Supporting Information

Unprecedented Metal-mediated *In-situ* Reactions of Heterocyclic Disulfide of Di[4-(pyridin-2-yl)pyrimidinyl]disulfide

Hai-Bin Zhu [a] *, Yan-Fang Wu [a], Yue Zhao [b] *, Jun Hu [b]

[a] *School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189 China*

[b] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China*

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1. ESI-MS characterization of **2**.

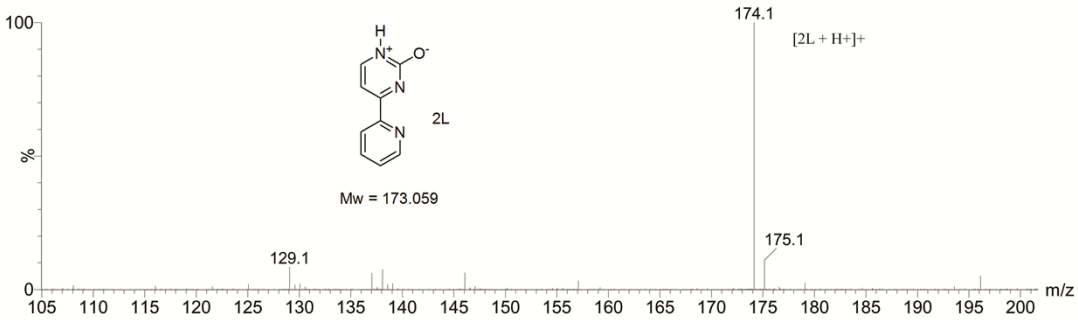

Fig. S1 ESI-MS spectrum of **2**

(The positive ion peak at m/z = 174.1 corresponds to the assignment of $[2L + H]^+$.)

2. Synthesis and crystal structure of **2a.**

Synthesis of 2a. A solution of $Cu(ClO_4)_2.6H_2O$ (0.2 mmol) in 5mL of CH_3CN was slowed added into a solution of **2-ppds** (0.1 mmol) in DCM (5mL) without stirring. Slow diffusion of Et2O into the above solution overnight afforded blue crystals of **2a**. Yield, 62% (based on **2-ppds**). Anal.Calcd for $C_{18}H_{14}Cl_2CuN_6O_9S_2$: C, 32.91; H, 2.15; N, 12.79%. Found: C, 32.87; H, 2.36; N, 12.88%. IR(KBr，cm^{-1}): 3424 (m) 3087 (w), 1581 (m), 1540 (m), 1482 (m), 1414 (m), 1345 (m), 1208 (w), 1169 (w), 1087 (s), 797 (w), 763 (w), 622 (m).

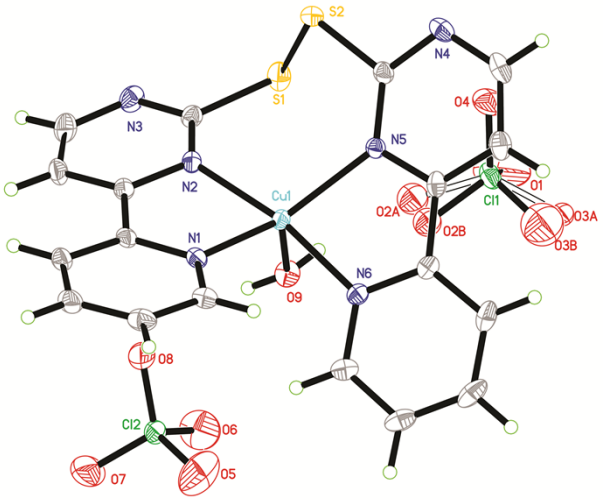

Fig. S2 Perspective view of crystal structure of **2a**.

X-ray crystallography. Diffraction intensity data for **2a** were collected at 298(2) K on a Bruker SMART CCD-4K diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were collected using SMART and reduced by the program SAINT. All the structures were solved by direct methods and refined by full-matrix least squares method on F^2obs by using SHELXTL-PC software package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated by geometrical methods and refined as a riding model. The crystallographic data for **2a** are summarized in **Table S1**. The perspective view of crystal structure of **2a** was shown in **Fig. S2**.

CCDC 1015426 (for **2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1223-336-033; or E-Mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystallographic data for **2a**.

Compound	**2a**
Formula	$C_{18}H_{14}Cl_2CuN_6O_9S_2$
Mr	656.94
Crystal System	Monoclinic
Space Group	*P*21/*n* (No. 14)
a (Å)	11.500(3)
b (Å)	12.721(3)
c (Å)	16.167(4)
α (º)	90
β	96.571(3)
γ	90
V (Å^3)	2350(1)
Z	4
D_{calc} (g cm^{-3})	1.857
F(000)	1324
Reflns collected	15955
Unique reflns	4120
R(int)	0.045

*R*1, *wR*2 [I >2σ(I)]	0.0538/ 0.1170
*R*1 *wR*2 (all data)	0.0592/ 0.1193
GOF	1.17

3. XPS characterization of **3.**

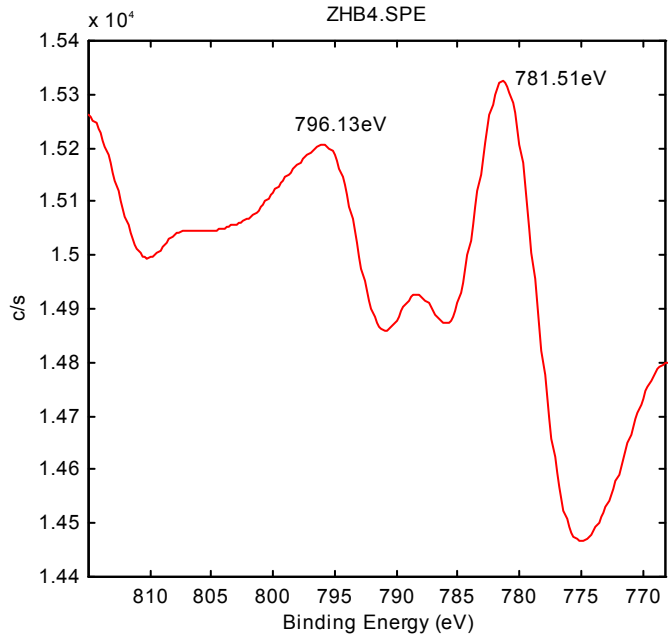

Fig. S3 XPS spectrum of **3**.

4. ESI-MS characterization of **3.**

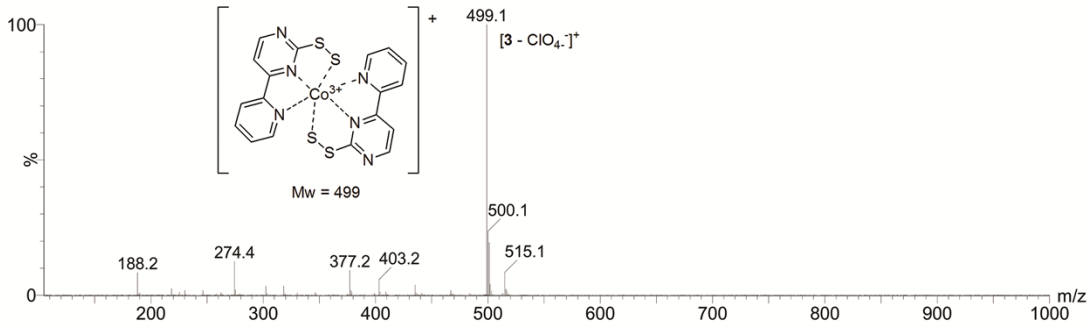

Fig. S4 ESI-MS spectrum of **3.**

5. Synthesis and crystal structure of **4a.**

Synthesis of 4a. A solutionof CuI (0.2mmol) in CH_3CN (5ml) was layered above a solution of n-ppds (0.1mmol) in toluene (5mL). Red block crystals of **4a** were formed in several weeks. Yield, 53.6 % (based on 2-ppds). IR (KBr, cm^{-1}) 3064 (w), 1593 (w), 1563 (s), 1535 (s), 1465 (w), 1446 (w), 1407 (m), 1332 (s), 1207 (m), 1186 (m), 1106 (w),1007 (w), 845 (w), 824 (w), 796 (m), 758 (m), 743 (m), 717 (w), 695 (w), 651 (w), 627 (w).

X-ray crystallography. Diffraction intensities for **4a** were collected at 298(2) K on a Bruker SMART CCD-4K diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71073Å). The data were collected using SMART and reduced by the program SAINT. Since the solvent molecules could not be satisfactorily modeled, they were removed from the atom lists for refinement and the PLATON SQUEEZE procedure was applied. The structure was then refined again using the data generated. All the structures were solved by direct methods and refined by full-matrix least squares method on F^2obs by using SHELXTL-PC software package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated by geometrical methods and refined as a riding model. The crystallographic data for **4a** are summarized in **Table S2**. The crystal structure of 4a was depicted in **Fig. S5**.

CCDC 832570 (for **4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1223-336-033; or E-Mail: deposit@ccdc.cam.ac.uk).

Table S2. Crystallographic data for **4a**.

Compound	**4a**
Formula	$C_{25}H_{20}Cu_2I_2N_6S_2$
Mr	849.50
Crystal System	Monoclinic
Space Group	C2/c (No. 15)
a (Å)	15.494(2)
b (Å)	12.435(1)
c (Å)	15.726(2)
α (o)	90

β	106.748(1)
γ	90
V (Å3)	2901.2(5)
Z	4
Dcalc (g cm-3)	1.734
F(000)	1432
Reflns collected	2889
Unique reflns	2889
R1[I >2σ(I)]	0.0359
wR2[I >2σ(I)]	0.0662
R1(all data)	0.0812
wR2 (all data)	0.0744
GOF	1.00

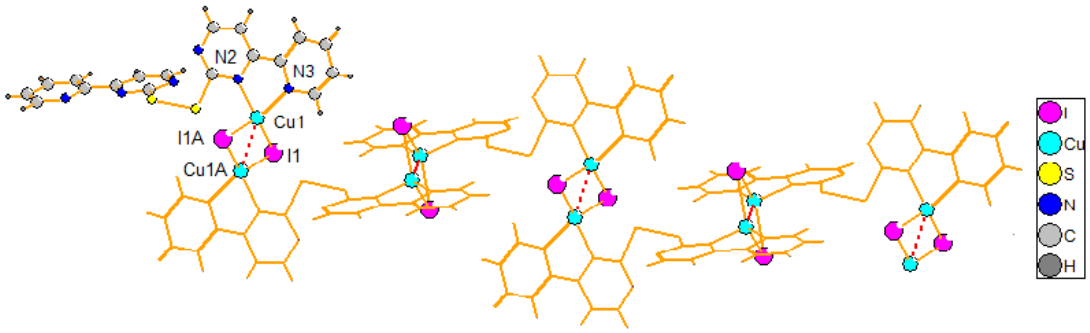

Fig. S5 A 1-D chain structure of **4a.**