

## Crystal structures and electronic states of metal-dithiolate–resorcinarene co-assemblies driven by hydrogen-bond formations

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**[Introduction]** Molecular assemblies driven by Hydrogen-bond (H-bond) formations have gathered attention in research fields of crystal engineering and supramolecular chemistry. As components of such assemblies, of interesting are molecules offering electronic structures impacted by protonation/deprotonation processes, such as quinone derivatives, because of potentials to develop materials exhibiting electronic functions depending on H-bond states.<sup>1</sup> Previously, I reported that bis(pyrazine-2,3-dithiolene)metal complexes;  $[M(\text{pdt})_2]^{2-}$  ( $M = \text{Ni}, \text{Pd}, \text{Pt}$ ) shows  $d$ -element dependency of electron-donor-ability changes by their protonation in solution states;<sup>2</sup> however, their potential to build H-bond assemblies dealing with proton and electron transfers remain an issue. Herein, I report that tetraethylammonium salts of  $[M(\text{pdt})_2]^{2-}$  ( $M = \text{Ni}, \text{Pd}, \text{Pt}$ ) are crystallized with tetra(isobutyl)resorcine[4]arene (**RCArene**) to afford a series of H-bonded 1:1 assemblies (**MArene**), and I discuss electronic states of metalladithiolate composing **MArene** by investigating their optical and magnetic properties.

**[Results and discussion]** As shown in Figure 1, crystal structures of **MArene** are an isotypic structure containing head-to-head arranged **RCArene** pairs linked by six  $[M(\text{pdt})_2]^{2-}$  units with forming one-dimensional H-bonds between hydroxyl oxygen and pyrazine nitrogen atoms along  $c$  axis. With cooperation from intramolecular H-bonds of **RCArene** units, strongly bonded characters of the intermolecular H-bonds were indicated by broaden absorption bands of **MArene** from 3600 to 2000  $\text{cm}^{-1}$ . Electronic absorption spectra of all **MArene** shows both protonated and deprotonated states of metalladithiolate were composed. Partial oxidations of **NiArene** and **PdArene** provide different shapes of EPR signals, i.e. the Ni species has a large contribution of the metallacycle spin, and the Pd species contains both of metallacycle and hydroxyl radicals. These results are considered to come from a  $d$ -element dependency of pH-dependent redox of  $[M(\text{pdt})_2]^{2-}$ , where values of oxidation potentials of  $[Pd(\text{pdt})_2]^{2-}$  are reversed by those of **RCArene** with decreasing the activity of proton, as indicated by their Pourbaix Diagrams.

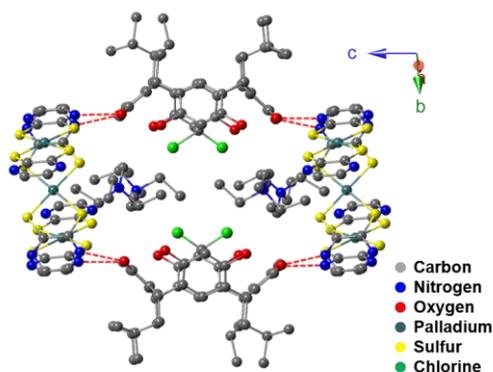


Figure 1 A key structure composed of **PdArene**.  $\text{CH}_2\text{Cl}_2$  are contained in the pair of **RCArene**. H-bonds are indicated as red dotted lines. Hydrogen atoms were omitted for clarity.

- 1) a) Y. Hirao, *et al. Angew. Chem. Int. Ed.* **2015**, *54*, 2402. b) K. Nakasuji, *et al. J. Am. Chem. Soc.* **1991**, *113*, 1862. 2) M Hayashi, *et al. J. Am. Chem. Soc.* **2019**, *141*, 11686.