Selective Formation of Conductive Network by Radical-Induced Oxidation

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1 Introduction
A redox-active porous coordination network can provide a potential-tunable space to achieve numerous benefits, including catalytic activity, selective molecular trapping, and tunable electronic/magnetic materials. We prepared various coordination networks based on tripyridyl hexaazaphenalene (TPHAP) which was designed to show the importance of multi-interactivity of the ligand for kinetic network formation.\(^1\) Because TPHAP is not redox-active, we designed new tripyridyl ligand, 2,5,8-tri(4-pyridyl)1,3-diazaphenalene (TPDAP or H\(^+\)\(^-\)) to introduce redox activity while keeping the same molecular shape as TPHAP. This change was achieved by replacing non-redox-active central hexaazaphenalene (HAP) with redox-active diazaphenalene (DAP) which possesses a higher HOMO level than does HAP. We revealed that H\(^+\)\(^-\) forms a neutral radical (\(1^*\)) by one-electron oxidation, and can possess two-step redox activity (Fig. 1a).\(^2\)

![Fig. 1: Features of TPDAP. a) TPDAP two-step redox activity. b) Schematic model of selective network formation based on redox active ligand H\(^+\)\(^-\). c) H\(^+\)\(^-\)-1\(^*\) dimer formation and HOMO increase.](image)

2 Results and Discussion
We report the selective formation of electron conductive/non-conductive coordination networks based on redox active ligand H\(^+\)\(^-\) (Fig. 1b). We also report an unexpected oxidation mechanism of TPDAP in CH\(_3\)OH. The experimental results suggested the formation of \(1^*\) \(\cdots\) H\(^+\)\(^-\) \(\pi\)-dimer which caused further oxidation of H\(^+\)\(^-\). Meanwhile, H\(^+\)\(^-\) was never oxidized in CH\(_3\)OH in the absence of \(1^*\) because no dimer formation occurred. We prepared redox active coordination networks having channels using TPDAP and Cd\(^{2+}\). We found significant structural differences depending on the presence/absence of \(1^*\). The \(1_{\text{ox}}\) powder produced a dark red block crystal of ESR active network, [Cd\(_{2.39}\)(NO\(_3\))\(_{3.8}\)(H\(^+\)\(^-\))\(_{2}\)(H\(_2\)O)\(_{0.95}\)(CH\(_3\)OH)\(_{1.1}\)] (Cd-1\(_{\text{mono}}\)) obtained by layering diffusion of a CH\(_3\)OH solution of Cd(NO\(_3\))\(_2\)-4H\(_2\)O into a CH\(_3\)OH-nitrobenzene solution of \(1_{\text{ox}}\) in air at 20±1 °C for 1 d (Fig. 2 a, b). In contrast, the layering diffusion of a CH\(_3\)OH solution of Cd(NO\(_3\))\(_2\)-4H\(_2\)O into a CH\(_3\)OH-nitrobenzene solution of non-oxidized H\(^+\)\(^-\) solid in air at 20±1 °C for 1 d yielded a single crystal of non-conductive, ESR-silent network, [Cd\(_2\)(NO\(_3\))\(_3\)(H\(^+\)\(^-\))\(_2\)(H\(_2\)O)\(_2\)(CH\(_3\)OH)\(_3\)] (Cd-1\(_{\text{ortho}}\)) (Fig. 2 c, d).

![Fig. 2: Crystal structures of Cd-1\(_{\text{mono}}\) and Cd-1\(_{\text{ortho}}\). networks. a) Structure of main triplex unit b) 1D columnar structure. c) Structure of main dimer unit of Cd-1\(_{\text{ortho}}\). d) Interpenetrated 2D zigzag sheet structure of Cd-1\(_{\text{ortho}}\).](image)

In summary, we selectively prepared Cd-based conductive/non-conductive coordination networks based on redox active ligand TPDAP by controlling the amount of the radical species \(1^*\). The experimental results indicated that selective network formation dependent on the amount of \(1^*\) was realized by the formation of H\(^+\)\(^-\)-\(1^*\) \(\pi\)-dimer followed by further oxidation of H\(^+\)\(^-\).

3 References

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