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Review

In situ construction of metal–organic sulfur-containing heterocycle frameworks

Hai-Bin Zhu[a,b], Shao-Hua Gou[a,b,*]

[a] *Pharmaceutical Research Center, and School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China*
[b] *Jiangsu Province Hi-Tech Key Laboratory for Bio-Medical Research, Nanjing 211189, China*

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ABSTRACT

This review outlines three types of *in situ* methods used for constructing metal–organic sulfur-containing heterocycle frameworks, *viz.*, *in situ* S–S function reactions, *in situ* C–S bond cleavage and *in situ* thiol-S atom reactions. Each method is described in detail in three respects, namely (i) reaction parameters, (ii) the organic transformation and coordination modes involved, and (iii) fascinating structures and functional properties of those *in situ*-generated metal-coordination compounds.

1. Introduction

The coordination chemistry of organic sulfur-containing heterocycles, especially those with thioamide moieties, has been of interest for a long time. One main reason is based on their diverse S, N-mixed coordination modes as documented in two earlier excellent reviews [1]. In the last decade, special interest has been given to their direct assembly with soft acid metal ions (e.g. Ag^+) [2], which have brought about new advances in this area. In general, metal–sulfur–organic network solids constitute a class of promising electronic materials due to their potential electronic properties (e.g. electrical conductivity) [3]. Analogously, metal–organic sulfur-containing heterocycle compounds with metal–sulfur bonds are also of particular appeal to inorganic and bioinorganic chemists. On the one hand, the incorporation of thiolate-S as a single atom bridge between adjacent transition metal sites would permit greater delocalization of spin density towards the bridging atom and contribute to strong super-exchange interactions if the selected metal orbital energies are better matched for the sulfur atom. This beneficial feature is highly desirable in terms of magnetic, conductive and luminescent behavior. On the other hand, these compounds have great biological relevance since there are a number of metalloen-

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[*] Corresponding author at: Pharmaceutical Research Center, and School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China. Tel.: +86 25 83272381.
E-mail address: sgou@seu.edu.cn (S.-H. Gou).

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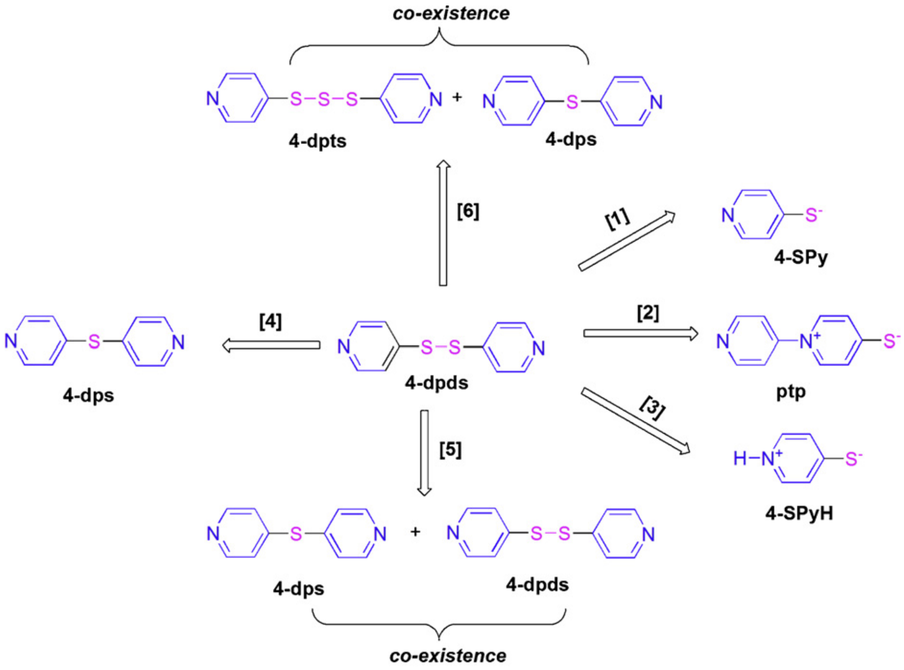


Scheme 1. *In situ* S–S function reactions of 4-dpds under hydro(solvo)thermal reactions.

zymes containing metal–sulfur bonds, of which the thiolate-S atom may act as not only coordination donors but also reactive sites. Consequently, these compounds may serve as good candidates for artificial mimics of metalloenzymes.

Generally, *in situ* metal/ligand reactions could open a new avenue towards the discovery of new organic reactions, the elucidation of reaction mechanisms, and the generation of novel functional materials, particularly for those that are inaccessible *via* the direct approach [4]. Likewise, the *in situ* construction of metal–organic sulfur-containing heterocycle frameworks has also attracted considerable attention during recent years. The direct method features the use of thiol-containing heterocycles as starting materials. Unfortunately, the intrinsic propensity of S atom to bridge multiple nuclei has always resulted in the rapid formation of oligomeric or polymeric compounds, which do not readily crystallize used for X-ray diffraction analysis. By contrast, *in situ* strategy offers a promising solution where the organic building blocks are gradually generated from *in situ* metal/ligand precursor reactions. Thus, by subtly adjusting reaction conditions, the reaction rate can be slowed down to some extent, benefiting crystal growth. Furthermore, *in situ* versatile reactions provide vast opportunities to create MOFs (MOFs = metal–organic frameworks) with unique structures and functional properties which are not attainable by the conventional method.

This review is intended to summarize recent advances in the *in situ* preparation of metal–organic sulfur-containing heterocycle frameworks, highlighting their preparative methods in addition to their special structures and interesting functional properties. However, it is not intended to be comprehensive but will provide an overview for chemists interested in this area.

2. *In situ* methods

MOFs with sulfur-containing heterocycles have been constructed by three types of *in situ* methods as (i) *in situ* S–S function reactions, (ii) *in situ* C–S bond cleavage, and (iii) *in situ* thiol-S atom reactions. The first is the most widely used tool in this area mainly due to the versatile S–S transformation through S–S reductive and oxidative cleavage. The second method is a recently developed efficient means, though it is principally concerned with hydrodesulferization (HDS). The third one may be viewed as a special direct method upon the starting ligands. Although reported occasionally, the rich chemistry associated with S atom would be expected to make it more fruitful in the future.

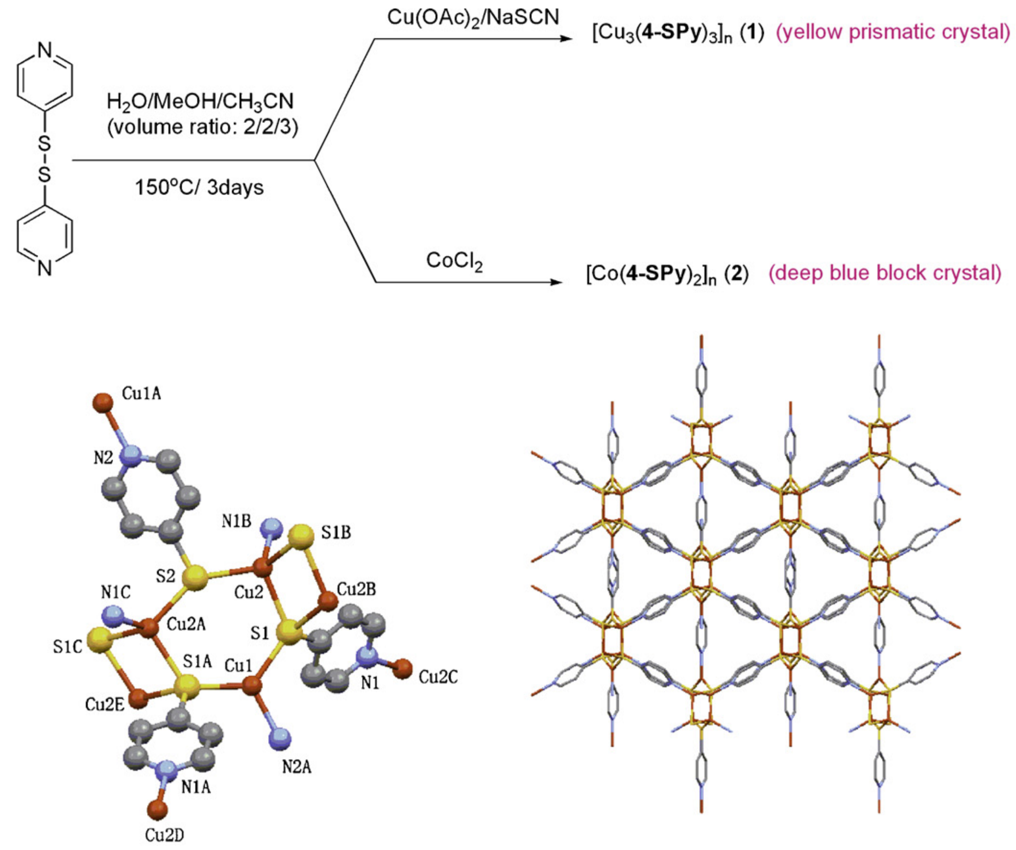
3. *In situ* S–S function reactions

The S–S function, also named disulfide, readily undergoes S–S bond scission under various thermal, chemical, photochemical and electrochemical conditions. Nevertheless, the mechanism of S–S bond cleavage is fairly complicated and may involve several routes [5]. Reductive cleavage of S–S bond has been frequently used as an efficient method for incorporating metal–sulfur bonds into molecular assemblies at an early stage. However, most examples in this aspect have been confined to the oxidative addition of disulfide bond to metal centers under *UV* or thermal treatments, and under ambient conditions [6]. Nowadays, much attention has moved to *in situ* S–S function reactions under hydro(solvo)thermal conditions primarily due to its reaction diversity under harsh circumstances. In this context, 4,4′-dipyridinedisulfide (4-dpds) and 2,2′-dipyridinedisulfide (2-dpds) are mostly discussed among the organic disulfide heterocycles.

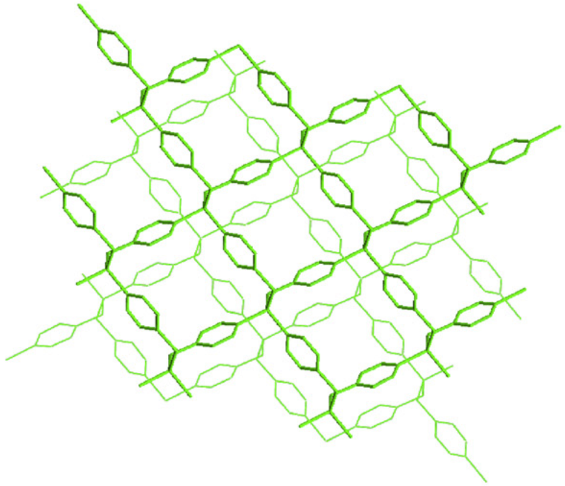
3.1. 4,4′-Dipyridinedisulfide

3.1.1. Under hydro(solvo)thermal reaction conditions

In the field of crystal engineering, hydro(solvo)thermal reactions of 4-dpds with transition metals have recently received increasing attention. Under hydro(solvo)thermal conditions, 4-dpds would be converted, through *in situ* S–S function reactions, into a variety of products including their mixtures. As shown in Scheme 1, by choosing different reaction parameters, 4-dpds may undergo *in situ* S–S cleavage to generate pyridinethiolate 4-SPy, its zwitterion 4-SPyH, or even the rearrangement zwitterion ptp. Furthermore, insertion or extrusion of one sulfur atom from S–S bond may also occur in 4-dpds, forming its trisulfide 4-dpts and monosulfide 4-dps, respectively. Sometimes, under suitable circumstance, 4-dpds and 4-dps may co-exist owing to incomplete *in situ* S–S



(a) Coordination enviroment of Cu^+ and **4-SPy** in compound **1** (b) 3D framework of compound **1** viewed down *c* axis



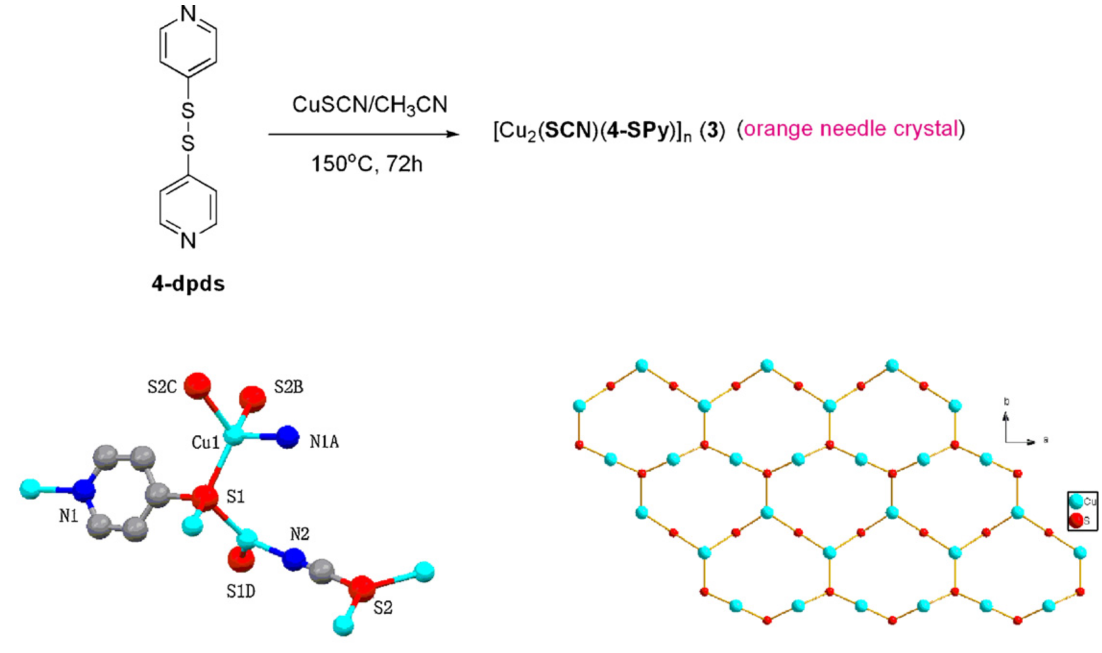
(c)Two adjacent layers with the square-grid-type structure in compound **2**

Scheme 2. Hydro(solvo)thermal reactions of 4-dpds with $Cu(OAc)_2$/NaSCN and $CoCl_2$.

reactions. Specially, 4-dpts and 4-dps may result from the same reaction.

Han et al. described the first example of MOFs fabricated through the S–S reductive cleavage of 4-dpds [7]. Under the same solvothermal conditions (Scheme 2), two novel coordination polymers **1** and **2** were obtained, accompanied by *in situ* generation of the 4-SPy ligand from 4-dpds. For compound **1**, the reduction of Cu^{2+} to Cu^+, simultaneously with the reductive cleavage of S–S bond, takes place possibly by the action of SCN^- ions. However, no valence state change of Co^{2+} ions occurs in compound **2**.

Compound **1** exhibits a three-dimensional (3,4)-connected network of which both metal sites or ligands alone can serve as 3-connected triangular and 4-connected tetrahedral nodes. It is topologically different from the known (3,4)-connected nets such as boracite and cubic C_3N_4, whose 3- and 4-connected nodes are not alternating. Moreover, a unique Cu–S chain is generated in compound **1** by means of alternative linkage of Cu_2S_2 four-ring and Cu_3S_3 six-ring structures by sharing a common edge. Compound **2** has a two-dimensional square-grid-type structure wherein each Co^{2+} ion is tetrahedrally linked to four adjacent Co^{2+} ions by four



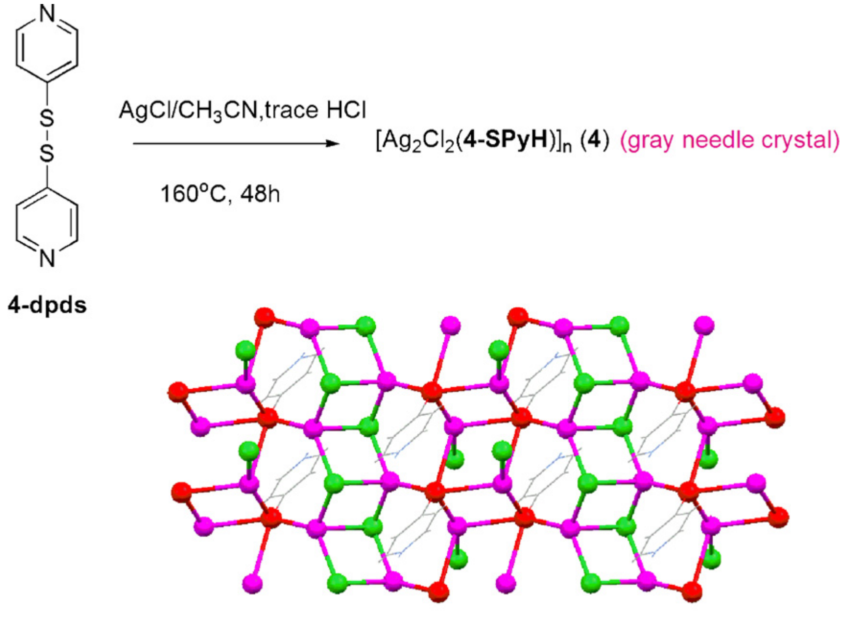
(a) Coordination enviroment of Cu$^+$ and **4-SPy** in compound **3** (b) A (6,3) Cu-S layer in compound **3**

Scheme 3. Hydro(solvo)thermal reaction of 4-dpds with CuSCN.

disparate 4-SPy ligands *via* two S and two N atoms. The coordination modes for 4-SPy ligands in both compounds are strikingly different. In compound **1**, there exist two kinds of coordination modes of μ_3: η^1N η^2S and μ_4: η^1N η^3S. There is only one single μ_2 (η^1N η^1S) bridging linkage in compound **2**.

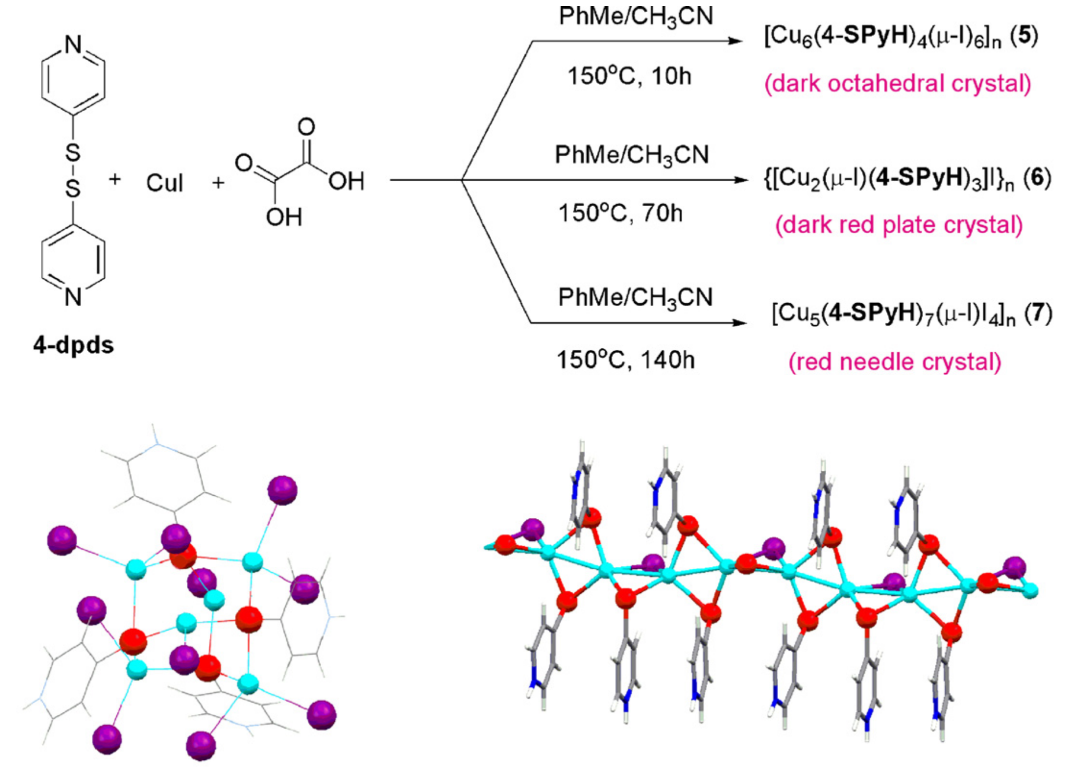
By using a similar strategy, Tong's group also reported a new coordination polymer **3** by solvothermal reaction of 4-dpds with CuSCN in acetonitrile [8] (Scheme 3). Similarly, *in situ* S–S reductive scission of 4-dpds led to the formation of 4-SPy. The SCN$^-$ ions act purely as building blocks in compound **3** instead of the reducing agent as is the case in compound **1**.

Compound **3** contains an intriguing inorganic Cu–S coordination layer in a (6,3) topology consisting of three tetrahedral Cu^I atoms, two trigonal Cu^I atoms, three μ_3-S (4-SPy) atoms, and two μ-S (SCN$^-$) atoms bound *via* Cu–S bonds to each other per ring. An infinite 3D coordination network in compound **3** results from further linking of adjacent inorganic layers by 4-SPy and SCN$^-$ ligands, which could be simplified as an unusual 3D (4,3)-connected

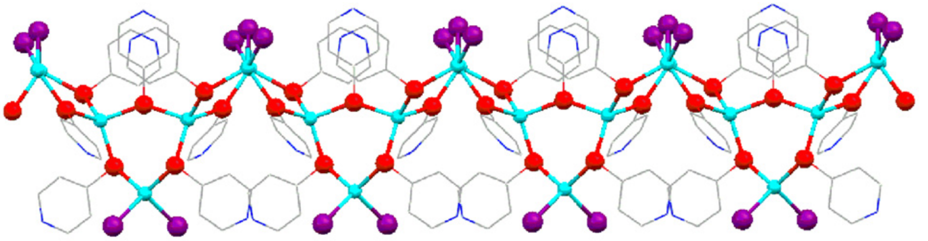


2D inorganic layer in compound **4**
(atom color code: Ag, pink; Cl, green; S, red)

Scheme 4. Hydro(solvo)thermal reaction of 4-dpds with AgCl in the presence of trace hydrochloric acid.



(a) The Cu_6S_4 core in compound **5** (b) 1D cationic chain in compound **6** extending along *c* axis



(c) 1D chain in compound **7** along *a* axis

(atom color code: Cu, light blue; I, violet; S, red)

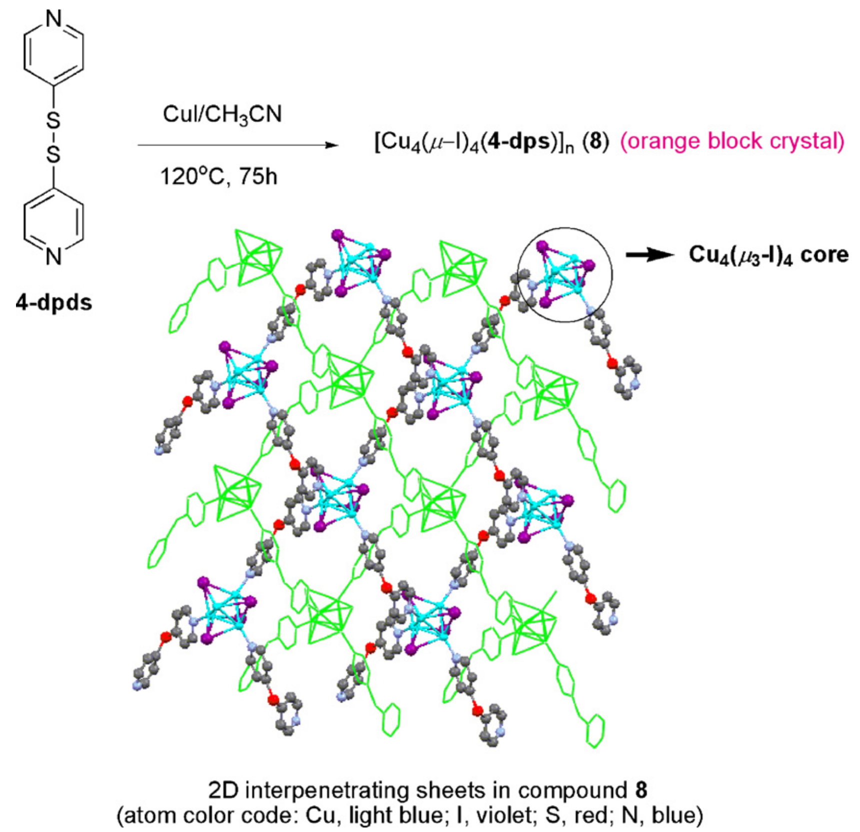
Scheme 5. Hydro(solvo)thermal reaction of 4-dpds with CuI in the presence of oxalic acid.

net with two types of four- and three-connected nodes in a ratio of 1:1:1:1. The 4-SPy ligand in compound **3** adopts a uniform μ_4: η^1N η^3S coordination pattern while the linear SCN^- ligands act as μ_3: η^1N η^2S bridges.

The same research group also found that *in situ*-generated 4-SPy may be present in its zwitterion form of 4-SPyH if the solvothermal reaction was carried out in a sub-acidic reaction medium [8] (Scheme 4). In compound **4**, the resultant 4-SPyH only takes advantage of the naked S atom to coordinate with Ag^+ ions in a μ_3-S coordination mode. Interestingly, the chloride ions have two distinct coordination modes, η^1-Cl end-on coordination and μ_3-Cl bridges. Connection between metal ions with μ_3-bridge chloride anions generated a one-dimensional $(AgCl)_n$ ladder chain, while two S atoms and two Ag^+ ions formed a square four-membered Ag_2S_2 ring. All the chains are further joined together by the Ag_2S_2 rings through Ag–S bonds, producing a two-dimensional (4,4) inorganic layer.

Lang's group introduced another example concerning the *in situ* formation of 4-SPyH from 4-dpds [9] (Scheme 5). The use of oxalic acid should be responsible for maintaining the reaction medium sub-acidic. It is also an interesting example that just by changing the solvothermal reaction period one can stepwise synthesize compounds **5**–**7**.

The resulting compounds **5**–**7** are all Cu/I/S-based coordination polymers. Compound **5** has an adamantine-type Cu_6S_4 core bearing four equatorial Cu(I) atoms and two apical ones, which works as a tetrahedral 4-connected node to link with other equivalent ones through four pairs of iodide bridges coordinated to equatorial Cu(I) atoms, forming a 3D diamond-like net. Compound **6** contains a slightly puckered Cu_2IS ring with two Cu(I) atoms bridged by one μ-I and μ-4-SPyH, which further connects with its neighboring ones through two pairs of μ-4-SPyH to produce a 1D cationic chain. Compound **7** possesses a repeating $[Cu_5(\mu\text{-}I)I_4(\mu\text{-}4\text{-}SPyH)_7]$ unit made up with a $[Cu_4(\mu\text{-}I)I_2(\mu\text{-}4\text{-}SPyH)_5]^+$



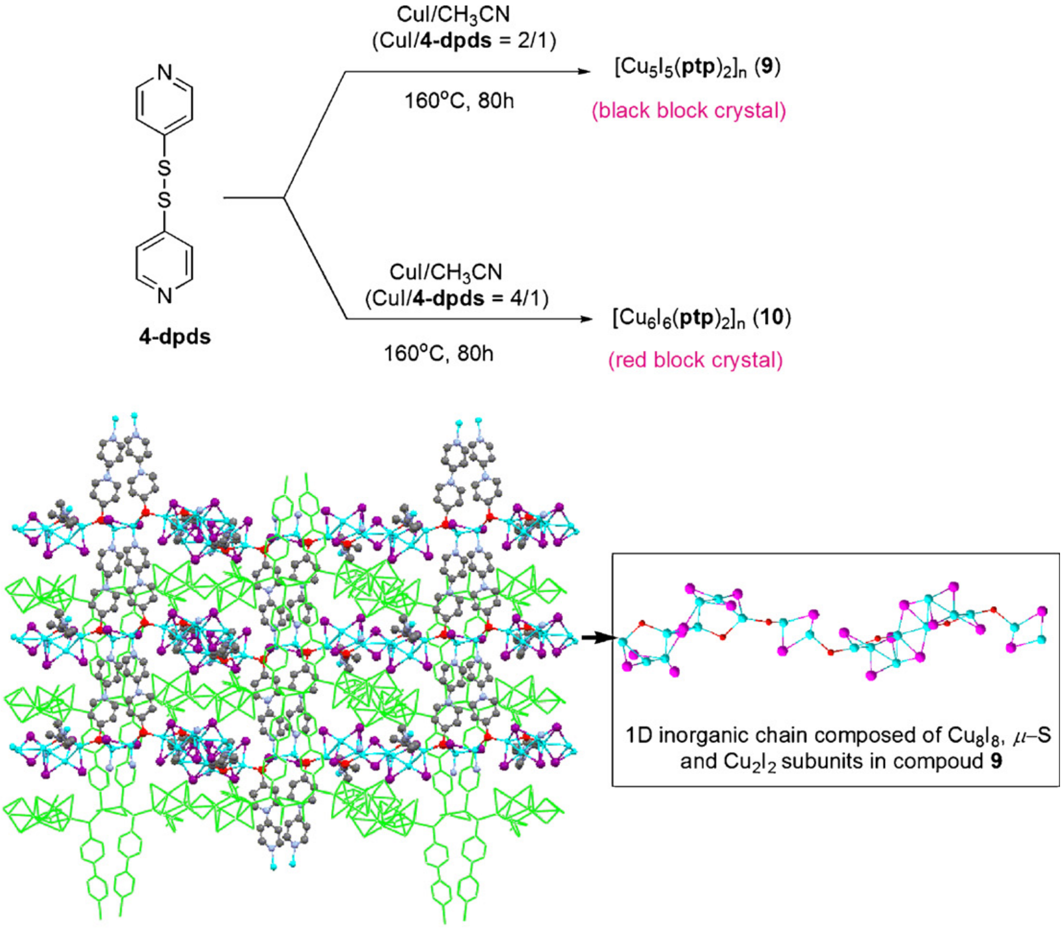
Scheme 6. Hydro(solvo)thermal reaction of 4-dpds with CuI at 120 °C.

fragment and $[CuI_2(\mu\text{-}4\text{-}SPyH)_2]^-$ fragment joined together by one μ-4-SPyH ligand, which further interconnects each other through a couple of μ-4-SPyH species to give a 1D chain. On the other hand, 4-SPyH is present in a μ_3-S coordination mode in compound **5**, and a μ_2-S coordination mode in compounds **6** and **7**. According to the Kubelka–Munk function, the absorption (α/S) data of crystalline solids **5**–**7** are calculated from the reflectance based on their ambient optical diffuse-reflection spectra. Followed by extrapolation of the linear portion of the absorption edges, the estimated energy band gaps of compounds **5**–**7** (**5**, 1.69 eV; **6**, 2.10 eV; **7**, 2.13 eV) lie between the band gaps of Cu_2S (1.2 eV) and CuI (3.1 eV), suggesting that these Cu/I/S-based coordination polymers be endowed with semiconductor characteristics of CuI and Cu_2S. Moreover, variable-temperature measurements of the conductivity of their single crystals show that they have a typical semiconducting behavior. With temperature increase from 293 to 443 K, the electrical conductivities of their single crystals change drastically from $1.97 \times 10^{-7}\,S\,m^{-1}$ to $6.32 \times 10^{-5}\,S\,m^{-1}$ (**5**), from $6.84 \times 10^{-6}\,S\,m^{-1}$ to $3.96 \times 10^{-4}\,S\,m^{-1}$ (**6**), and from $2.74 \times 10^{-7}\,S\,m^{-1}$ to $2.43 \times 10^{-5}\,S\,m^{-1}$ (**7**). The authors attribute the best performance of compound **6** to the larger density of states or effective mass of compound **6** compared with compounds **5** and **7**.

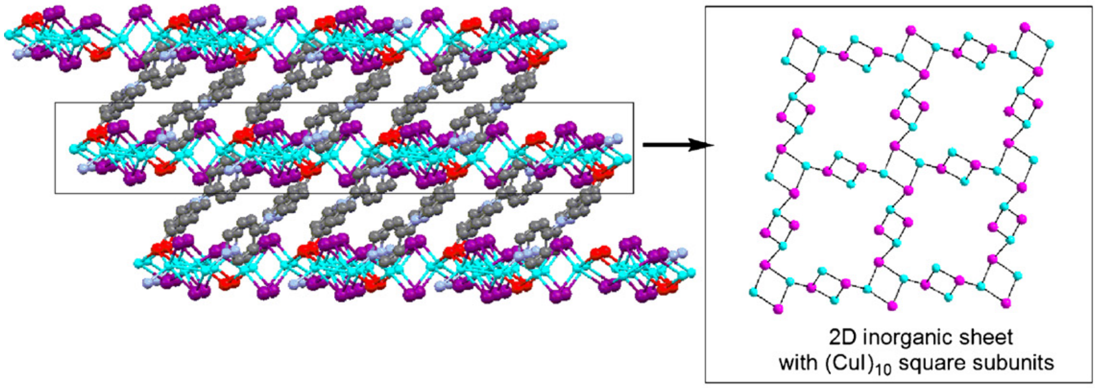
In addition to the aforementioned S–S reductive cleavage, 4-dpds may also be converted into its monosulfide (4-dps) through a disproportionation reaction. Tong first reported that the solvothermal reaction between 4-dpds and CuI at 120 °C in CH_3CN resulted in an unprecedented coordination polymer (**8**) (Scheme 6), of which 4-dps was *in situ* generated and believed to be from the disproportionation reaction of 4-dpds since the formation of the elemental sulfur was observed [10]. Compound **8** is a 2D coordination network of 2-fold interpenetration, in which the 2D undulating (4,4)-net is made up of cubane-like $Cu_4(\mu_3\text{-}I)_4$ cores as four-connected nodes and 4-dps as angular spacers. The resultant 4-dps works as a common N,N-bridging linker with the sulfur atom intact.

More surprisingly, 4-dps could even be converted into an exceptional zwitterionic product ptp if the same solvothermal reaction was performed at an elevated temperature. Thus, only by changing the reaction temperature from 120 °C to 160 °C, the same reaction system for compound **8** would produce a wholly different coordination architecture (**9**) with the *in situ* resultant ptp ligand [10] (Scheme 7). The ptp is speculated to be transformed from its isomeric 4-dps through subsequent S–C(sp) bond cleavage and rearrangement reactions at the higher temperature. The ptp in compound **9** serves as a μ_3 linker with the S atom bridging two Cu^+ ions and the N atom bound to the third Cu^+ ion. Compound **9** could be described as a 3D coordination network of 2-fold interpenetration with 1D inorganic chains assembled by ptp-connection, which is constructed by alternative linkage of Cu_8I_8 and Cu_2I_2 clusters *via* the μ_2-sulfur bridges. Furthermore, another compound **10** was obtained by additional change of CuI/4-dpds molar ratio from 2/1 to 4/1 [10] (Scheme 7). Unlike compound **9**, ptp ligand in compound **10** acts as a μ_4 bridge with the sulfur atom connecting three Cu^+ ions. Compound **10** is one of the limited examples containing 2D inorganic copper(I) halide sheets, and has a rare 2D inorganic $(CuI)_n$ layer in (4,4) topology, comprising two different kinds of Cu_2I_2 dimeric units linked mutually *via* Cu–I bonds: four-connected ones and two-connected ones. A non-interpenetrating 3D coordination network of compound **10** was eventually installed by the means of 2D inorganic layers pillared by ptp ligands.

In situ generation of 4-dps from 4-dpds under solvothermal condition has also been demonstrated by two other groups. One group revealed that solvothermal reaction between $Co(OAc)_2$ and mixed ligands of 4-dpds and H_2tbip (H_2tbip = 5-tert-butyl isophthalic acid) would turn out remarkably distinct results under variable temperatures [11] (Scheme 8(a)). Solvothermal reaction at 120 °C



(a) 3D coordination network with 2D interpeneration in compound **9**

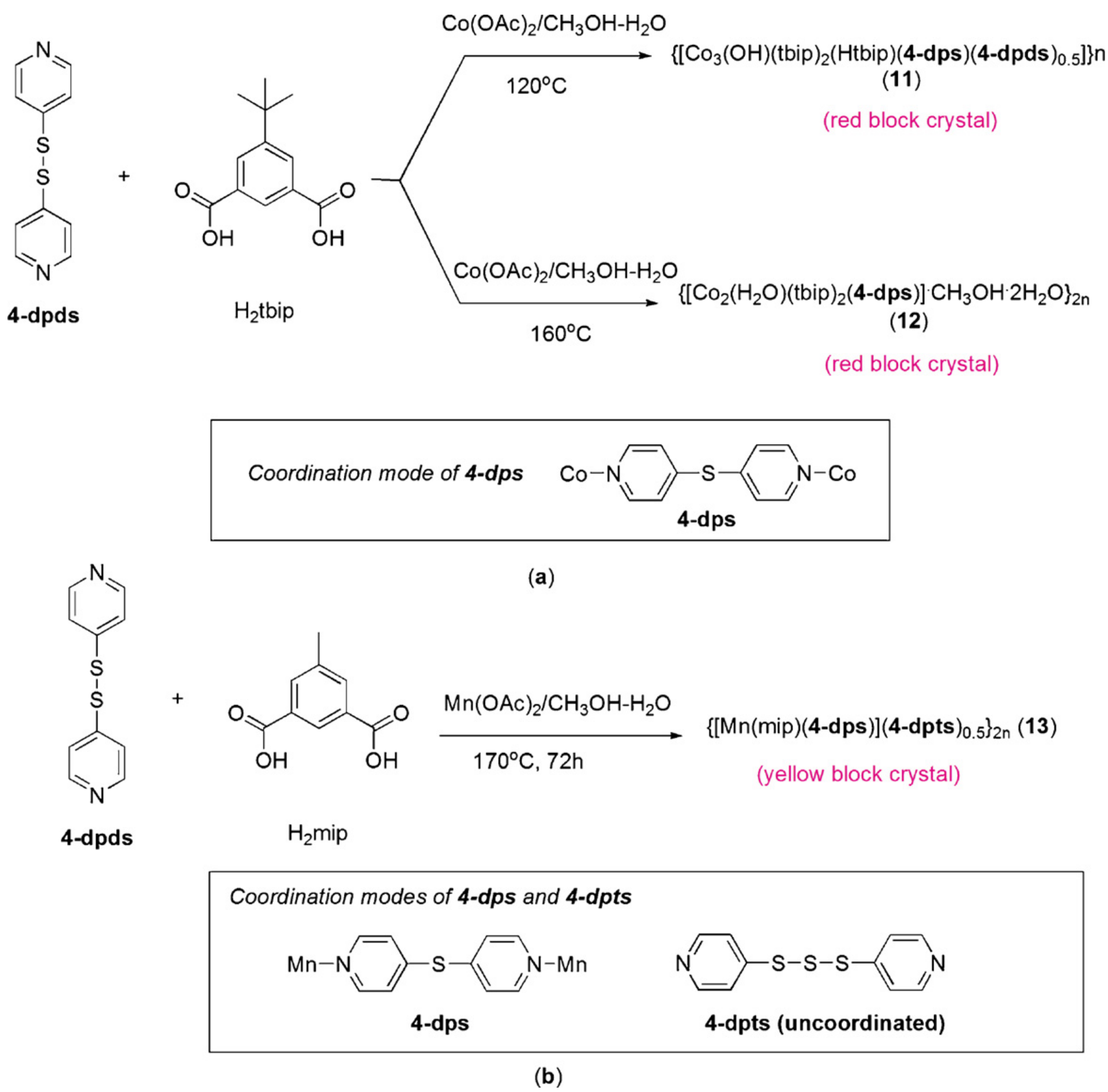


(b) 3D coordination network pillared by **ptp** in compound **10**

(atom color code: Cu, light blue; I, violet; S, red)

Scheme 7. Hydro(solvo)thermal reaction of 4-dpds with CuI at 160 °C.

afforded compound **11** with mixed ligands of tbip, Htbip, 4-dps and 4-dpds, whereas the same reaction at 160 °C generated compound **12** that contains only tbip and 4-dps. It is quite interesting to find that 4-dpds was, unpredictably, partially transformed into 4-dps in compound **11**, providing a unique example containing mixed ligands of 4-dps and 4-dpds. Compound **11** is a 3D network composed of trinuclear $[Co_3(\mu_3\text{-OH})]^{5+}$ clusters as 5-connected nodes, which are linked to two others by single tbip bridges, to two more by both tbip and a 4-dps bridge, and to a fifth by two Htbip and one 4-dpds bridge. Compound **12** is also a non-interpenetrating 3D network consisting of $Co_3(CO_2)_6$ trimeric clusters supported by six carboxylate groups, which act as a 6-connecting node to connect two other trimers (*via* two pairs of tbip ligands) and four independent Co^{2+} atoms as 4-connecting nodes (*via* single tbip and 4-dps bridges). 4-dps and 4-dpds in both compounds **11** and **12** appear in the N, N-bridging mode.



Scheme 8. (a) Hydro(solvo)thermal reaction of mixed ligands (4-dpds and H_2tbip) with $Cu(OAc)_2$; (b) Hydro(solvo)thermal reaction of mixed ligands (4-dpds and H_2mip) with $Mn(OAc)_2$.

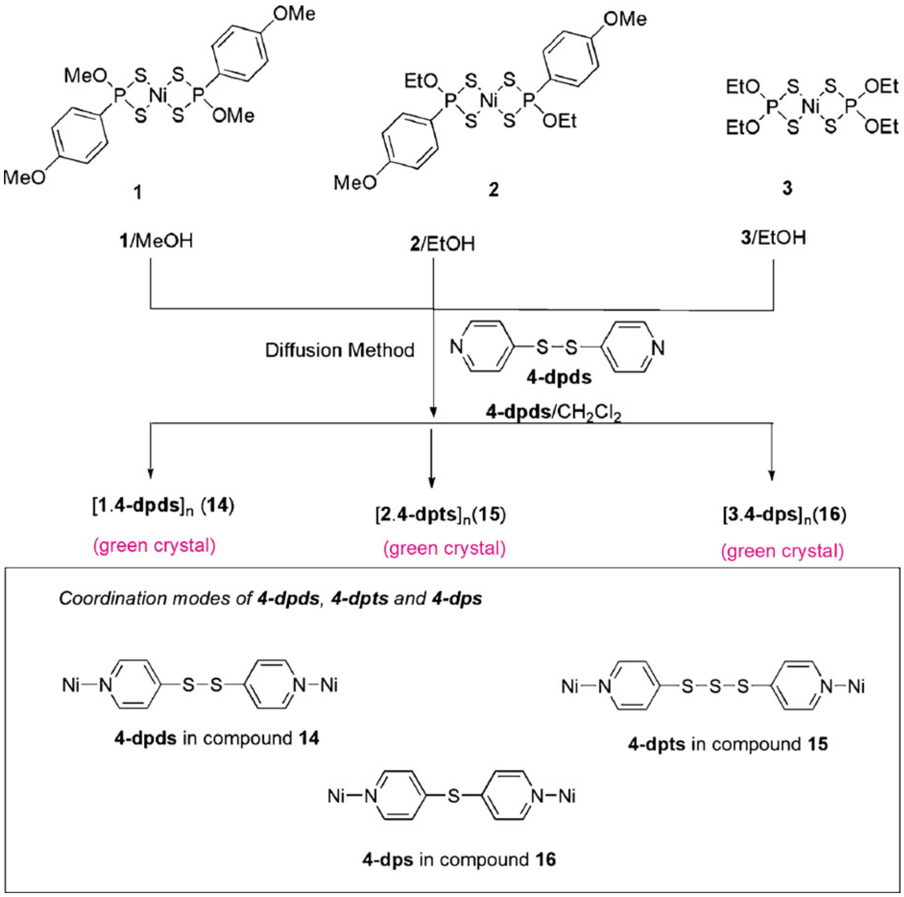
Another group discovered that both 4-dps and trisulfide 4-dpts could be *in situ* generated in a one-pot solvothermal reaction [12]. Hydrothermal reaction of 4-dpds and 5-methylisophthalate (H_2mip) with $Mn(OAc)_2$ in CH_3OH/H_2O at 170 °C for 3 days produced an unprecedented coordination polymer (**13**) (Scheme 8(b)), which contains mip, 4-dps and 4-dpts. It is the first report on *in situ* generation of 4-dpts from 4-dpds under solvothermal conditions. Nevertheless, the resultant 4-dpts ligands, unlike 4-dps, are not involved into metal-coordination but lattice molecules in compound **13**. Mip anions here serve as tridentate ligands to join Mn(II) ions to form a 1D polymeric motif, which consequently are interlinked by 4-dps spacers to generate a complicated 3D coordination network. In fact, compound **13** is a rare example of a metal–organic coordination network with mixed (3,5)-connectivity, of which Mn(II) ion works as a 5-connected trigonal bipyramidal node while the mip anion as a planar 3-connected node.

3.1.2. Under ambient conditions in solution

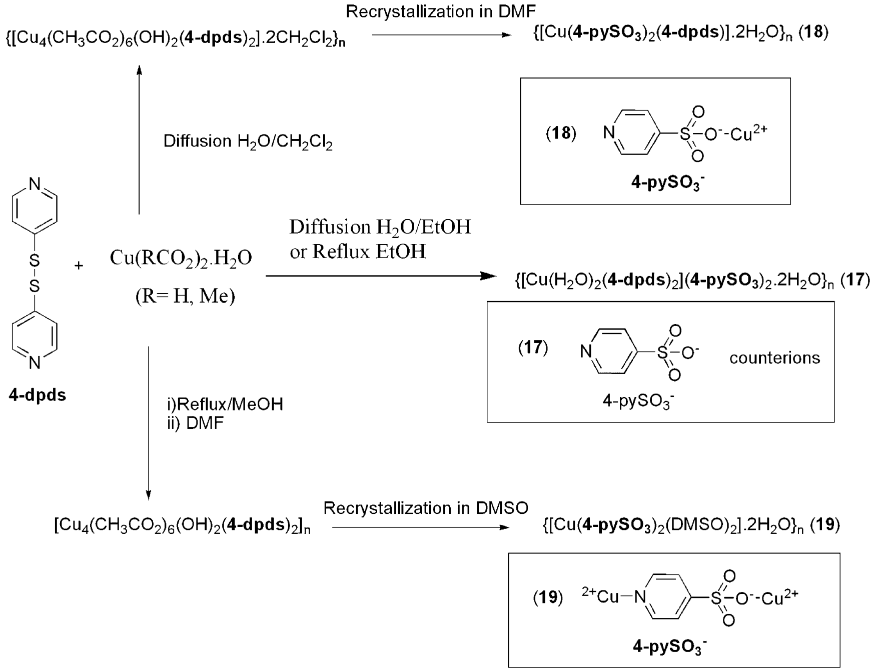
Under mild conditions, extrusion or insertion of one S atom from S–S bond may happen within 4-dpds as well, yielding its monosulfide 4-dps and trisulfide 4-dpts, respectively. Three novel 1D Ni^{II} coordination polymers (**14**)–(**16**), with different N,N-bridging spacers ((**14**): 4-dpds; (**15**): 4-dps; (**16**): 4-dpts), are obtained by the diffusion method at room temperature [13] (Scheme 9). Undoubtedly, both 4-dps and 4-dpts were generated through *in situ* chemical rearrangement of the starting 4-dpds, the isolation of which proved the existence of pyridyldisulfide and pyridylsulfide radicals.

In the normal solution reaction, oxidative cleavage of S–S bond within 4-dpds has been observed in the presence of basic copper(II) salts (formate and acetate), which is the first example of direct oxidation of 4-dpds to its sulfonate without the use of a strong oxidizing agent [14] (Scheme 10).

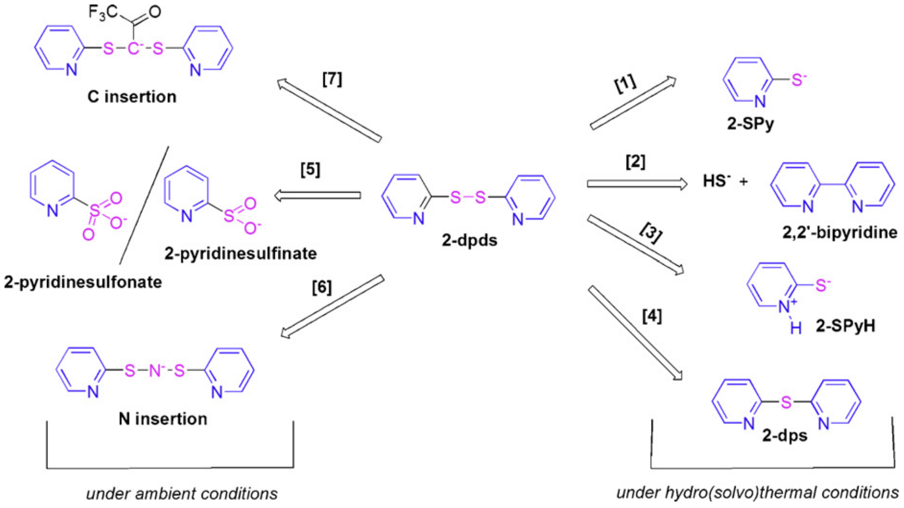
As depicted in Scheme 10, compound **17** could be prepared by several direct methods such as the diffusion method or under refluxing conditions, wherein the starting material, 4-dpds, is partly oxidized to its sulfonate, 4-pyridylsulfonate (4-PySO_3^-). In compound **17**, copper(II) ions are bridged by a pair of the remaining 4-dpds ligands, forming a chiral repeated rhomboid chain, whereas 4-PySO_3^- only acts as a counter-ion. In comparison, compounds **18** and **19** can only be accessible in a stepwise manner. Reaction of 4-dpds with copper(II) salts first produces copper(II) coordination compounds with 4-dpds, $\{[Cu_4(HCO_2)_6(OH)_2(4\text{-dpds})_2]{\cdot}2CH_2Cl_2\}_n$ and $[Cu_4(CH_3CO_2)_6(OH)_2(4\text{-dpds})_2]\}_n$, followed by recrystalliza-



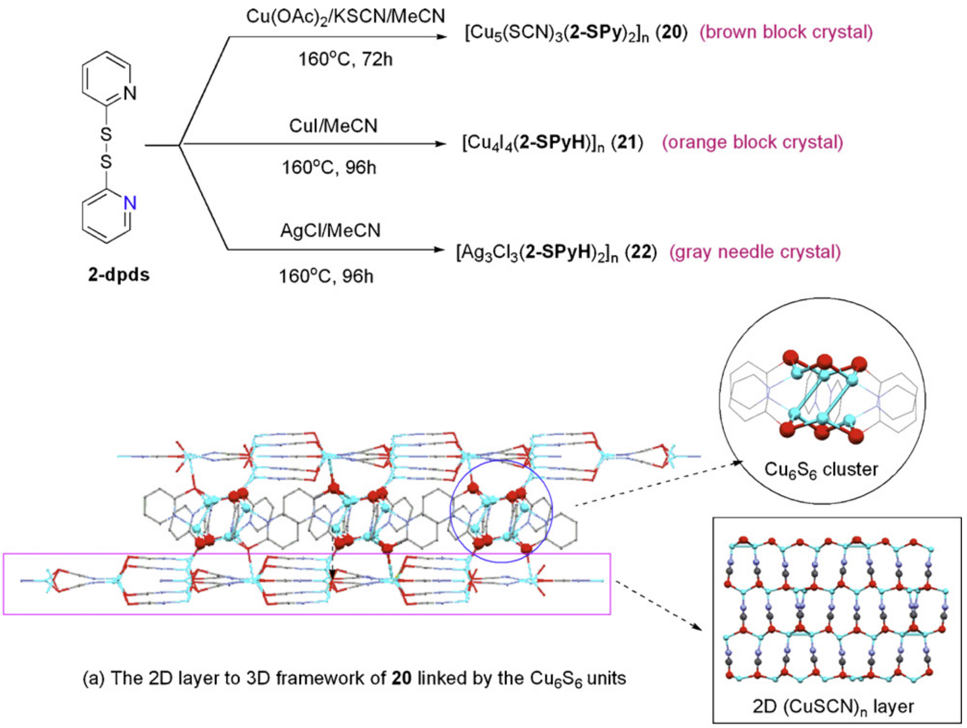
Scheme 9. Extrusion or insertion of one S atom from S–S bond within 4-dpds.



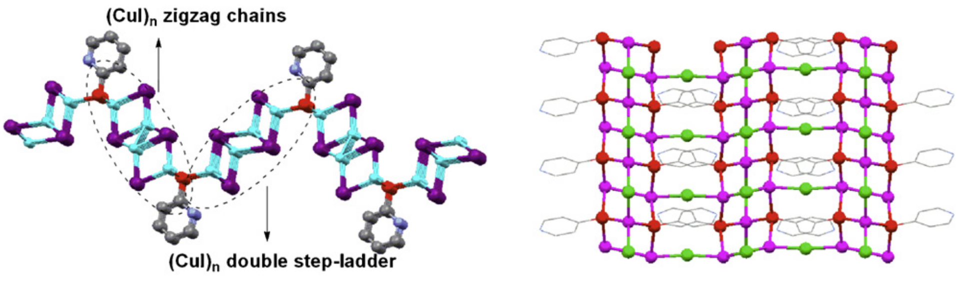
Scheme 10. *In situ* oxidative cleavage of S–S bond of 4-dpds mediated by copper(II) salts (coordination modes of 4-pySO$_3^-$ in compounds **17–19** (blue crystals) marked in square grid).



Scheme 11. *In situ* S–S function reactions of 2-dpds.



(a) The 2D layer to 3D framework of **20** linked by the Cu_6S_6 units



(b) 2D Cu··· Cu-S-Cu··· Cu layers in compound **21**

(c) 2D inorganic sheet structure in compound **22**

(atom color code: Cu, light blue; I, violet; S, red; N, blue)

Scheme 12. Hydro(solvo)thermal reactions of 2-dpds with $Cu(OAc)_2$/KSCN, CuI and AgCl.

tion from DMF and DMSO to give compounds **18** and **19**, respectively. Compound **18**, with mixed ligands of 4-dpds and 4-$PySO_3^-$ resulted from incomplete oxidation. It also exhibits a chiral rhomboid $[Cu(4\text{-dpds})_2]_n$ chain as compound **17**, and 4-$PySO_3^-$ appears as a terminal coordination ligand *via* one of sulfonate oxygen atoms. In compound **19**, 4-dpds was fully oxidized to 4-$PySO_3^-$, which exhibits bidentate N,O-bridging coordination behavior, linking copper(II) ions to give a polymeric repeated rhomboid chain.

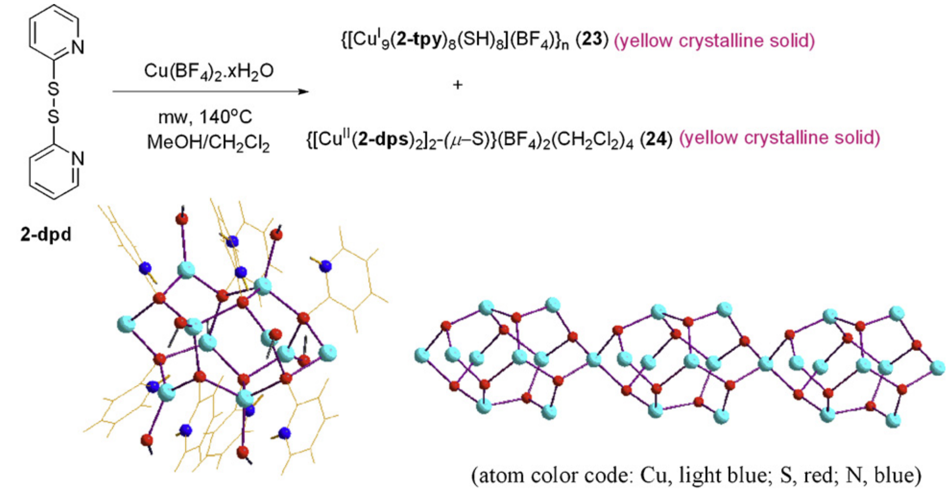
3.2. 2,2′-Dipyridinedisulfide

As the analogue of 4-dpds, 2,2′-dipyridinedisulfide (2-dpds) has often been employed in the crystal engineering of metal–organic frameworks (Scheme 11). Similarly, under hydro(solvo)thermal conditions, 2-dpds may be turned into either its pyridinethiolate 2-SPy or zwitterion 2-SPyH *via in situ* S–S bond cleavage, or its monosulfide 2-dps through concurrent *in situ* S–S and C–S cleavage. Strikingly, the subsequent C–S cleavage may even generate HS^- anions, concomitantly with the formation of 2,2′-bipyridine. Meanwhile, under ambient conditions, oxidative cleavage of S–S bond may also take place within 2-dpds to generate its pyridinesulfonate (2-$PySO_3^-$), pyridinesulfinate (2-$PySO_2^-$), or even their mixture, generally triggered by the action of basic copper(II) salts. Notably, it is unique in 2-dpds that an N or C atom except for the S atom may unpredictably insert into the S–S bond in special reaction systems, as proven by X-ray studies.

3.2.1. Under solvo(hydro)thermal reaction conditions

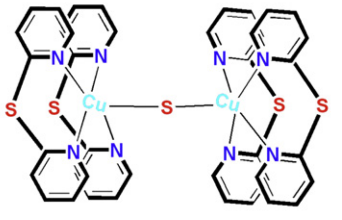
Solvothermal reaction of 2-dpds, $Cu(OAc)_2$ and KSCN in MeCN produced compound **20** with 2-SPy as organic building blocks [8], while solvothermal reactions with CuI and AgCl in the sub-acidic environment generated compounds **21** and **22** both based on the 2-SPyH ligands [8] (Scheme 12). Compound **20** is a complicated 3D coordination polymer where 2D $(CuSCN)_n$ layers are linked by pseudo (Cu_6S_6) clusters containing two sets of (Cu_3S_3) units joined by Cu–Cu interactions. The 2-SPy ligands formed *in situ* adopt the μ-4 coordination mode while SCN^- anions work as μ-3 and μ-4 coordination modes. Compound **21** is a novel 2D network composed of Cu···Cu–S–Cu···Cu layers made by two distinct $(CuI)_n$ zigzag chains and double step-ladder chains interlinked each other by μ-3 S from the 2-SPyH ligands. The iodide ions adopt three types of coordination modes, μ-2, μ-3 and μ-4. Compound **22** has an inorganic sheet structure, in which the $(Ag_5S_2Cl_2)_n$ double step-ladder chains are linked to each other by μ_2-Cl atoms. The coordination mode of 2-SPyH in compound **22** is identical with that in compound **21**.

Surprisingly, under microwave solvothermal conditions, an unusual 1D Cu^I coordination polymer (**23**) together with a novel discrete binuclear Cu^{II} complex (**24**) was obtained by reaction of $Cu(BF_4)_2$ with 2-dpds [15] (Scheme 13). In the course of solvothermal reaction, *in situ* S–S and C–S bond scission occurred at 2-dpds, unprecedentedly leading to the formation of 2-pyridylthione (2-tpy), 2-dps, elemental sulfur S_8 and even HS^-. Compound **23** is an interesting quasi-1D Cu^I polymer based on the assembly of Cu_9 cages which comprise nine copper(I) cations bridged to each other by μ-3 sulfur atoms from 2-tpy. Complex **24**, as the minor product, has two centrosymmetric $[Cu^{II}(2\text{-dps})]$ units connected by a linear sulfur bridge, which constitutes one of a few examples containing a linear sulfur bridge between two transition metals. It is assumed that 2-dpds may undergo homolytic rupture of S–S and S–C(sp^2) bonds to release [2-py·] and [2-pyS·] radicals. The formation of 2-dps is ascribed to the combination of two above



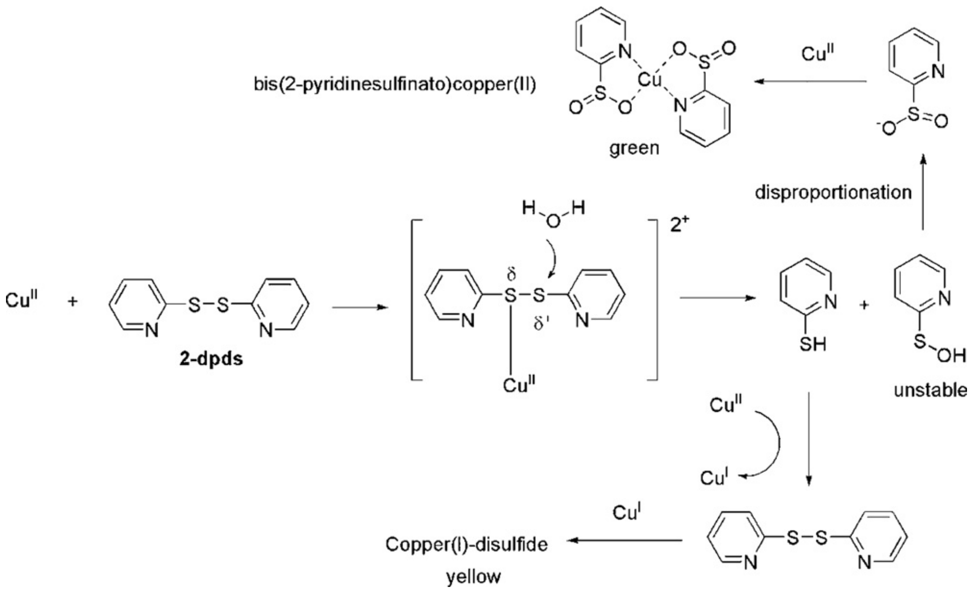
(atom color code: Cu, light blue; S, red; N, blue)

(a) The $[Cu_9(C_5H_5NS)_8(SH)_8]^+$ cluster in compound **23** (b) 1D coordination chain of **23** based on Cu_9 cage

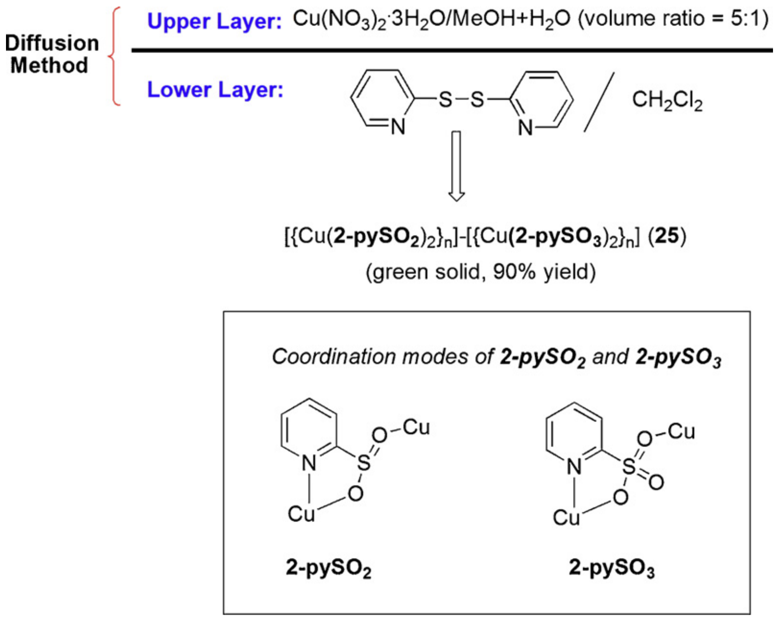


(c) Coordination enviroment of Cu^{2+} and **2-dps** in compound **24**

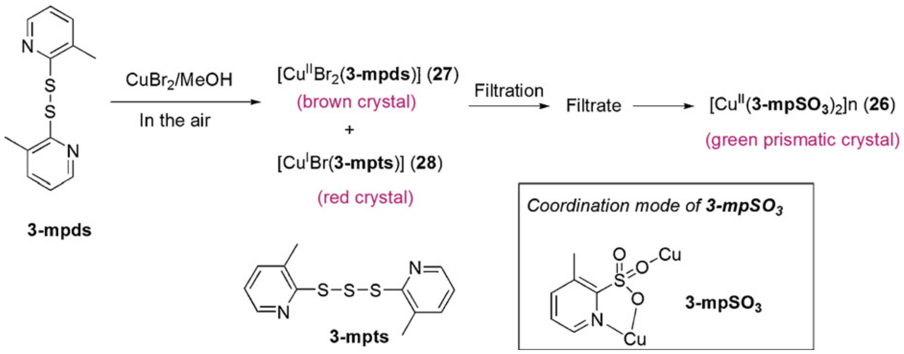
Scheme 13. Microwave solvothermal reaction of 2-dpds with $Cu(BF_4)_2$.



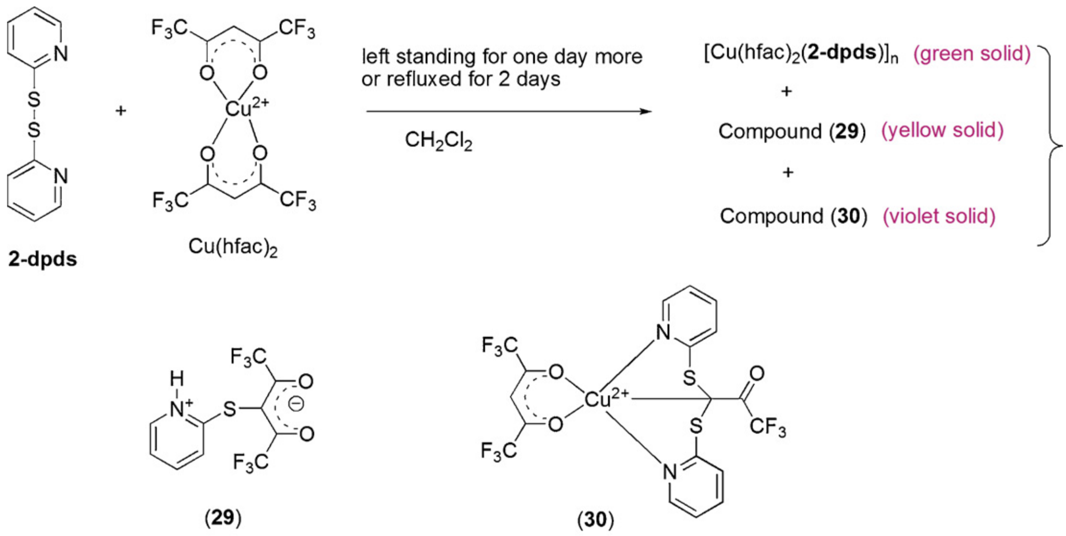
Scheme 14. Oxidative S–S bond cleavage of 2-dpds mediated by $Cu(ClO_4)_2$.



Scheme 15. Oxidative S–S bond cleavage of 2-dpds mediated by $Cu(NO_3)_2$.



Scheme 16. Oxidative S–S bond cleavage of 3-mdps mediated by $CuBr_2$.



Scheme 17. Carbon atom insertion of S–S bond within 2-dpds.

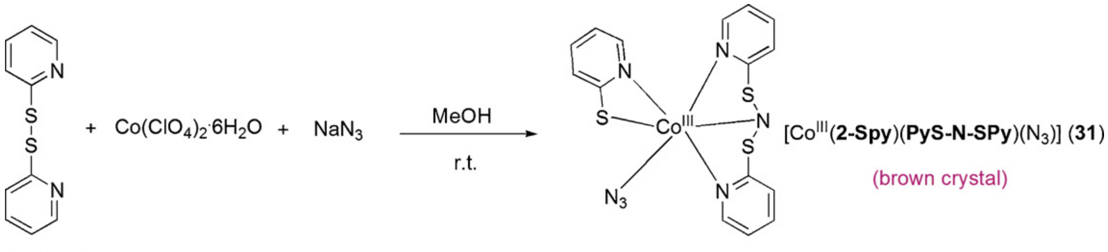
radicals whereas self-combination of [2-py·] radicals should give 2,2′-bipyridine, which has been confirmed by means of electrospray ionization mass spectrometry. The reduction of Cu^{II} to Cu^{I} in compound **23** is probably related to the presence of N-containing ligands or thiolate groups. It is the first report of the application of microwave technique for preparing new coordination networks, and that compound **23** is one of the very few coordination polymers exhibiting conductivity in the solid state. Measurements of the dc electrical conductivity of compound **23** were conducted on two different single crystals with the four contact methods. (The contacts were made with Pt wires (25 μm diameter) along the long axis of the needles using graphite paste and the samples were examined in a Quantum Design PPMS-9 with dc currents between 5 and 100 nA.) Both crystals exhibit similar conductivity characteristics (1.0×10^{-3} and 1.6×10^{-3} S cm^{-1} at room temperature) as well as thermal behavior (with activation energies of 109 and 110 meV).

3.2.2. Under ambient conditions in solution

Under ambient conditions in solution, 2-dpds also exhibits diverse reactions, of which oxidative cleavage of S–S bond would be the most general type. In fact, the earliest report, dating back to 1977, revealed that reaction of 2-dpds with Cu(ClO$_4$)$_2$ yielded a yellow product and a green product, which were structurally determined as a Cu^{I}–disulfide complex and bis(2-pyridinesulfinate) copper(II) complex, respectively [16]. In this reaction, 2-dpds is believed to be oxidized into 2-pyridinesulfinato by Cu(II) ions, which may proceed by a concomitant electrophilic and nucleophilic attack on the S–S bond by the Cu(II) ion and water molecules (Scheme 14).

Similarly, by treatment of 2-dpds with Cu(NO$_3$)$_2$·3H$_2$O in both aerobic and anaerobic conditions, an unexpected sulfinate-sulfonate mixed coordination polymer of copper(II) (**25**) was obtained [17] (Scheme 15), which should follow an analogous reaction route to that for Cu(ClO$_4$)$_2$. However, the remarkable difference is that the oxidized product of 2-dpds is a mixture of its sulfonate and sulfinate derivatives. Compound **25** possesses an infinite 1D polymeric chain consisting of [Cu(C$_5$H$_4$N)$_2$] building units connected by SO$_2$/SO$_3$ groups.

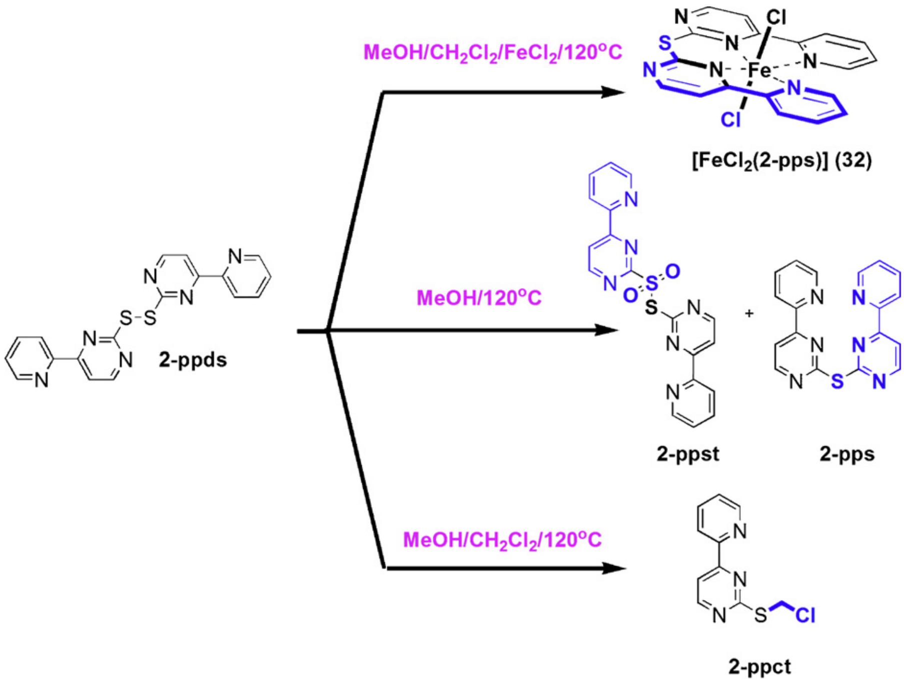
Another example utilizing such a reaction is described by a 1D Cu(II) coordination polymer (**26**) with 2-pyridinesulfonate donors which was formed *via* the air oxidation of 3-mpds (3-mpds = (2,2′-bis(3-methylpyridyl)disulfide)) in the presence of CuBr$_2$ [18] (Scheme 16). In this reaction, 3-mpds is completely oxidized into its sulfonate derivative. Nevertheless, the oxidation reaction could be terminated at the stage of sulfinate if CuBr$_2$ is replaced with Cu(ClO$_4$)$_2$. Moreover, the yield of compound **26** is only 5%, and the major products, initially formed from this reaction, are compound **27** with 3-mpds and compound **28** with 3-mpts (3-mpts = (2,2′-bis(3-methylpyridyl)trisulfide). Quite close to compound **25**, compound **26** also consists of an infinite 1D chain, of which the NOCuON core in the basic unit of [Cu(3-mpySO$_3$)$_2$] is bridged by the use of its two oxygen atoms from two 3-mpySO$_3$



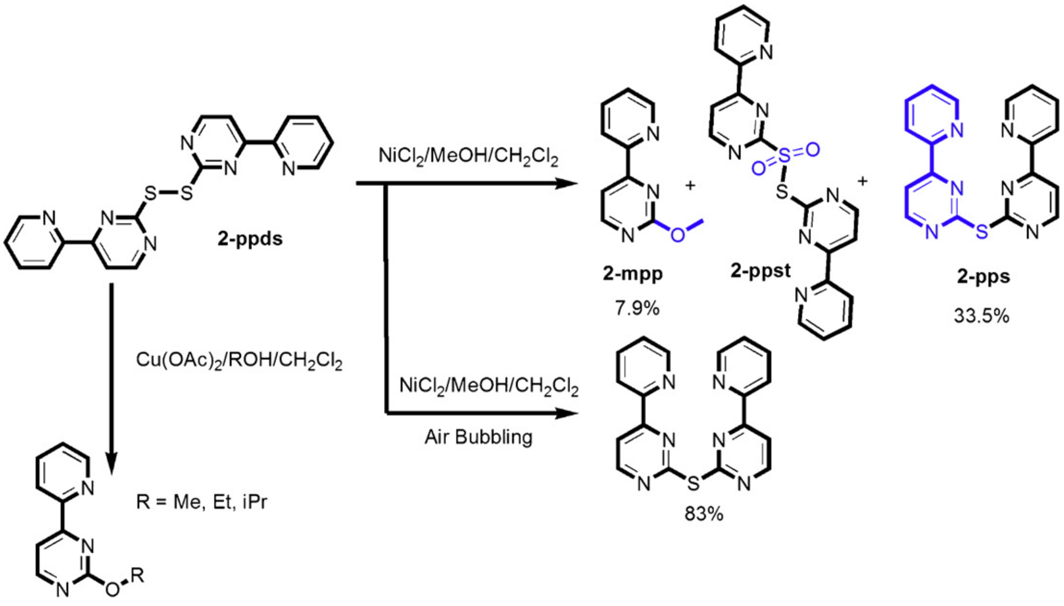
A possible reaction equation:

$$Co^{II} + 1.5(\textbf{2-dpds}) + 2N_3^{-} \longrightarrow [Co^{III}(\textbf{2-Spy})(\textbf{PyS-N-SPy})(N_3)] + N_2$$

Scheme 18. Nitrogen atom insertion of S–S bond within 2-dpds.



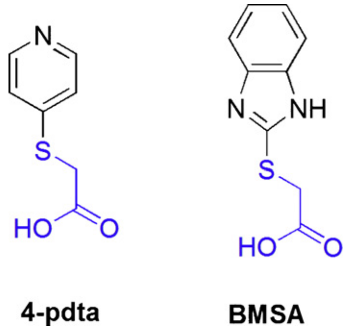
Scheme 19. *In situ* S–S function reactions of 2-ppds under solvolysis conditions.



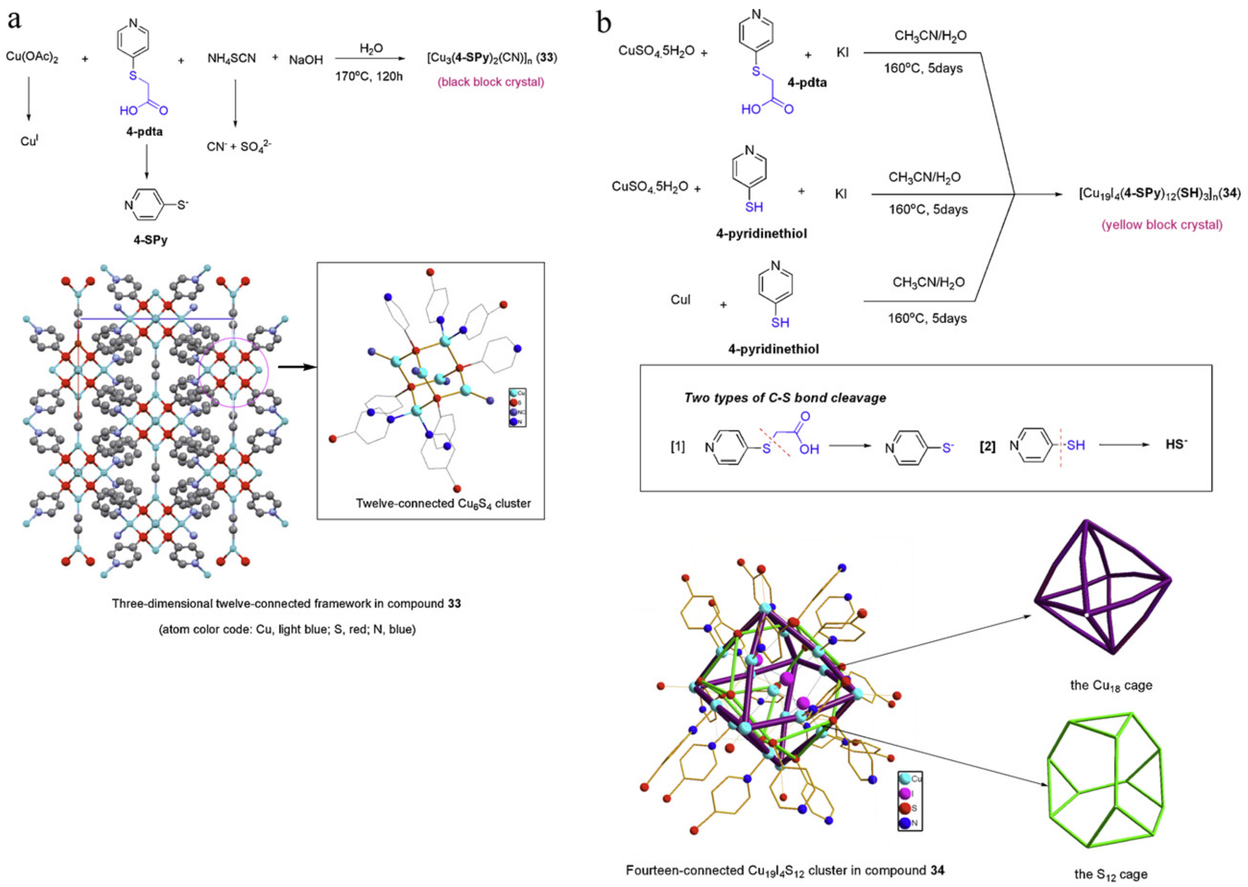
Scheme 20. Metal-coordination induced *in situ* S–S function reactions of 2-ppds.

donors to coordinate with the Cu(II) atom belonging to adjourning cores at the apical position.

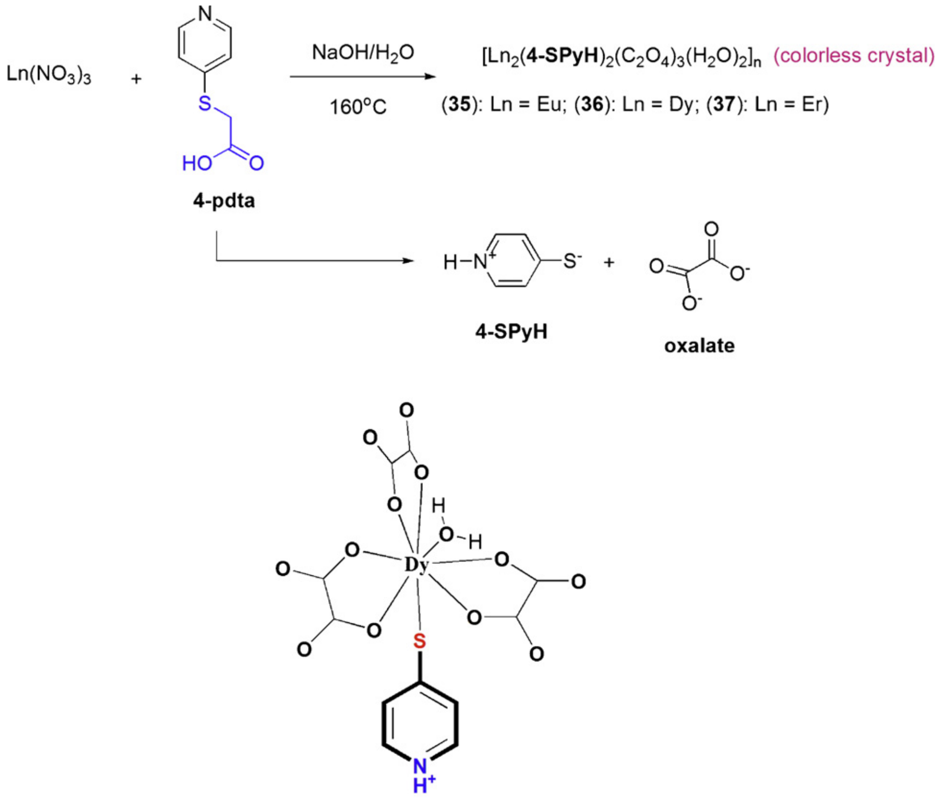
Remarkably different from 4-dpds, one C atom insertion into the S–S bond has occurred in 2-dpds. The mixture of 2-dpds and Cu(hfac)$_2$ (hfac = hexafluoroacetylacetonate) in CH_2Cl_2, which was left standing for longer than one day or refluxed for two days, would give two new rearrangement products (**29**) and (**30**) rather than the expected copper(II) compound with 2-dpds [19] (Scheme 17). Compound **29** is a new organic compound bearing a (1-hydro-2-pyridinio)thiol group that is bound to a hexafluoroacetylacetonate anion through a S–C bond, and compound **30** is a mononuclear compound wherein the Cu^{II} ion is pentacoordinated to two oxygen atoms of the hfac anion, two nitrogen atoms of two 2-pyridyl sulfide fragments, and one carbon atom of the CC(O)CF$_3$ fragment, which has been inserted into the S–S bond of 2-dpds. A plausible mech-



Scheme 21. Two common ligands with the structure of HOOC–CH$_2$–S-Het (Het: heterocycle).



Scheme 22. *In situ* C–S bond cleavage of 4-pdta mediated by Cu(II) and Cu(I).



Coordination enviroment of Dy^{3+} in compound **37**

Scheme 23. *In situ* C–S bond cleavage of 4-pdta triggered by lanthanide ions.

anism was suggested by the authors to explain the formation of compounds **29** and **30**. The Cu^{II} coordination effect in $[Cu(hfac)_2(2\text{-dpds})]_n$ may promote homolytic cleavage of 2-dpds, generating [2-pyS·] radicals. The attack of the methine carbon atom of the $hfac^-$ anion on the pyridyl sulfide radical leads to the formation of compound **29** while some $hfac^-$ is broken apart and $C(H)C(O)CF_3$ fragments are bonded to the sulfur atom of pyridyl sulfide to give compound **30**. The reaction pathway towards **29** should predominate with regard to compound **30** given that the yield of compound **29** is higher than that of compound **30**.

Besides the above-mentioned examples of S and C atom insertion, N-insertion into the disulfide bond would even happen within 2-dpds. Reaction of Co^{II} ions and 2-dpds in the presence of azide produced a peculiar mononuclear complex (**31**) [20] (Scheme 18). Two primary reactions were observed in this case. On the one hand, 2-dpds undergoes reductive cleavage of disulfide bond accompanied by the oxidation of Co^{II} to Co^{III}. On the other hand, it is extraordinary that the azide anion decomposes and donates a nitrogen atom to 2-dpds, installing an unusual N-inserted ligand of PyS-N-Spy stabilized by electropositive Co^{III} ion coordination. As a result, the Co^{III} ion in compound **31** is surrounded by three disparate ligands, viz. 2-PyS^-, N_3^- and $[PyS\text{-}N\text{-}Spy]^-$, which in turn adopt the N,S-chelation, end-on coordination and NNN-chelation modes, respectively. It is proposed that the driving force of the insertion may be associated with both the expansion from the strained four-membered ring to the strain-free five-membered rings and the subsequent stabilization of the N-inserted ligand by coordination to the electropositive Co^{III} ion.

3.3. *Other disulfide ligands*

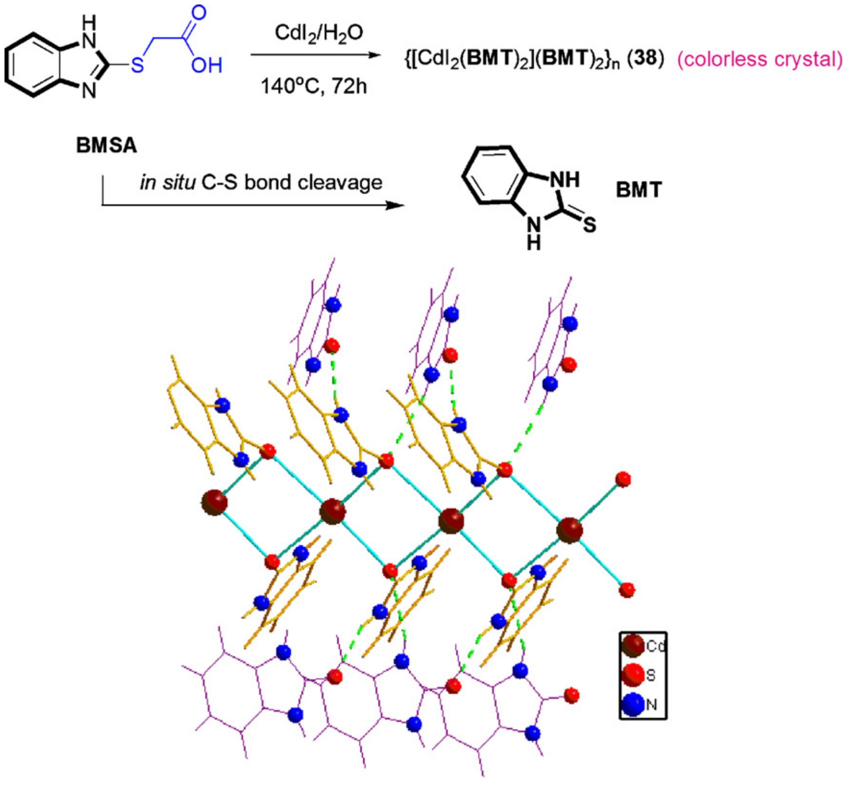
Recently, we have showed that the disulfide ligand of 2-dpds (2-dpds = bis(4-(pyridin-2-yl)pyrimidin-2-yl)disulfide) exhibits some very interesting *in situ* S–S function reactions either under solvothermal conditions [21] or in normal solution reactions [22].

The solvothermal reaction between 2-dpds and $FeCl_2$ in the mixed solvent of $MeOH/CH_2Cl_2$ afforded a mononuclear compound $[FeCl_2(2\text{-pps})]$ (**32**) with newly generated organic ligand 2-pps (2-pps = bis(4-(pyridin-2-yl)pyrimidin-2-yl)sulfane). Surprisingly, metal-free solvolysis of 2-dpds in pure MeOH or $MeOH/CH_2Cl_2$ solvent gave different products. In the former case, 2-ppds was partially transformed into a mixture of *S*-(4-pyridin-2-yl)pyrimidin-2-yl(4-pyridin-2-yl)pyrimidine-2-sulfonothioate (2-ppst) and 2-pps, while in the latter one, 2-(chloromethylthio)-4-(pyridin-2-yl)pyrimidine (2-ppct) was obtained as the main product (Scheme 19). According to the results from these parallel comparative experiments, we supposed that the oxidation product of 2-ppst may be an crucial intermediate towards 2-pps, and the Fe^{2+}-coordination to 2-pps helps prevent 2-pps from further reaction with CH_2Cl_2 solvent.

More interestingly, normal solution reaction between $NiCl_2$ and 2-dpds in $MeOH/CH_2Cl_2$ resulted in three new components identified as 2-mpp (2-methoxy-4-(pyridine-2-yl)pyrimidine), 2-ppst and 2-pps (bis(4-(pyridin-2-yl)pyrimidin-2-yl)sulfane), respectively (Scheme 20). More importantly, such *in situ* reactions could be efficaciously controlled to proceed in a highly selective manner. With the aid of continuous air bubbling through the reaction $NiCl_2$-mediated *in situ* reaction of 2-ppds selectively produced 2-pps, whereas replacement of $NiCl_2$ with $Cu(OAc)_2$ gave 2-mpp exclusively. 2-ppst serves as a decisive intermediate in these *in situ* transformations.

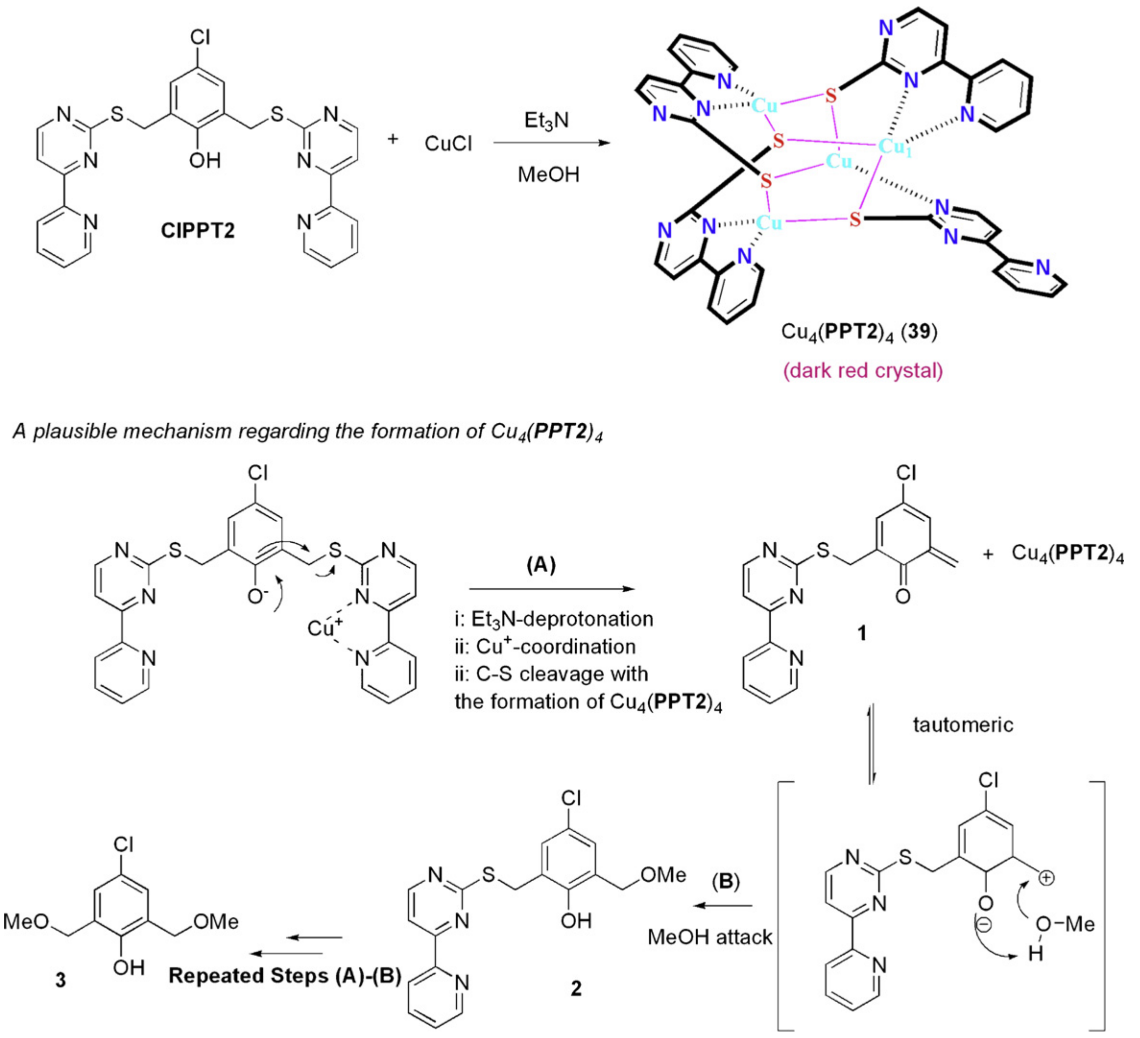
4. ***In situ*** **C–S cleavage**

Transition-metal-mediated cleavage of a C–S bond is a subject of current interest due to its importance in synthetic chemistry, petro-



One-dimensional chain structure of (**38**)

Scheme 24. *In situ* C–S bond cleavage of BMSA promoted by CdI_2.

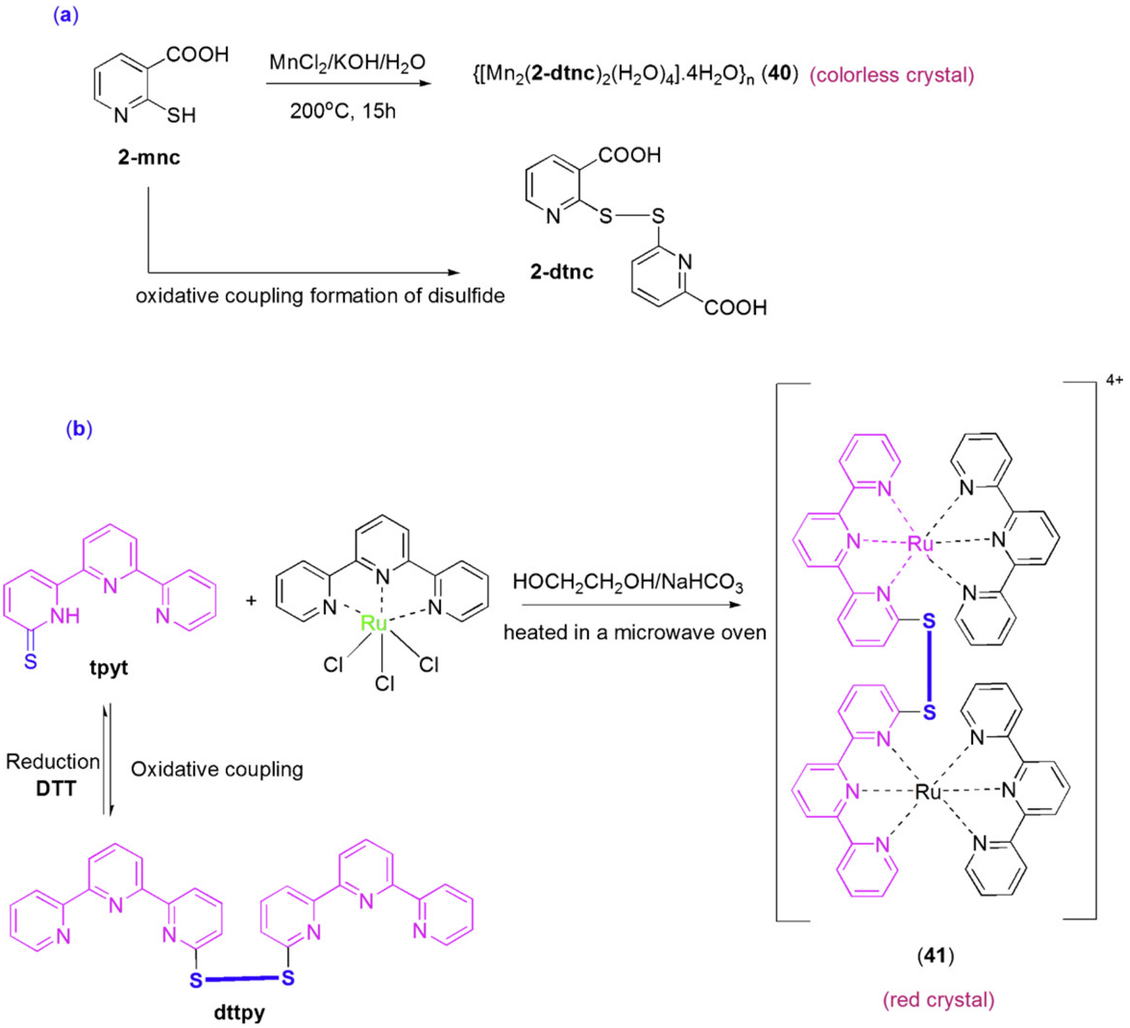


Scheme 25. *In situ* C–S bond cleavage of ClPPT2 induced by Cu(I).

chemical hydrodesulfurization (HDS), bioorganic and bioinorganic chemistry. Several examples concerning C–S bond cleavage within organic molecules by different metal ions have been reported [23]. Nevertheless, the conscious use of C–S cleavage for preparation of metal–sulfur-containing coordination polymers is still less developed, and only a few reports have appeared mainly in the type of organic ligand, HOOC–CH_2–S-Het (Het: heterocycle) (Scheme 21).

The first report on this aspect was made from Zhang's research group. They found that hydrothermal reaction of 4-pdta with $Cu(OAc)_2$ produced a unique twelve-connected Cu_6S_4 cluster-based coordination polymer (**33**) [24] (Scheme 22(a)). In this reaction, 4-pdta is ambiguously converted into 4-SPy, of which the S-attached carboxymethyl group is removed through C–S bond cleavage. At the same time, SCN^- ions are converted to CN^- and SO_4^{2-}, indicating that both C–S cleavage and S-oxidation have happened. Moreover, the Cu^{II} is reduced to Cu^{I}. Based on these experimental facts, the authors speculated that the formation of compound **33** proceeded through two steps. The first step is probably a redox reaction involving Cu(II) and SCN^- ions, generating Cu(I), cyanide and sulfate ions. The second step may involve the assembly of Cu(I), CN^- and 4-pdta *via* coordination interactions, during which in situ C–S cleavage occurs in 4-pdta presumably because of steric hindrance caused by the coordination of the S atom to the Cu(I) atom at a relatively high reaction temperature. In compound **33**, the Cu_6S_4 cluster node has its six Cu(I) ions arranged in an octahedral manner with four μ-3 S distributed at the centers of trigonal faces. Each Cu_6S_4 cluster is connected to adjacent Cu_6S_4 clusters via four cyanide ions and eight pyridine rings to form a three-dimensional twelve-connected face-centered cubic topological framework. It is the first observation of twelve-connectivity in a metal–organic framework. The successful production of compound **33** is dependent on subtle control of reaction parameters, among which the use of ligand precursor 4-pdta rather than 4-pyridinethiol is a key point.

As an extension of this methodology, the same group prepared a $Cu_{19}I_4S_{12}$-based fourteen-connected body centered cubic topological coordination polymer (**34**) by reaction of 4-pdta with $CuSO_4$ under solvothermal conditions [25] (Scheme 22(b)) Unlike compound **33**, compound **34** could also be obtained by employing other reactants (e.g. $CuSO_4$/4-pyridinethiol/KI, or CuI/4-pyridinethiol). Particularly, two types of C–S bond cleavage were observed in a one-pot reaction, which corresponded to C–S(sp) cleavage of 4-pyridinethiol and C–S(sp^3) cleavage within 4-pdta, and C–S(sp) cleavage of 4-pyridinethiol. Similar to compound **33**, compound **34** also has clusters of $Cu_{19}I_4S_{12}$ as nodes but with fourteen-connectivity, and triple pyridines and hydrosulfides as connectors. Conspicuously, the $Cu_{19}I_4S_{12}$ cluster node is made up with a centered CuI_4 unit and a $Cu_{18}S_{12}$ shell. In the $Cu_{18}S_{12}$ shell, six Cu(I) atoms constitute a Cu_6 octahedron with the remaining 12 Cu(1) atoms located at the midpoint of 12 edges, and 12 μ-3 S atoms from 4-Spy ligands arrayed into a truncated tetrahedron. In addi-



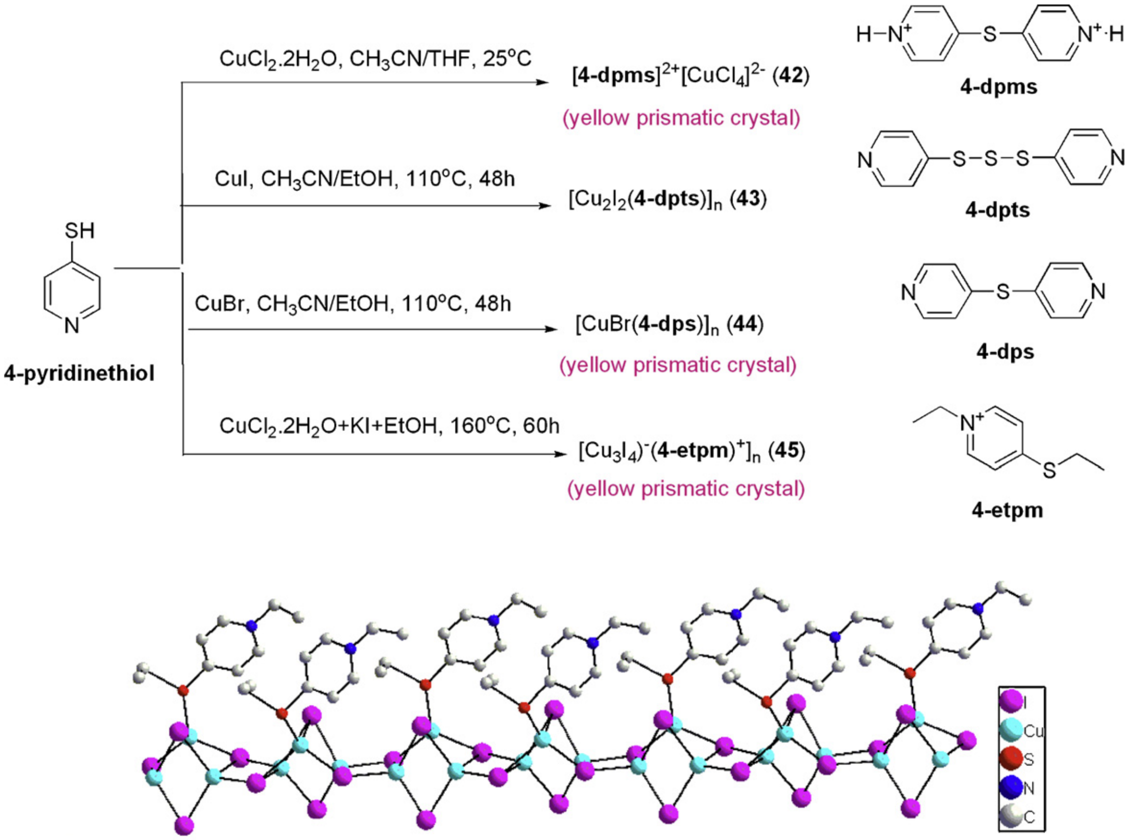
Scheme 26. *In situ* S–S oxidative coupling to disulfide.

tion, the $Cu_{19}I_4S_{12}$ cluster in compound **34** is the exclusive example of a nano-sized chiral sulfur-bridged copper cluster.

Following an analogous strategy, another group obtained a series of lanthanide (Ln = Eu, Dy, Er) coordination polymers (**35**–**37**) by taking advantage of *in situ* C–S cleavage with 4-pdta precursor [26] (Scheme 23). Distinctively, *in situ* C–S cleavage into 4-pdta releases 4-SPyH zwitterions and unexpected oxalate ions, which are considered to be triggered by lanthanide-coordination. All compounds are isomorphous, wherein each lanthanide ion is surrounded by one sulfur atom of a 4-SPyH ligand, one water molecule and six oxygen atoms of chelating oxalate groups. Each lanthanide ion is further linked to adjacent three lanthanide ions through three bound oxalate groups, giving an infinite two-dimensional honeycomb layer along the *c*-axis.

Inspired by these successes, our group also employed a similar carboxymethyl-modified benzoimidazole-2-thiol (BMT), namely BMSA, as the starting ligand precursor and attempted to prepare novel coordination polymers with BMT ligands through *in situ* C–S bond cleavage. Indeed, hydrothermal reaction of BMSA with CdI_2 resulted in a unique 1D Cd^{2+} coordination polymer (**38**), which is composed of an inorganic skeleton chain $[CdS_2]_n$ with BMT anchoring on both sides like wings [27] (Scheme 24). The ligand precursor of BMSA undergoes *in situ* C–S cleavage as expected, generating BMT ligands all in the form of the thione-tautomer. In addition, two kinds of BMT ligands are present in compound **38**, of which one adopts a μ-2 S bridge mode connecting two Cd^{2+} ions whereas the other, though uncoordinated, is involved into N–H···S hydrogen bonding interactions.

Apart from *in situ* C–S cleavage with 4-pdta, a serendipitous discovery was previously made in our group when a unique discrete Cu_4S_4 cluster (**39**) was obtained via *in situ* C–S cleavage of the organic molecule ClPPT2 [28] (Scheme 25). In this reaction, the new PPT2 ligand was formed as the result of C–S bond rupture within ClPPT2. In compound **39**, two disparate coordination modes are found for the resultant PPT2, one is involved with two N atoms chelating one Cu^+ ion and one sulfur atom bridging two additional Cu^+ ions, the other is concerned with one exo-N atom connecting one Cu^+ except for one bridging S atom. The spatial arrangement of the Cu_4S_4 cluster is rather similar to the Cu_z active site of N_2OR ($N_2OR = N_2O$ reductase), which may be treated as a model compound mimicking the enzyme in biological system. A reasonable mechanism regarding the C–S bond cleavage has been proposed based on the ESI-MS detected reaction intermediates. It is suggested that base-deprotonation of the phenol group in cooperation with metal-coordination facilitates the charge transfer from oxygen to sulfur atoms, promoting the C–S cleavage and the formation of a stable quinone structure. The presence of the phenolic hydroxyl group is indispensible for inducing this reaction since no similar reaction occurs with the counterpart without a phenolic hydroxyl group.



Linear chain structure of compound **45**

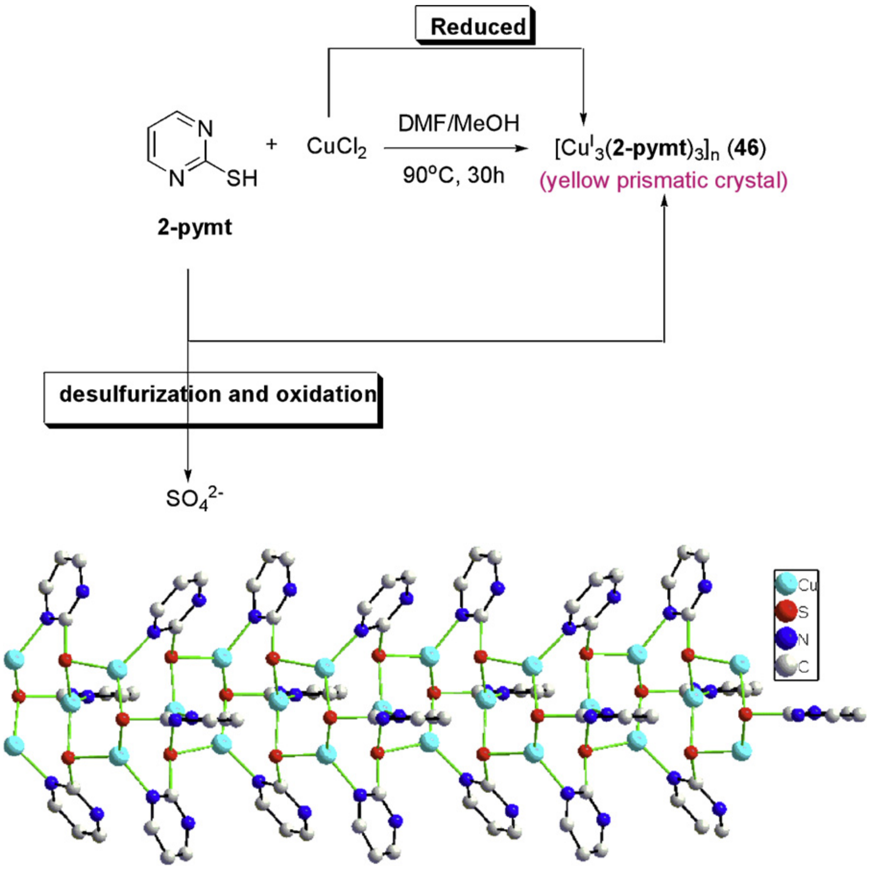
Scheme 27. *In situ* thiol-S atom reactions under different conditions.

5. *In situ* thiol-S atom reactions

Under some conditions, the thiol-group shows some interesting reactions, for constructing some intriguing coordination complexes. Notwithstanding the direct use of thiol-group, *in situ* thiol-S atom reactions distinguish this method from the direct one. The most common is the oxidative coupling formation of disulfide from the thiol-group. Such *in situ* reactions associated with the thiol-group provide an attractive route for elaborating metal-coordination complexes with the disulfide, especially those unattainable directly from the disulfide. Hydrothermal treatment of $MnCl_2$ with 2-mnc (2-mnc = 2-mercaptonicotinic acid) deprotonated with KOH produced a polymeric compound (**40**), which exhibited disulfide formation and oxygen-only metal interactions [29] (Scheme 26(a)). Compound **40** shows a stepped 2D sheet motif which is composed of isolated chains of *syn*, *anti*-carboxylate bridged Mn(II) ions forming 8-membered rings consisting of the repeated unit (–Mn–O–C–O–), with the disulfide bridge in between. Compound **40** could not be synthesized directly from the disulfide. If coupled with metal-centered redox chemistry, reversible thiol(thione)-disulfide redox chemistry may provide new reaction sequences for eventual incorporation into a self-replicating system. Reaction of tpyt (tpyt = 2,2′:6′,2″-terpyridine-6(1*H*)-thione) with $[Ru(tpy)Cl_3]$ heated in a microwave oven produced a dinuclear compound (**41**) as programmed, in which the initial tpyt was changed into dttpy *via* an oxidative coupling reaction of the thiol-group, concurrent with the reduction of Ru^{3+} to Ru^{2+} [30]. Furthermore, reduction of compound **41** with DTT (DTT = dithiothreitol) could return the complexes to the starting tpyt, indicating the reversibility of thiol-disulfide transformation (Scheme 26(b)).

Additionally, *in situ* thiol-group reactions of 4-pyridinethiol, systematically investigated by Yao's group, are indicative of reaction diversity (Scheme 27).

Reaction of 4-pyridinethiol with $CuCl_2$ in CH_3CN/EtOH produced an adduct (**42**) comprising a 4-dpms and $[CuCl_4]^{2-}$ ion pair, both of which formed a closed chain conformation *via* N–H···Cl hydrogen-bonding interactions [31]. The presence of 4-dpms in compound **42** is apparently derived from 4-pyridinethiol, which undergoes desulfurization and simultaneous coupling. Hydrothermal treatment of 4-pyridinethiol with CuI in the mixed solvent of CH_3CN and EtOH resulted in a 2D inorganic–organic hybrid framework (**43**) with infinite $[Cu_2I_2]_n$ double-chain separated by 4-dpts ligands. H_2S gas and I_2 were generated from this reaction, implying that the presence of CuI is crucial to the formation of 4-pdts. In fact, no 4-dpts was isolated in a blank experiment without CuI. Additionally, replacement of CuI with CuBr in this reaction produced a different compound (**44**), of which 4-dps instead of 4-dpts was *in situ* formed [32]. More surprisingly, solvothermal reaction of 4-pyridinethiol with $CuCl_2{\cdot}2H_2O$ in the presence of KI and EtOH gave the first example of a linear chain (**45**) formed by trinuclear Cu_3I_4 units [33] (Scheme 27). In this reaction, ethylation on both N and S atoms occurred on 4-pyridinethiol to afford the new species of 4-etpm. A converse induction has been applied to explain the formation of compound **45**. It is deduced that 4-etpm is the alkylated product of 4-pyridinethiol and EtI. The source of EtI should be from the reaction of EtOH and HI derived from I_2 afforded by the redox reaction of KI. Notably, a small amount of K_2SO_4 was also synchronously obtained, indicating that 4-pyridinethiol has partly undergone desulfurization reaction, followed by oxidation of S^{2+} to S^{6+}.



One-dimensional chain structure of compound **46**

Scheme 28. *In situ* thiol-S atom reaction under hydro(solvo)thermal conditions.

Similar to the case of compound **45**, the formation of SO_4^{2-} was also found in the solvothermal reaction between 2-pymt (pyrimidine-2-thiolate) and $CuCl_2$ [34] (Scheme 28). In this case, 2-pymt serves not only as the building units but also as reducing reagents, *in situ* reducing Cu^{2+} to Cu^+. The resultant Cu^I organosulfide polymeric compound (**46**) has an infinite one-dimensional chain structure. Three independent Cu^I ions are bound together by S,N-donors of 2-pymt to form a trinuclear repeating unit, which is further extended into a one-dimensional chain through S, N atoms of 2-pymt by bridging Cu^I ions from adjacent units. More strikingly, the chain is practically a distorted helix generated around crystallographic 2_1 screw axis that crystallizes in the chiral space group $P2_12_12_1$. The most fascinating feature of compound **46** is its rich red photoluminescence, displaying the lowest energy emission hitherto observed in luminescent d^{10} transition metal-coordination polymers. Moreover, compound **46** is the first example of a structurally characterized Cu^I–thiolate coordination polymer generated under solvothermal conditions by the redox reaction of Cu^{II} with one single thiol group.

6. Conclusions

In situ metal/ligand reactions offer an attractive route for constructing metal compounds with organic sulfur-containing heterocycles. To date, three kinds of *in situ* methods have been reported for this purpose, that is, *in situ* S–S function reactions, *in situ* C–S bond cleavage and *in situ* thiol-S atom reactions. The first method takes full advantage of the susceptible S–S functions. Taking 4-dpds as an example, *in situ* S–S function reactions would lead to a variety of transformations (4-SPy, 4-SPyH, 4-dpts, 4-dps, etc.) under various conditions, and further result in the formation of diverse architectures. Reaction diversities with S–S functions create tremendous opportunities for construction of metal–sulfur-containing heterocycles with novel structures, especially those inaccessible by the direct method. For the second method, limited examples are restricted into the use of carboxymethyl-modified thiol group at present. By appropriate choice of reaction parameters the removal of carboxymethyl unit would be readily realized, releasing thiol coordination donors. This orientated strategy is quite similar to the protection–deprotection sequence in organic synthesis. The third method is based on the reactions of thiol-S atom, which would be a promising tool coupled with the rich sulfur chemistry in this area.

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