha L)} \cdot \chi_r^{(3)} \qquad (1)$$

where the subscripts "*s*" and "*r*" represent the parameters for the sample and CS_2. And α is the linear absorption coefficient. The last fraction comes from the sample absorption and equals to 1 while the sample has no absorption around the employed laser wavelength. The values of $\chi_r^{(3)}$ and n_r for CS_2 are 6.7×10^{-14} esu and 1.632, respectively.[2]

The third-order nonlinear refractive index n_2 in isotropic media is estimated through eq. 2:[3]

$$n_2(esu) = \frac{12\pi\chi^{(3)}}{n^2} \qquad (2)$$

where *n* is the linear refractive index of the solution.

The second-order hyperpolarizability γ of a molecule in isotropic media is related to the solution $\chi^{(3)}$ by Equation (3):[4]

$$\gamma = \frac{\chi^{(3)}}{Nf^{4}} \qquad (3)$$

where N is the number density of the solute per milliliter, and f^4 is the local field correction factor which is $[(n^2 + 2)/3]^4$ (n is the linear refractive index of solution).

References

[1] Yang, Y.; Samoc, M.; Prasad, P. N. *J. Chem. Phys*. **1991**, *94*, 5282.

[2] Orezyk, M. E.; Samoc, M.; Swiatkiewicz, J.; Prasad, P. N. *J. Chem. Phys*. **1993**, 98, 2524.

[3] Jenekhe, S. A.; Lo, S. K.; Flom, S. R. *Appl. Phys. Lett*. **1989**, *54*, 2524.

[4] Mandal, B. K.; Bihari, B.; Sinha, A. K.; Kamath, M.; Chen, L. *Appl. Phys. Lett*. **1995**, *66*, 932.

Table S1. Summary of crystallographic data for **2**·2DMF·MeCN and **3**·4DMF·2MeCN**.**

Compound	**2**	**3**
Empirical Formula	$C_{50}H_{75}B_2Cu_8N_{23}O_4S_6W_2$	$C_{62}H_{78}B_2Cu_{10}KN_{28}O_6S_6W_2$
Formula Weight	2152.31	2567.80
Crystal System	monoclinic	monoclinic
Space Group	C2/*c*	C2/*c*
a (Å)	26.200(5)	15.165(3)
b (Å)	16.905(3)	26.907(5)
c (Å)	19.395(4)	23.715(5)
β (°)	117.36(3)	106.91(3)
V (Å^3)	7629(3)	9258(4)
Z	4	4
ρ_{calc} (g/cm^3)	1.859	1.730
F(000)	4148	5004
μ (MoKα,mm^{-1})	5.402	2.136
R^a	0.0718	0.0720
$R_w{}^b$	0.2040	0.2040
GOF^c	1.189	1.120

[a]$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$R_w = \{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [c]GOF = $\{\Sigma w((F_o^2-F_c^2)^2)/(n-p)\}^{1/2}$, where

M is the number of reflections and N is the number of parameters.

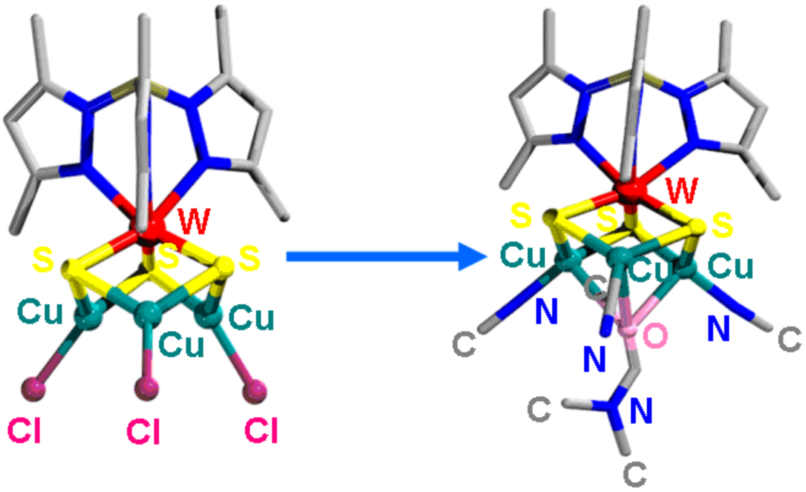

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Figure S1. The terminal chlorides of the anion of the precursor cluster **1** are replaced by cyanide ligands while the O-atom of the DMF molecule completes the cubanelike strutcure.

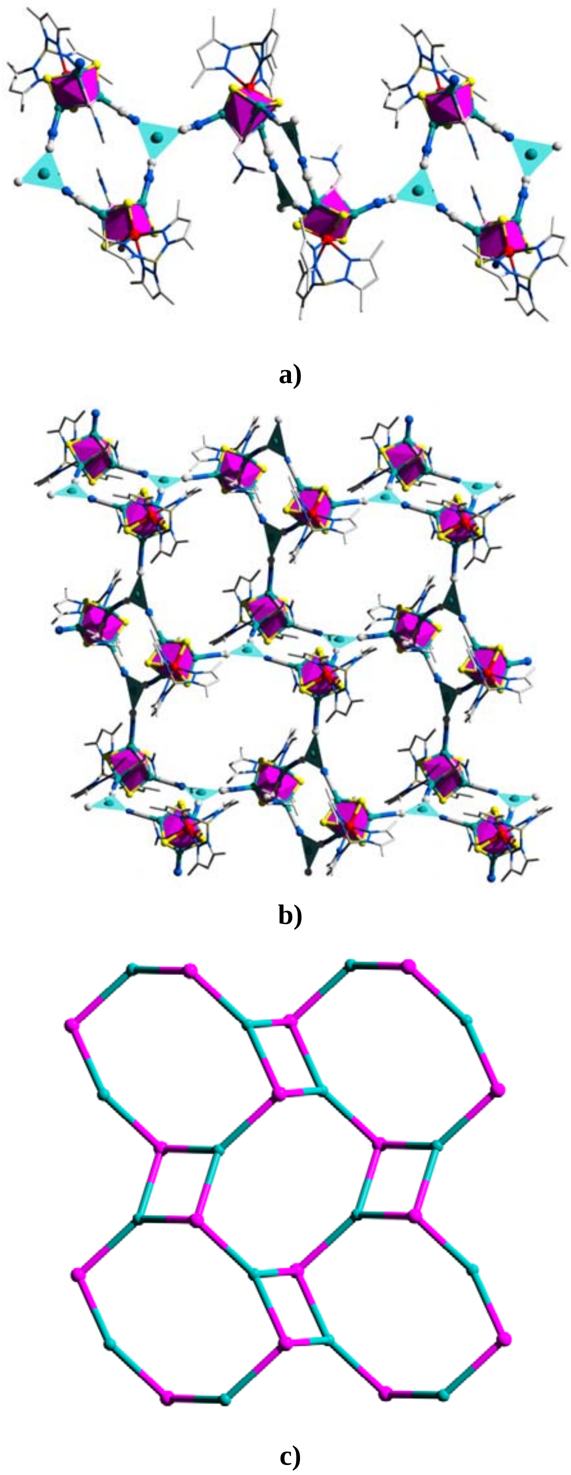
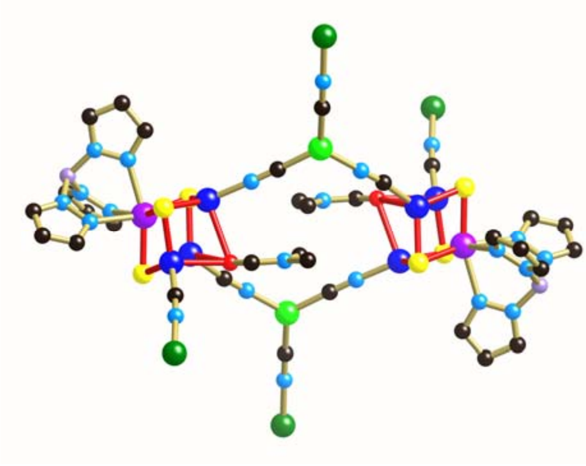
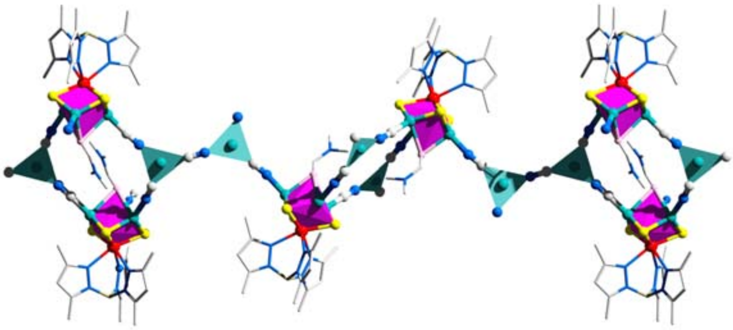


Figure S2. The structure of **2**. a) 1D zigzag chain linked by the $Cu_{cluster}$-μ-CN-$Cu_{metalloligand}$ bridges. b) The 2D layer structure of **2** with 4 and 8-membered metallomacrocycles. C gray, N blue, O pink, B gray green, S yellow, W red, Cu bluish green. **c)** Schematic view of the structure. Rose and bluish green balls represent W/Cu/S clusters and Cu sites respectively.



a)



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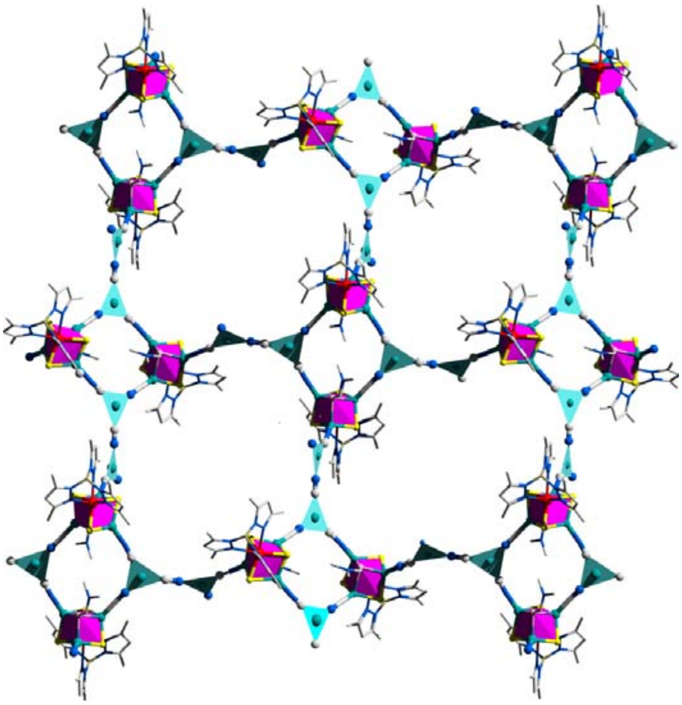

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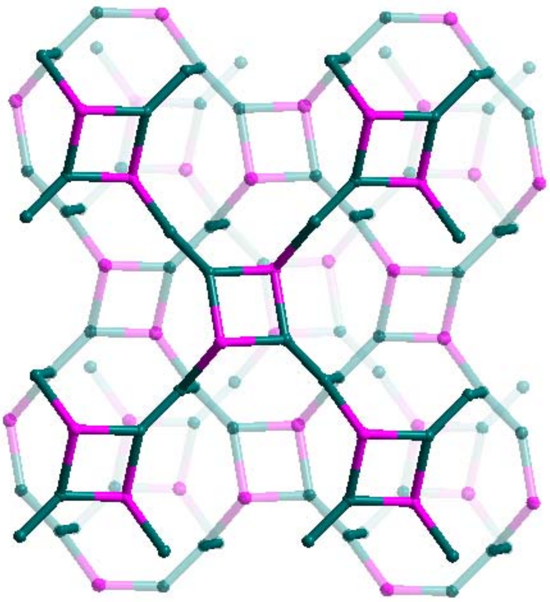

d)

Figure S3. The structure of **3**. a) The [Tp*WS$_3$Cu$_3$(μ_3-DMF){Cu(CN)$_3$}]$_2$ dicubane-like cluster unit of **3**; the dark green Cu at the top and bottom of the figure belong to two further cubane units; for clarity, methyl groups have been omitted. b) The 1D chain linked through the Cu$_{\text{cluster}}$-μ-CN-Cu$_{\text{metalloligand}}$-μ-CN-Cu$_{\text{metalloligand}}$ expanded bridges. c) The 2D layer structure of **3** with 4 and 12-membered metallmacrocycles**.** C gray, N blue, O pink, B gray green, S yellow, W red, Cu bluish green. d) Schematic view that the 2D layers interconnected in the ABAB mode to the 3D anion network. Rose and bluish green balls represent W/Cu/S clusters and Cu sites respectively.

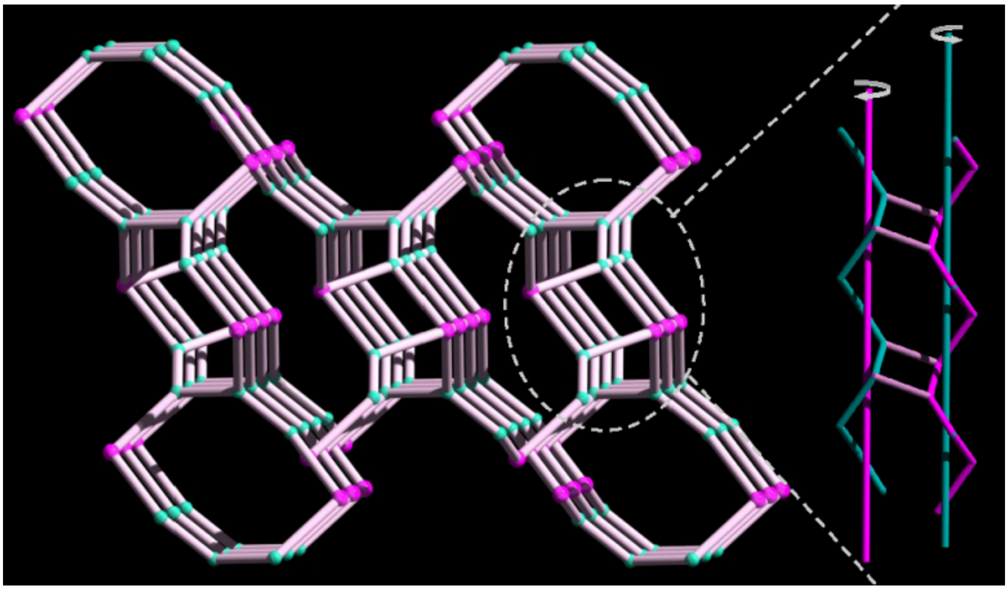

Figure S4. 3-connected topological network of **3** with unprecedented Schläfli symbol $(4.8.10)_2(8.8.12)$ (left) and double-stranded helixes with the opposite handless, right-and left-handed helicates are simplified to green and rose respectively (right). Rose and bluish green balls represent W/Cu/S clusters and Cu sites.

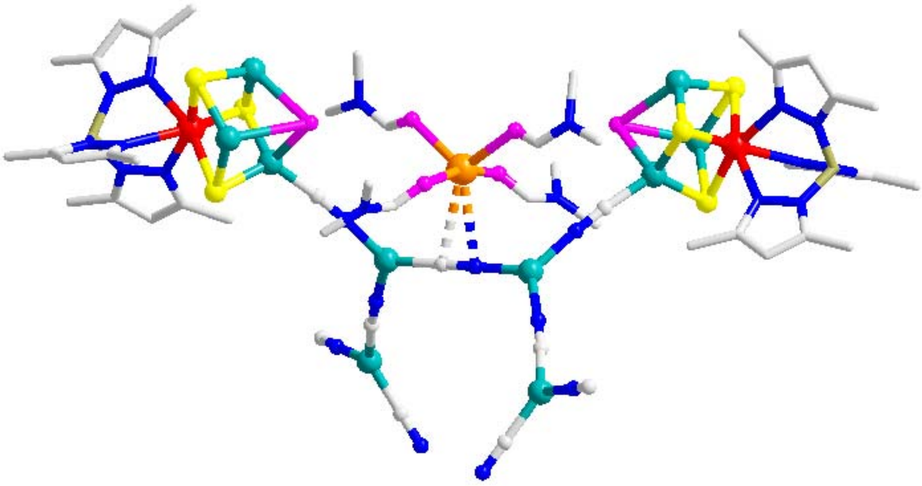

Figure S5. Coordination environment of the potassium ion in **3**. C gray, N blue, O pink, B gray green, S yellow, W red, Cu bluish green, K, brown.

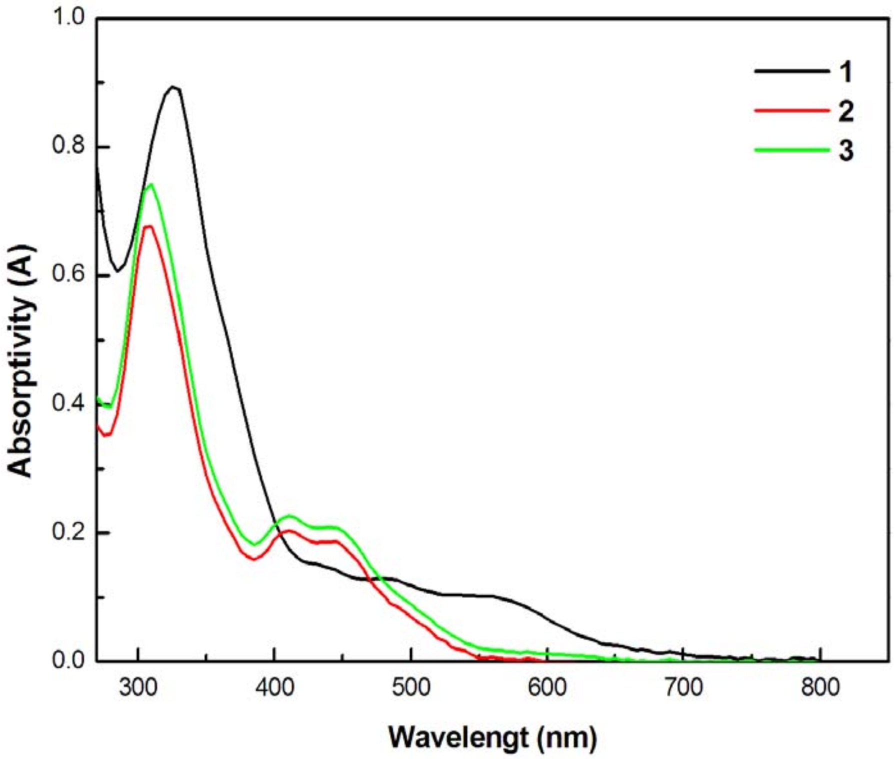

Figure S6. Electronic spectra of **1** (7.1 × 10^{-5} M), **2** (1.8 × 10^{-5} M) and **3** (2.5 × 10^{-5} M) in DMF in a 1-cm-thick glass cell.

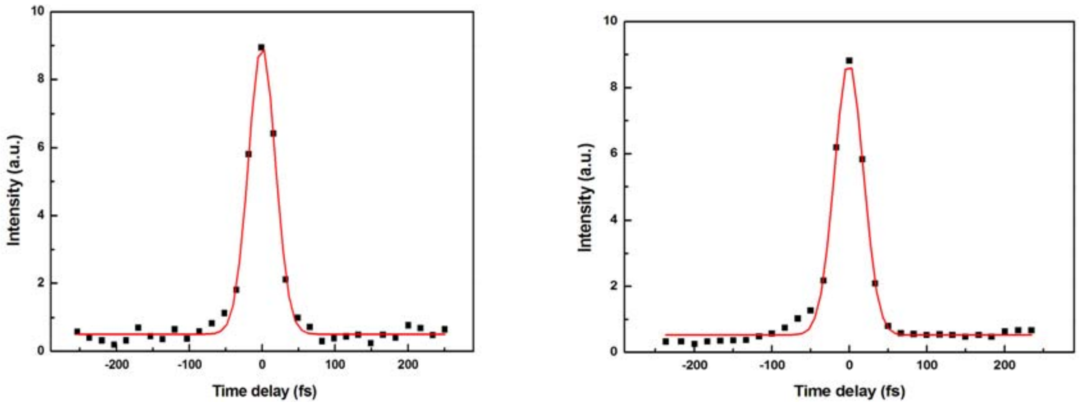

Figure S7 The DFWM signal for the DMF solutions of 1.87 × 10^{-5} M for 2 (Left) and 2.32 × 10^{-5}M for 3 (Right) with 80 fs and 1.5 mm cell. The black solid squares are experimental data, and the red solid curves are the theoretical fit.

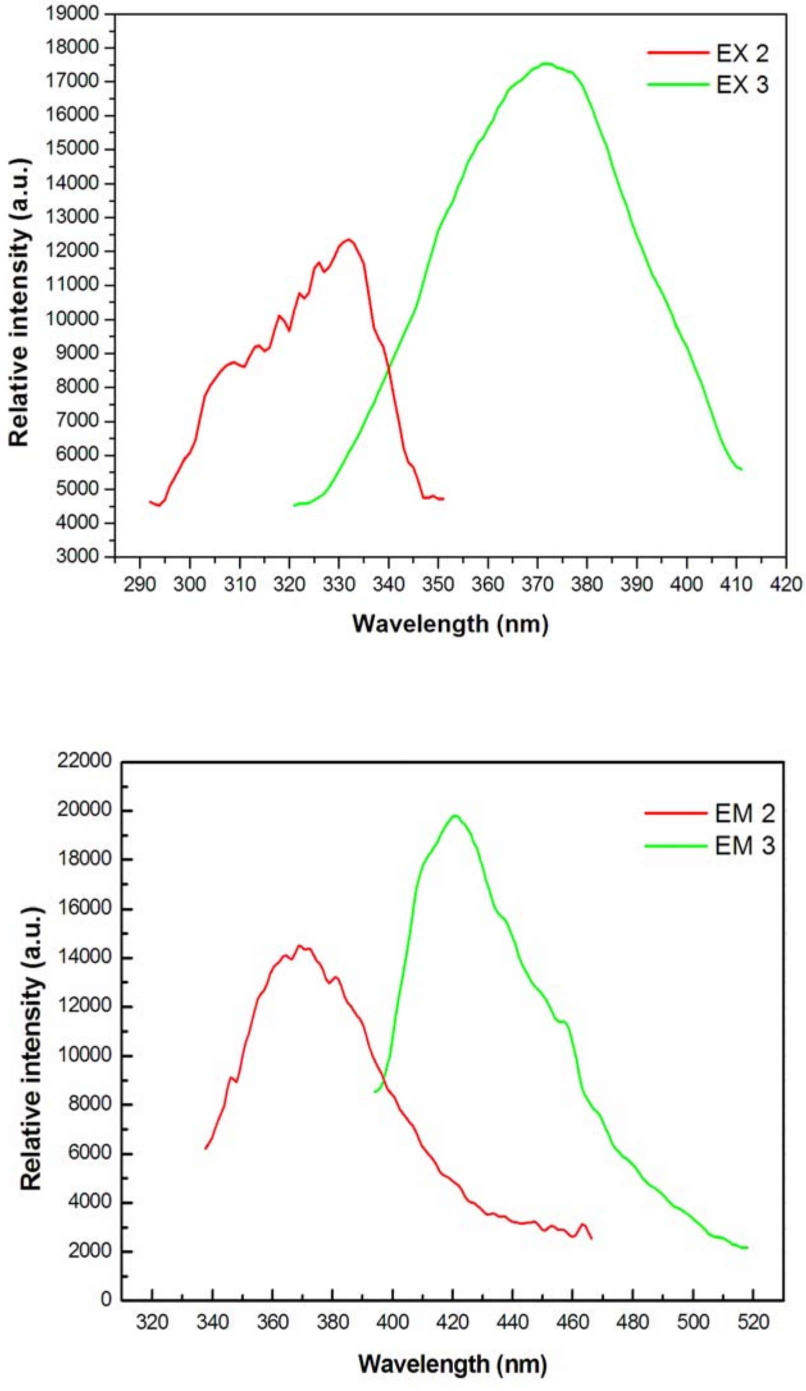

Figure S8. Excitation (top) and emission (bottom) spectra of **2** and **3** in the solid state at ambient temperature.

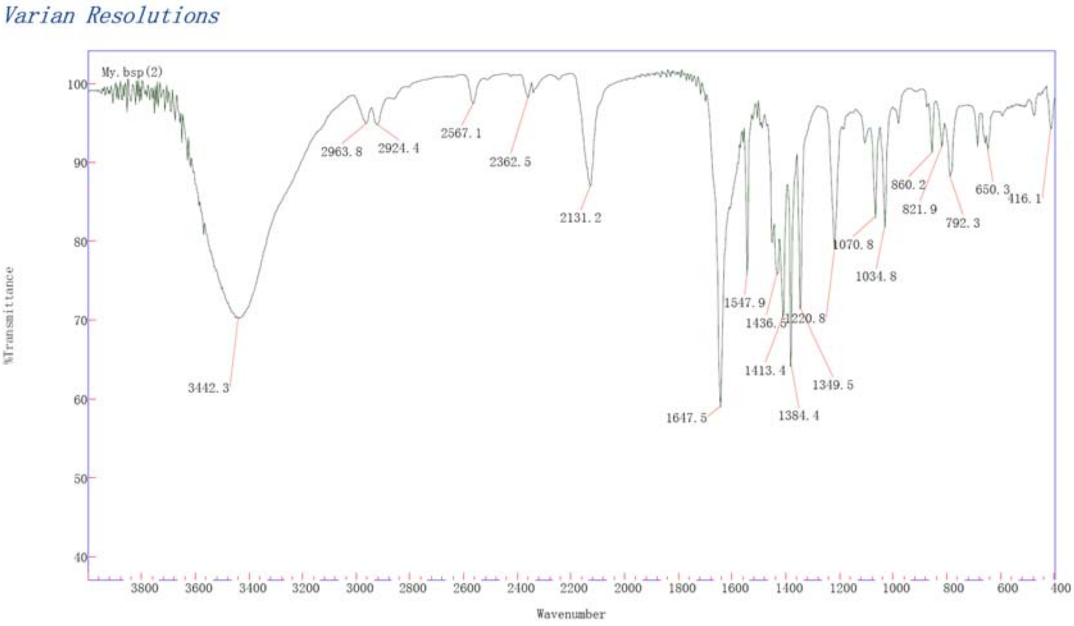

Figure S9. IR spectrum of compound **2**.

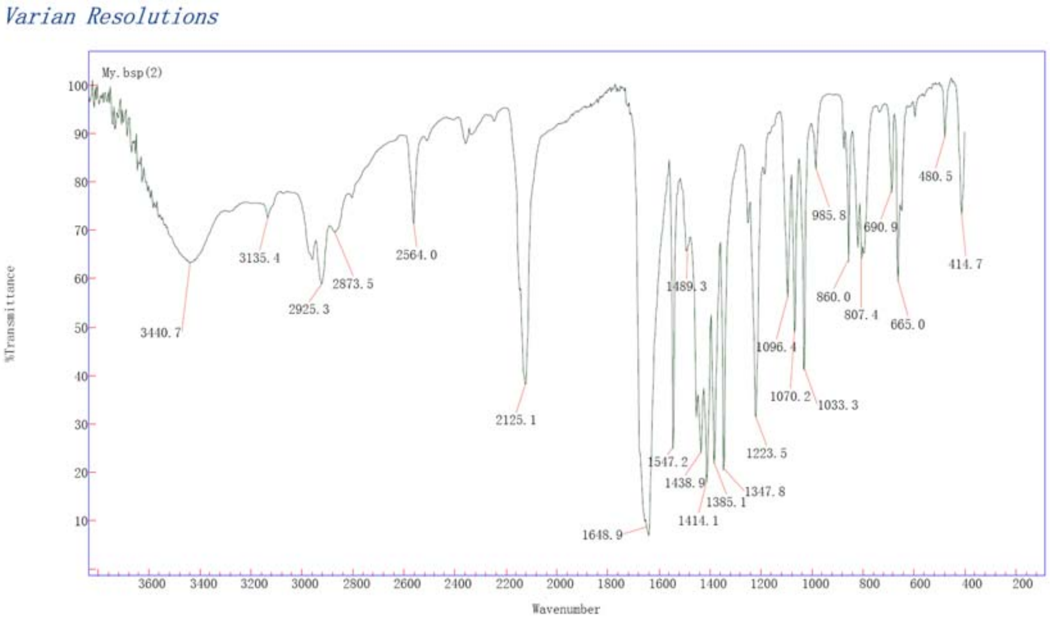

Figure S10. IR spectrum of compound **3**.