

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 hexaazaphenylene (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-diazaphenylene (TPDAP or $\mathbf{H}^+\mathbf{1}^-$) to introduce redox activity while keeping the same molecular shape as TPHAP. This change was achieved by replacing non-redox-active central hexaazaphenylene (HAP) with redox-active diazaphenylene (DAP) which possesses a higher HOMO level than does HAP. We revealed that $\mathbf{H}^+\mathbf{1}^-$ forms a neutral radical ($\mathbf{1}^\bullet$) by one-electron oxidation, and can possess two-step redox activity (Fig. 1a).²

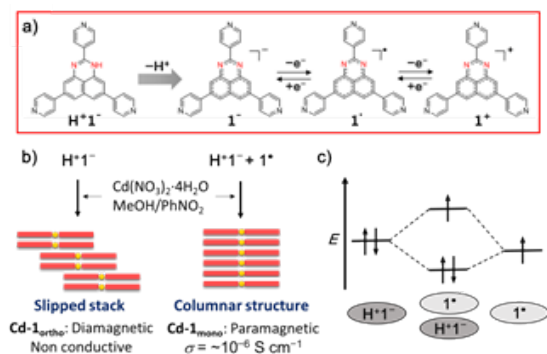


Fig. 1: Features of TPDAP. a) TPDAP two-step redox activity. b) Schematic model of selective network formation based on redox active ligand $\mathbf{H}^+\mathbf{1}^-$. c) $\mathbf{H}^+\mathbf{1}^-$ - $\mathbf{1}^\bullet$ dimer formation and HOMO increase.

2 Results and Discussion

We report the selective formation of electron conductive/non-conductive coordination networks of redox-active TPDAP (Fig. 1b). We also report an unexpected oxidation mechanism of TPDAP in CH_3OH . The experimental results suggested the formation of $\mathbf{1}^\bullet \cdots \mathbf{H}^+\mathbf{1}^-$ π -dimer which caused further oxidation of $\mathbf{H}^+\mathbf{1}^-$. Meanwhile, $\mathbf{H}^+\mathbf{1}^-$ was never oxidized in CH_3OH in the absence of $\mathbf{1}^\bullet$ 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 $\mathbf{1}^\bullet$. The $\mathbf{1}_{\text{ox}}$ powder produced a dark red block crystal of ESR active network, $[\text{Cd}_{2.39}(\text{NO}_3^-)_{3.8}(\mathbf{H}^+\mathbf{1}^-)_2(\mathbf{1}^\bullet)(\text{H}_2\text{O})_{6.95}(\text{CH}_3\text{OH})_{1.5}]$ ($\mathbf{Cd-1}_{\text{mono}}$) obtained by layering diffusion of a CH_3OH solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ into a CH_3OH -nitrobenzene solution of $\mathbf{1}_{\text{ox}}$ in air at 20 ± 1 °C for 1 d (Fig. 2 a, b). In contrast, the layering diffusion of a CH_3OH solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ into a CH_3OH -nitrobenzene solution of non-oxidized $\mathbf{H}^+\mathbf{1}^-$ solid in air at 20 ± 1 °C for 1 d yielded a single crystal of non-conductive, ESR-silent network, $[\text{Cd}_2(\text{NO}_3^-)_4(\mathbf{H}^+\mathbf{1}^-)_2(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})_5]$ ($\mathbf{Cd-1}_{\text{ortho}}$; Fig. 2 c, d).

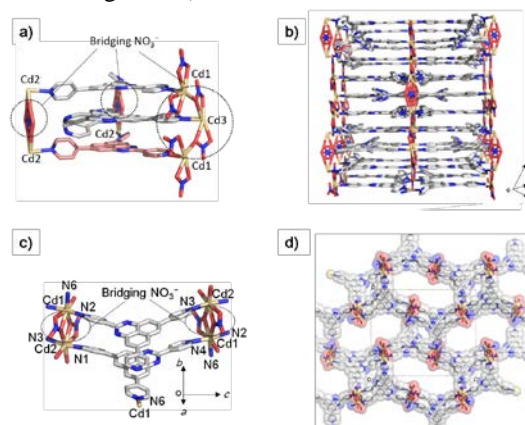


Fig. 2: Crystal structures of $\mathbf{Cd-1}_{\text{mono}}$ and $\mathbf{Cd-1}_{\text{ortho}}$ networks. a) Structure of main triplex unit b) 1D columnar structure. c) Structure of main dimer unit of $\mathbf{Cd-1}_{\text{ortho}}$. d) Interpenetrated 2D zigzag sheet structure of $\mathbf{Cd-1}_{\text{ortho}}$. Gray, C; blue, N; yellow, Cd; red, O. Hydrogen atoms are omitted for clarity.

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 $\mathbf{1}^\bullet$. The experimental results indicated that selective network formation dependent on the amount of $\mathbf{1}^\bullet$ was realized by the formation of $\mathbf{H}^+\mathbf{1}^-$ - $\mathbf{1}^\bullet$ π -dimer followed by further oxidation of $\mathbf{H}^+\mathbf{1}^-$.

3 References

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- [2] J. Y. Koo, Y. Yakiyama, G. R. Lee, J. Lee, H. C. Choi, Y. Morita, M. Kawano, *J. Am. Chem. Soc.*, **138**, 1776 (2016)

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