Supplemental Material

Two new inorganic-organic hybrid zinc phosphite and their derived ZnO/ZnS heterostructure for efficient photocatalytic hydrogen production

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(1) X-ray crystallography

The crystallographic diffraction data of **1** and **2** were collected with an Agilent Technologies Gemini A Ultra diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. All absorption corrections were applied using the multiscan program SADABS. The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97 [1] within Olex2 [2]. All non-hydrogen atoms of two crystal structures were refined with anisotropic thermal parameters. The positions of hydrogen atoms were geometrically placed. The crystallographic data and structural refinement parameters of the five CPs are summarized in Table S1 and the selected bond lengths and angles are given in Table S2.

(2) Table S1 Crystal data and structure refinements for compound 1 and 2.

Comound	**1**	**2**
Empirical formula	$C_7H_8N_2O_3PZn$	$C_8H_{10}N_2O_3PZn$
Formula weight	264.49	277.51
T, K	293(2)	293(2)
crystal system	orthorhombic	monoclinic
space group	*Pbcn*	$P2_1/c$
a (Å)	8.8182(5)	5.2103(2)
b (Å)	10.1110(4)	11.7634(5)
c (Å)	21.4930(9)	17.4168(8)
α (deg)	90	90
β (deg)	90	99.315(4)
γ (deg)	90	90
V (Å^3)	1916.33(15)	1053.41(8)
Z	8	4
D_c (g/cm^3)	1.834	1.750
μ (mm^{-1})	2.710	2.470
F (0 0 0)	1064.0	560.0
R_{int}	0.0453	0.0513
GOF on F^2	1.030	1.156
R_1[a]/wR_2[b] I > 2σ(I)	R_1 = 0.0317, wR_2 = 0.0714	R_1 = 0.1745, wR_2 = 0.4731
R_1, wR_2 (all data)	R_1 = 0.0442, wR_2 = 0.0782	R_1 = 0.1774, wR_2 = 0.474

[a]$R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$. [b]$wR_2 = [\Sigma w(|F_0|^2 - |F_c|^2)^2/\Sigma(F_0^2)^2]^{1/2}$

(3) Table: S2 Selected bond lengths (Å) and angles (deg) for 1 and 2

Complex **1**			
Zn1-O1	1.951(2)	Zn1-O2^{i}	1.933(2)
Zn1-N1	2.002(3)	Zn1-O3^{ii}	1.910(2)
O1-Zn1-N1	107.78(11)	O3^{ii}-Zn1-O1	110.53(10)
O2^{i}-Zn1-O1	108.49(11)	O3^{ii}-Zn1-N1	113.89(11)
O2^{i}-Zn1-N1	112.98(11)	O3^{ii}-Zn1-O2^{1}	103.05(10)
Symmetry code: (i) 1-x, 1-y, 1-z; (ii) -1/2+x, 1/2-y, 1-z; (iii) -x, y, 3/2-z; (iv) 1/2+x, 1/2-y, 1-z.			
Complex **2**			
Zn1-O1	1.941(2)	Zn1-N1	2.007(17)
Zn1-O3^{i}	1.929(15)	Zn1-O2^{ii}	1.933(15)
O1-Zn1-N1	111.1(7)	O2^{ii}-Zn1-O1	109.9(8)
O3^{i}-Zn1-O1	113.0(7)	O2^{ii}-Zn1-O3^{i}	112.3(7)
O3^{i}-Zn1-N1	109.7(8)	O2^{ii}-Zn1-N1	100.2(7)
Symmetry code: (i): 1-x, 1-y, 1-z; (ii): -x, 1-y, 1-z; (iii): -x, 1-y, -z.			

(4) Table: S3 Hydrogen bonds for 2

D-H…A(Å)(symmetry mode)	H…A(Å)	D…A(Å)	D-H...A(deg)
Complex **2**			
C5-H5A···O2 (-1+x, 0.5-y, 0.5+z)	2.502(2)	3.412(4)	155.7(2)
C4-H4···O1 (x, 0.5-y, 0.5+z)	2.343(2)	3.267(4)	173.4(2)

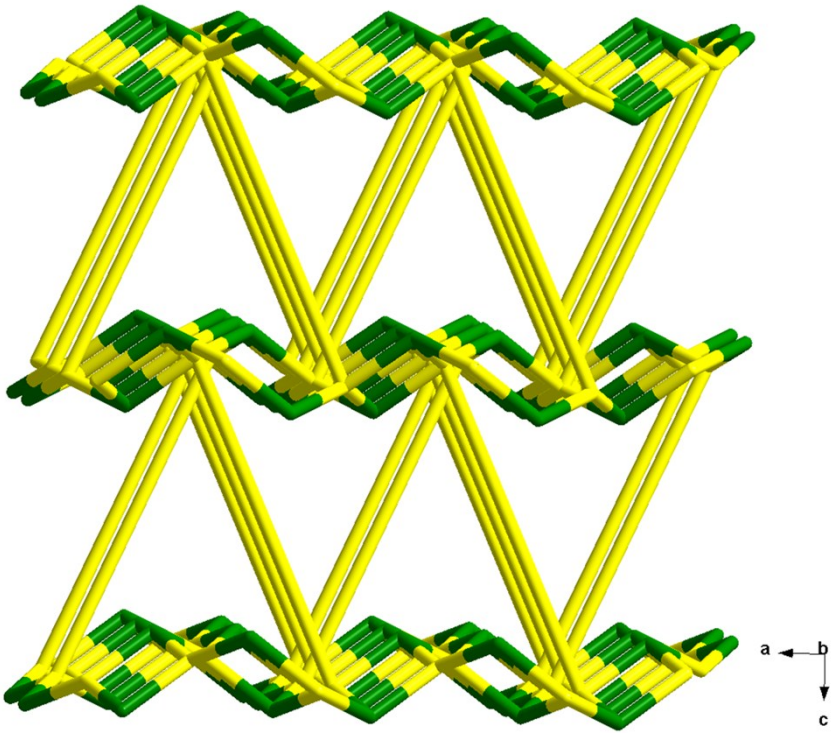

Fig. S1. The 3D 2-nodal 3,4-connected ***3,4L83*** topology of compound **1** with point symbol of $\{4.8^2.10^3\}\{4.8^2\}$.

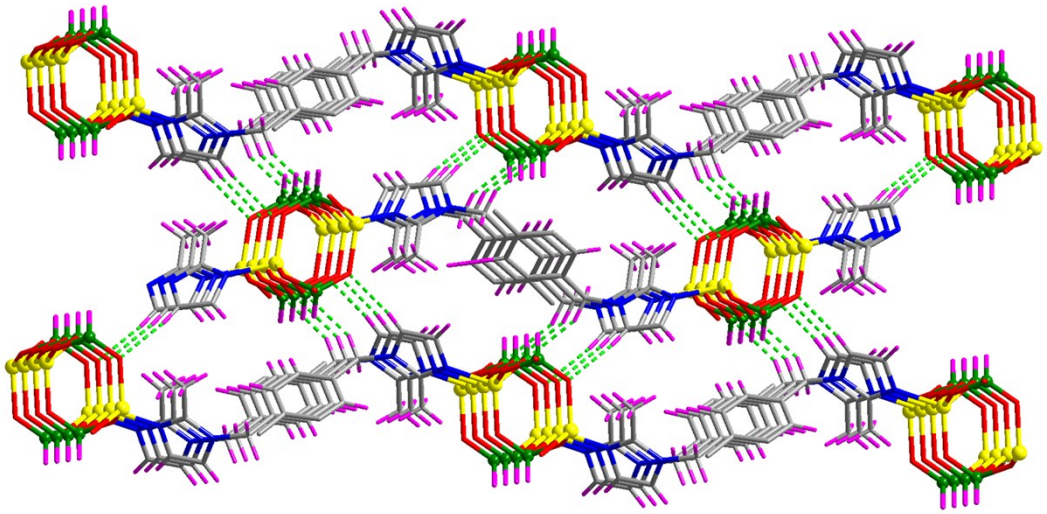

Fig. S2. 3D hydrogen bonding surpramolecule of compound **2**.

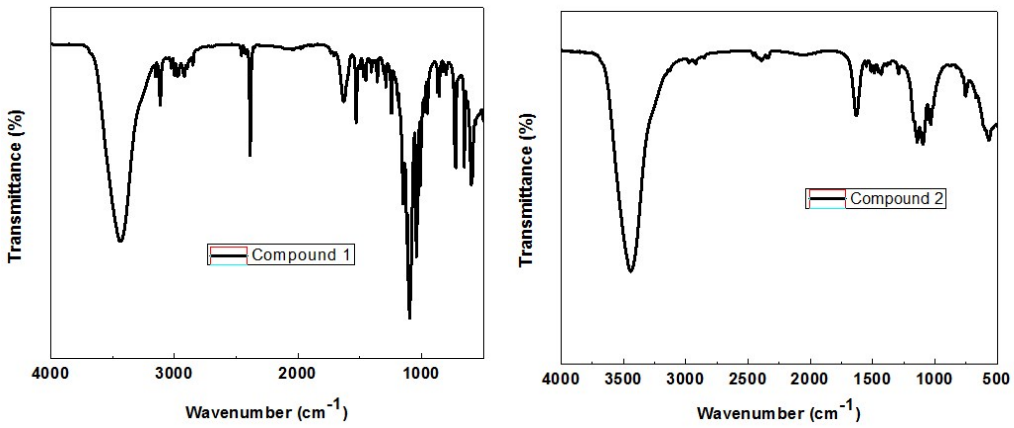

Fig. S3: IR spectra of **1** and **2**

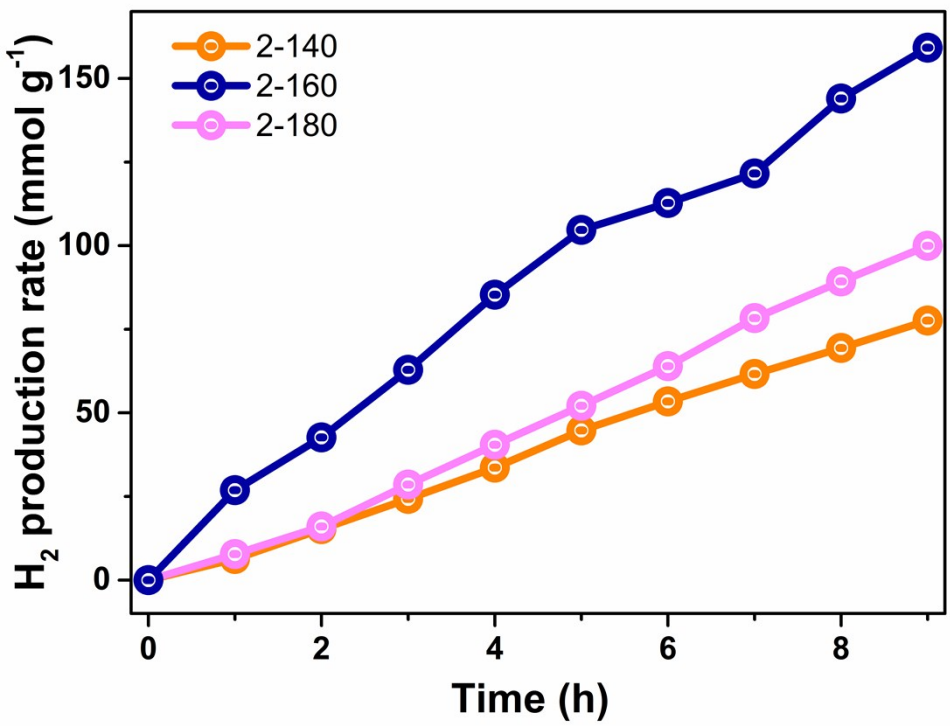

Fig. S4: Plots of photocatalytic H_2 evolution amount of **2-140**, **2-160** and **2-180**.

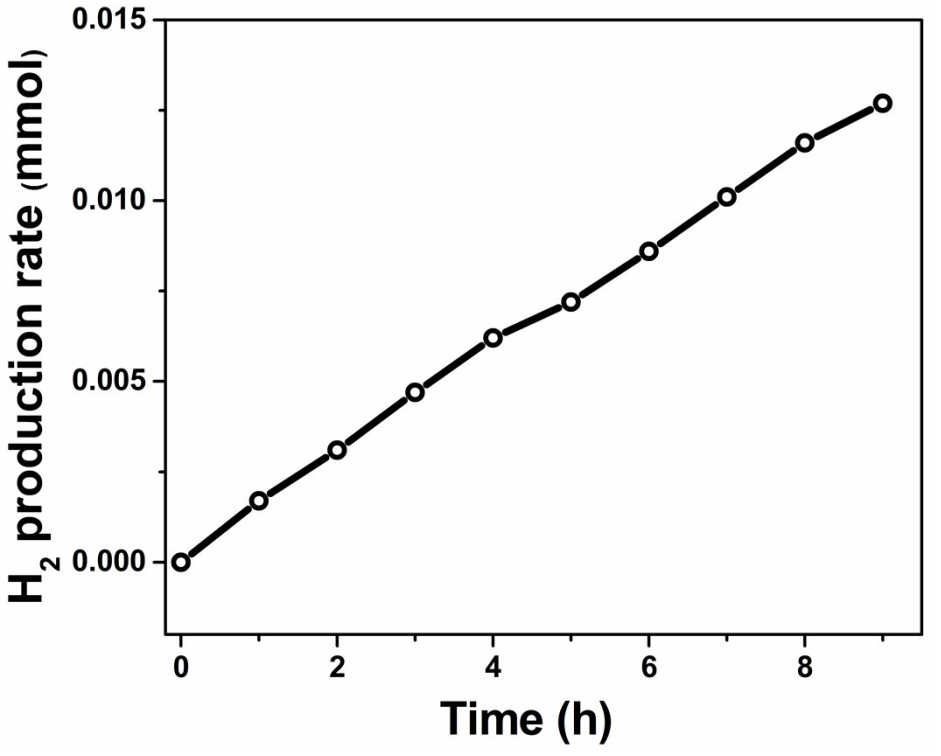

Fig. S5: Plots of photocatalytic H_2 evolution amount of the controlled experiment by merely irradiating Na_2S/Na_2SO_3 solution.

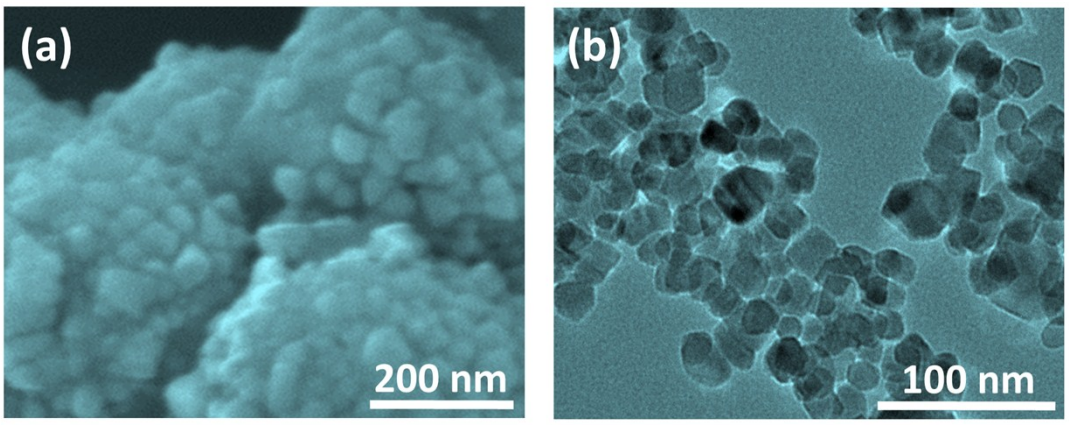

Fig. S6: a) The SEM and b) TEM images of **2-160**.

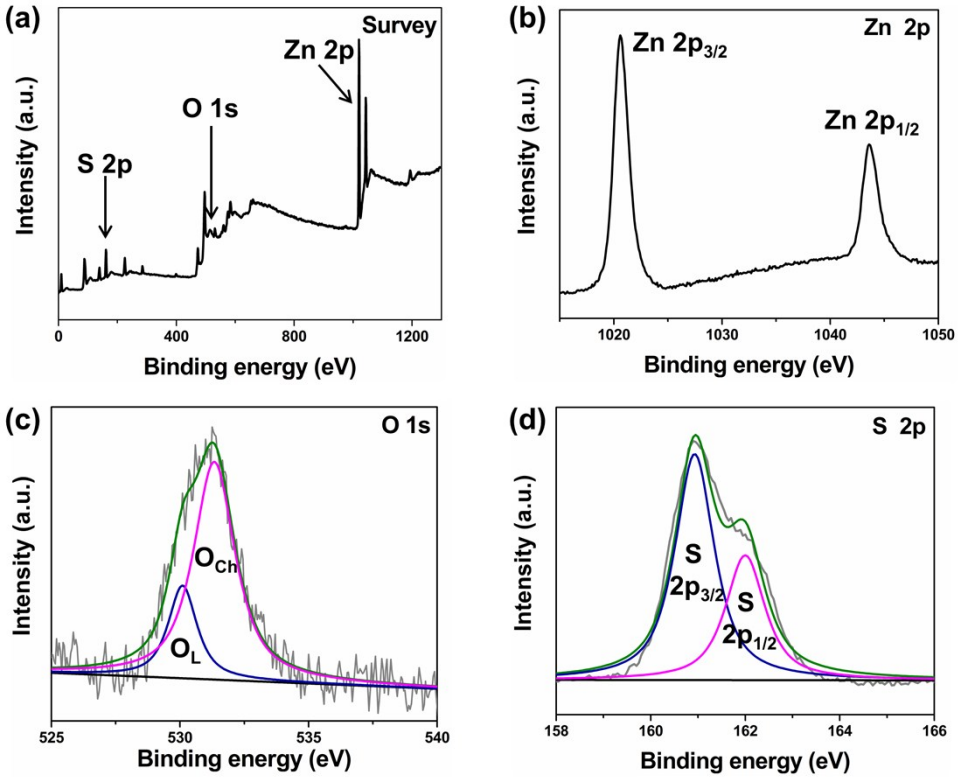

Fig. S7: (a) The XPS Survey spectrum and high resolution spectra of Zn 2p (b), O 1s (c) and S 2p (d) in **1-160** sample.

Equation S1:

$$\text{The apparent quantum yield} = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\%$$

$$= \frac{2 \times \text{number of evolved } H_2 \text{ molecules}}{\text{Number of incident photons}} \times 100\%$$

$$= \frac{2 \times n_{H_2}}{n_p} \times 100\%$$

$$= \frac{2 \times n_{H_2}}{n_p} \times 100\%$$

Where n_{H_2} and n_p stand for the number of H_2 molecules and photons, respectively; P is the light power; t = 3600 s represents the irradiation time; λ = 420 nm is the wavelength of incident light; h = 6.63 × 10^{-34} J s is the Planck constant; and c = 3.0 × 108 m s^{-1} is the light speed.

References

[1]. G.M. Sheldrick., Acta Cryst., A64 (2008) 112.

[2]. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann., J. Appl. Cryst. 42 (2009) 339.