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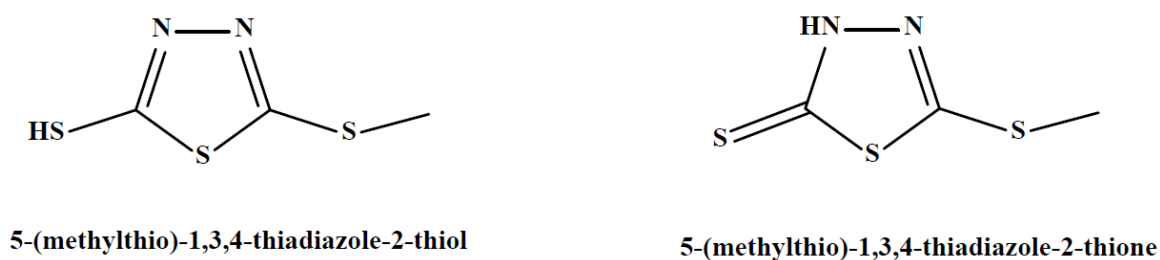
**Supporting information for article:**

**A sulfur coordination polymer with wide bandgap semiconductority  
formed from zinc(II) and 5-methylsulfanyl-1,3,4-thiadiazole-2-thione**

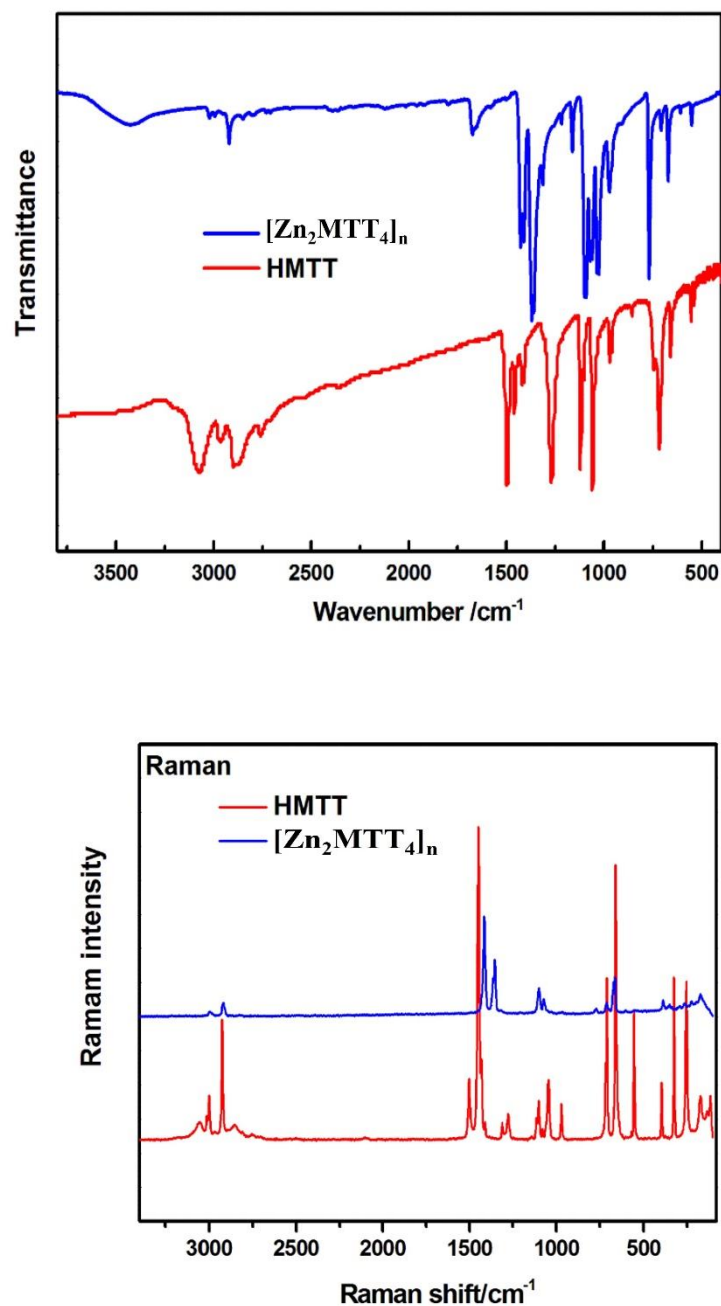
**Jun Zhang, Xiaofan Ma, Weili Kong, Fazhi Xie, Shizhen Yuan, Xiaojie Song,  
Zhansheng Lu and Xiaopeng Xuan**

## 1. Discussion of synthesis

In this work, the organic base triethylamine was used to remove the proton of HMTT (Figure S1), resulting in the more conveniently coordinated  $\text{MTT}^-$  anion. After mixed the  $\text{Zn}^{2+}$  with HMTT in DMF, white precipitate of  $[\text{Zn}_2\text{MTT}_4]_n$  is rapidly formed, and is difficult to structurally determine. Infrared and Raman spectroscopy were used to verify the formation of target compound, and to estimate the coordination mode. From IR and Raman spectra depicted in Figure S2, it can be found that the vibrational bands of  $\nu_{\text{N-H}}$  ( $3100\text{ cm}^{-1}$  in IR and  $3060\text{ cm}^{-1}$  in Raman),  $\nu_{\text{C-N}}$  ( $1270\text{ cm}^{-1}$  in IR and  $1276\text{ cm}^{-1}$  in Raman),  $\nu_{\text{C=S}}$  ( $725\text{ cm}^{-1}$  in IR) and  $\nu_{\text{C-S}}$  ( $554\text{ cm}^{-1}$  in Raman) disappear in the spectra of  $[\text{Zn}_2\text{MTT}_4]_n$ . The shift of  $\nu_{\text{C=N}}$  ( $1448\text{ cm}^{-1}$ ) band and the splitting of  $\nu_{\text{C=S}}$  ( $657\text{ cm}^{-1}$ ) also reveal that both N atom on the ligand ring and S atom of -thione group are involved in coordination. According to the Hard Soft Acid Base theory, hardness parameter of  $\text{Zn}^{2+}$  (10.08) is more closer to that of thione (5.3, derived from  $\text{H}_2\text{S}$ ) than that of thiol (4.1), thus thione more easily coordinates with  $\text{Zn}^{2+}$  (Parr & Chattaraj, 1991). This agrees with the previous results (Mistry et al., 2014, Pang et al., 2017, Mohamed et al., 2015) and determined C-N and C-S bond lengths. Since  $[\text{Zn}_2\text{MTT}_4]_n$  is insoluble in general solvents such as ethanol, methanol, acetonitrile, acetone, chloroform and dichloromethane, the clear filtrate of reaction was quietly stood for the growth of single crystals at room temperature. After two weeks, only a small number of colorless block-shaped single crystals suitable for X-ray diffraction studies were collected from the filtrate.



**Figure S1** Tautomer Structures of HMTT

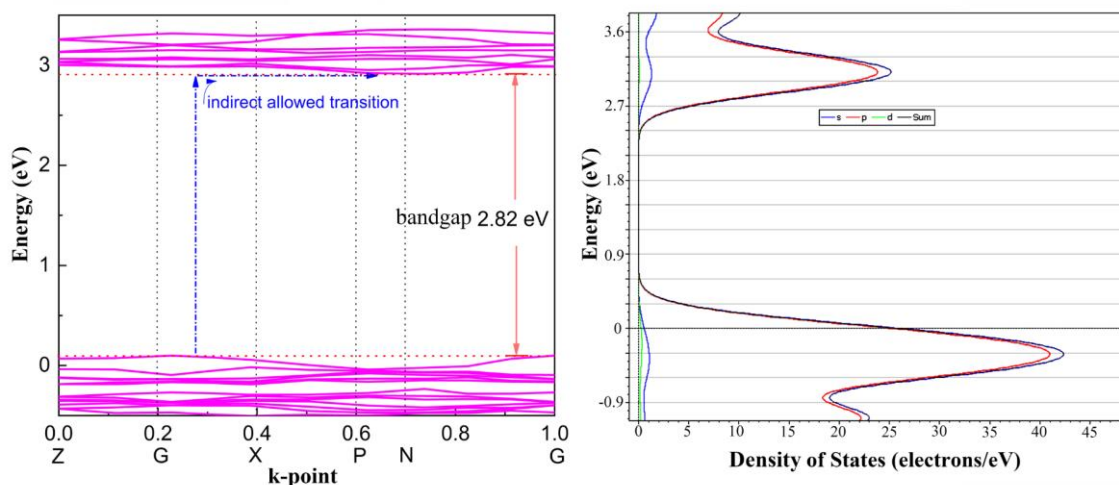


**Figure S2** FT IR/ Raman spectra of [Zn<sub>2</sub>MTT<sub>4</sub>]<sub>n</sub> and ligand (HMTT)

## 2. Theoretical calculation of [Zn<sub>2</sub>MTT<sub>4</sub>]<sub>n</sub>

Electronic band structure together with density of states (DOS) was calculated using the Castep module based on the density functional theory (DFT) applying a plane-wave expansion of the wave functions. The norm-conserving pseudopotential was used to describe the interactions between the ionic cores and the electrons. The Zn charge was set as +2, and the orbital electrons of Zn-3d<sup>10</sup>4s<sup>2</sup>, S-3d<sup>2</sup>3p<sup>4</sup>, C-2s<sup>2</sup>2p<sup>2</sup>, H-1s<sup>1</sup>, N-2s<sup>2</sup>2p<sup>3</sup> were treated as the valence electrons. A cutoff energy E<sub>c</sub> of 285.0 eV determined the number of plane waves was included

in the basis, and a  $3 \times 3 \times 2$  Monkhorst Pack k-point sampling was used to perform the numerical integration of the Brillouin zone. As shown in Figure S3, Theoretical calculation of bandgap reveals that both the valence band top and conduction band bottom mainly consist of  $p$  orbitals with minor  $s$  orbitals and bare  $d$  orbitals. The transition is indirect allowed because of the different k-point located by the valence band top and conduction band bottom.



**Figure S3** Theoretical bandgap calculation of  $[\text{Zn}_2\text{MTT}_4]_n$ .

### 3. Bandgap-temperature dependence and selective response for $[\text{Zn}_2\text{MTT}_4]_n$

In the practical application of a semiconductor, the effect of working temperature must be considered. High thermal stability of semiconductor materials ensures that device can work stably at a higher temperature. As previously identified by PXRD and TG measurements,  $[\text{Zn}_2\text{MTT}_4]_n$  can remain stable at 270 °C without obvious loss in weight, this provides the possibility to investigate the dependence of bandgap on temperature. From Figure 8b, it can be found that the bandgap keeps basically constant before 210 °C, steadily drops from 210 °C to 280 °C, and sharply decreases after 280 °C. The upper limit of temperature window is about 364 °C due to the full collapse of the entire structure, and at this point its bandgap value is near 0 eV, which is consistent with TG and PXRD analyses.

In addition, the structure and bandgap of  $[\text{Zn}_2\text{MTT}_4]_n$  are stable in the strongly acidic/basic condition (Figure S4 and Figure S5). We added some drops of different solvents on  $[\text{Zn}_2\text{MTT}_4]_n$ , and observed with the naked eyes that its colour in the ammonia ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) became darker, while no change in any other common solvents (Figure S6). PXRD studies (Figure S7) showed that the principal peaks of the  $[\text{Zn}_2\text{MTT}_4]_n$  still retained and only few weak new peaks appeared as mixed with ammonia water. After being immersed in the ethanol to remove the ammonia,  $[\text{Zn}_2\text{MTT}_4]_n$  can recover its initial structure as confirmed by PXRD in Figure S7. Therefore, the

selective response to ammonia was presumably resulted from the reversible interactions between the skeleton and the ammonia, especially ammonium.

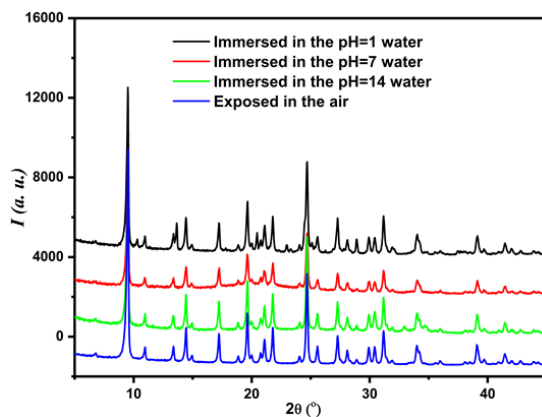


Figure S4 PXRD of  $[\text{Zn}_2\text{MTT}_4]_n$  in the water with different pH values

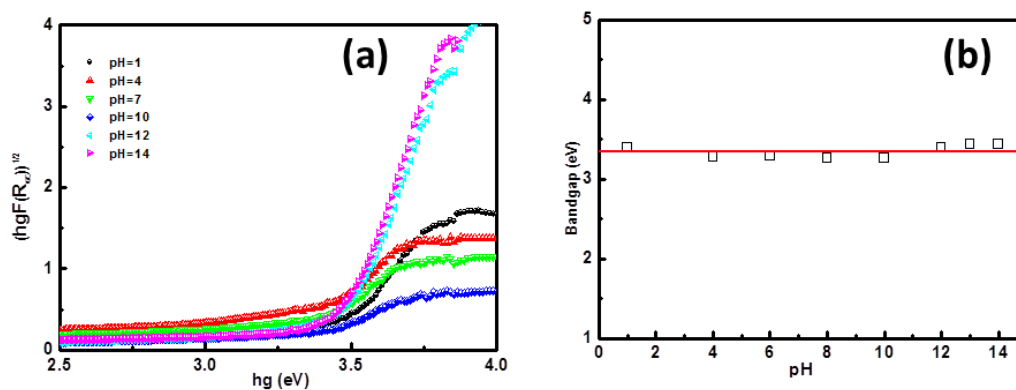


Figure S5 Tauc plots of transformed Kubelka-Munk function vs the light energy for  $[\text{Zn}_2\text{MTT}_4]_n$  in the different pH conditions (a); Bandgap of  $[\text{Zn}_2\text{MTT}_4]_n$  in the different pH conditions at room temperature (b).

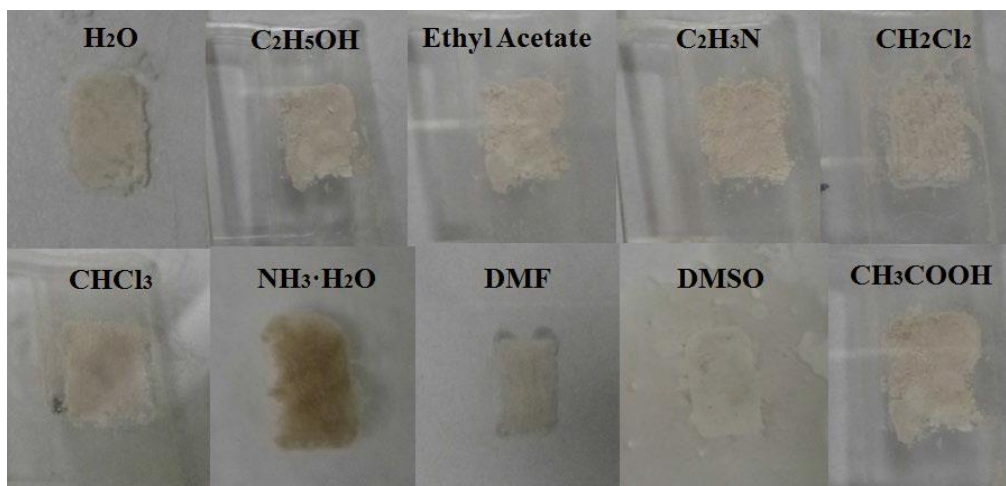


Figure S6 Color change of the sample of  $[\text{Zn}_2\text{MTT}_4]_n$  after adding various solvents

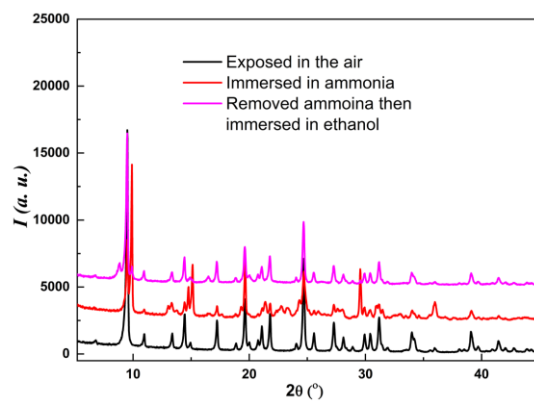


Figure S7 PXRD of  $[\text{Zn}_2\text{MTT}_4]_n$  with and without ammonia water.

**Table S1** Selected geometric parameters (Å, °) of  $[\text{Zn}_2\text{MTT}_4]_n$ 

Zn4—N4	2.036 (4)	Zn2—N2	2.004 (4)
Zn4—N4 <sup>i</sup>	2.036 (4)	Zn2—N2 <sup>vi</sup>	2.004 (4)
Zn4—N4 <sup>ii</sup>	2.036 (4)	Zn2—N2 <sup>vii</sup>	2.004 (4)
Zn4—N4 <sup>iii</sup>	2.036 (4)	Zn2—N2 <sup>viii</sup>	2.004 (4)
Zn3—S4	2.355 (1)	Zn1—S1	2.344 (1)
Zn3—S4 <sup>iv</sup>	2.355 (1)	Zn1—S1 <sup>ix</sup>	2.344 (1)
Zn3—S4 <sup>v</sup>	2.355 (1)	Zn1—S1 <sup>vii</sup>	2.344 (1)
Zn3—S4 <sup>i</sup>	2.355 (1)	Zn1—S1 <sup>x</sup>	2.344 (1)
S4—C4	1.730 (5)	S1—C1	1.728 (5)
S5—C4	1.722 (5)	S2—C2	1.730 (5)
S5—C5	1.732 (5)	S2—C1	1.736 (5)
S6—C5	1.730 (5)	S3—C2	1.734 (5)
S6—C6	1.787 (8)	S3—C3	1.798 (6)
N4—C4	1.324 (7)	N1—C2	1.299 (6)
N4—N3	1.391 (5)	N1—N2	1.383 (5)
N3—C5	1.304 (6)	N2—C1	1.311 (6)
C6—H6A	0.9600	C3—H3A	0.9600
C6—H6B	0.9599	C3—H3B	0.9600
C6—H6C	0.9600	C3—H3C	0.9600
N4—Zn4—N4 <sup>i</sup>	120.3 (2)	N2—Zn2—N2 <sup>vi</sup>	106.0(1)
N4—Zn4—N4 <sup>ii</sup>	104.4(1)	N2—Zn2—N2 <sup>vii</sup>	116.7 (2)
N4 <sup>i</sup> —Zn4—N4 <sup>ii</sup>	104.4(1))	N2 <sup>vi</sup> —Zn2—N2 <sup>vii</sup>	106.0(1)
N4—Zn4—N4 <sup>iii</sup>	104.4(1)	N2—Zn2—N2 <sup>viii</sup>	106.0(1)
N4 <sup>i</sup> —Zn4—N4 <sup>iii</sup>	104.4(1)	N2 <sup>vi</sup> —Zn2—N2 <sup>viii</sup>	116.7 (2)

N4 <sup>ii</sup> —Zn4—N4 <sup>iii</sup>	120.3 (2)	N2 <sup>vii</sup> —Zn2—N2 <sup>viii</sup>	106.0 (1)
S4—Zn3—S4 <sup>iv</sup>	110.44 (3)	S1—Zn1—S1 <sup>ix</sup>	107.61 (3)
S4—Zn3—S4 <sup>v</sup>	110.44 (3)	S1—Zn1—S1 <sup>vii</sup>	113.26 (7)
S4 <sup>iv</sup> —Zn3—S4 <sup>v</sup>	107.55 (6)	S1 <sup>ix</sup> —Zn1—S1 <sup>vii</sup>	107.61 (3)
S4—Zn3—S4 <sup>i</sup>	107.55 (6)	S1—Zn1—S1 <sup>x</sup>	107.61 (3)
S4 <sup>iv</sup> —Zn3—S4 <sup>i</sup>	110.44 (3)	S1 <sup>ix</sup> —Zn1—S1 <sup>x</sup>	113.26 (7)
S4 <sup>v</sup> —Zn3—S4 <sup>i</sup>	110.44 (3)	S1 <sup>vii</sup> —Zn1—S1 <sup>x</sup>	107.61 (3)
C4—S4—Zn3	97.2 (2)	C1—S1—Zn1	97.8 (2)
C4—S5—C5	88.3 (3)	C2—S2—C1	87.9 (2)
C5—S6—C6	101.7 (3)	C2—S3—C3	99.8 (3)
C4—N4—N3	114.7 (4)	C2—N1—N2	111.3 (4)
C4—N4—Zn4	126.2 (3)	C1—N2—N1	114.8 (4)
N3—N4—Zn4	119.1 (3)	C1—N2—Zn2	130.5 (3)
C5—N3—N4	110.7 (4)	N1—N2—Zn2	114.5 (3)
N4—C4—S5	111.7 (4)	N2—C1—S1	126.2 (4)
N4—C4—S4	124.8 (4)	N2—C1—S2	111.6 (4)
S5—C4—S4	123.5 (3)	S1—C1—S2	122.2 (3)
N3—C5—S6	125.7 (4)	N1—C2—S2	114.4 (4)
N3—C5—S5	114.6 (4)	N1—C2—S3	124.2 (4)
S6—C5—S5	119.7 (3)	S2—C2—S3	121.4 (3)
S6—C6—H6A	109.5	S3—C3—H3A	109.5
S6—C6—H6B	109.5	S3—C3—H3B	109.5
H6A—C6—H6B	109.5	H3A—C3—H3B	109.5
S6—C6—H6C	109.5	S3—C3—H3C	109.5
H6A—C6—H6C	109.5	H3A—C3—H3C	109.5
H6B—C6—H6C	109.5	H3B—C3—H3C	109.5



C4—N4—N3—C5	-1.1 (6)	C2—N1—N2—C1	1.1 (6)
Zn4—N4—N3—C5	177.0 (3)	C2—N1—N2—Zn2	-174.1 (3)
N3—N4—C4—S5	0.9 (5)	N1—N2—C1—S1	179.5 (3)
Zn4—N4—C4—S5	-177.2 (2)	Zn2—N2—C1—S1	-6.2 (7)
N3—N4—C4—S4	179.6 (3)	N1—N2—C1—S2	-1.2 (5)
Zn4—N4—C4—S4	1.5 (6)	Zn2—N2—C1—S2	173.1 (3)
C5—S5—C4—N4	-0.3 (4)	Zn1—S1—C1—N2	-82.5 (4)
C5—S5—C4—S4	-179.0 (4)	Zn1—S1—C1—S2	98.2 (3)
Zn3—S4—C4—N4	89.0 (4)	C2—S2—C1—N2	0.7 (4)
Zn3—S4—C4—S5	-92.5 (3)	C2—S2—C1—S1	-179.9 (3)
N4—N3—C5—S6	-179.0 (4)	N2—N1—C2—S2	-0.6 (5)
N4—N3—C5—S5	0.9 (6)	N2—N1—C2—S3	178.3 (3)
C6—S6—C5—N3	8.9 (6)	C1—S2—C2—N1	-0.1 (4)
C6—S6—C5—S5	-170.9 (4)	C1—S2—C2—S3	-179.0 (3)
C4—S5—C5—N3	-0.4 (4)	C3—S3—C2—N1	-4.7 (5)
C4—S5—C5—S6	179.5 (4)	C3—S3—C2—S2	174.1 (3)

Symmetry code(s): (i)  $-x+1, -y+1, z$ ; (ii)  $-y+1, x, -z+1$ ; (iii)  $y, -x+1, -z+1$ ; (iv)  $-y+1, x, -z+2$ ; (v)  $y, -x+1, -z+2$ ; (vi)  $-y+3/2, x-1/2, -z+3/2$ ; (vii)  $-x+2, -y+1, z$ ; (viii)  $y+1/2, -x+3/2, -z+3/2$ ; (ix)  $y+1/2, -x+3/2, -z+5/2$ ; (x)  $-y+3/2, x-1/2, -z+5/2$ .

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