

Synthesis of a quinone-functionalized macrocyclic ligand and the intense fluorescence of its zinc complex†

Michael Ruf‡, William S. Durfee§ and Cortlandt G. Pierpont*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA.

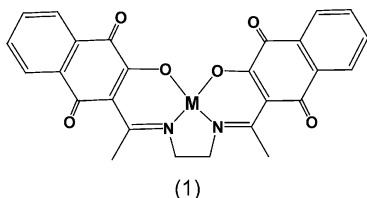
E-mail: Pierpont@Colorado.edu

Received (in West Lafayette, IN, USA) 29th January 2004, Accepted 2nd March 2004

First published as an Advance Article on the web 23rd March 2004

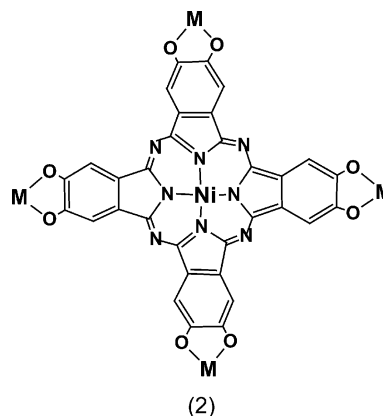
The redox-active quinone-functionalized macrocyclic ligand 1,4,14,17-tetrahydroxyhemiporphyrzine, $H_2hp(OH)_4$, has been synthesized and its zinc complex, $[Zn\{hp(OH)_4\}(py)]$, found to exhibit intense fluorescence.

Studies on the coordination chemistry of transition metal complexes containing catecholate and semiquinone ligands have shown uniquely interesting properties resulting from the similarity in energy of the quinone π -electronic levels with the metal d-orbitals.¹ These properties have included equilibrium studies on metal–ligand electron transfer,² metal–ligand and ligand–ligand magnetic exchange involving radical semiquinone ligands,³ and redox chemistry involving both the metal and quinone within a narrow range of electrochemical potential.⁴ Most of this research has been carried out on complexes containing one or more separate quinone ligands. An approach taken in the interest of extending electrochemical versatility within a single complex unit involves the synthesis of macrocyclic ligands containing peripheral quinone functionalities in electronic contact through the conjugated framework of the ligand. In these complexes, the quinone does not interact directly with the central metal ion of the macrocyclic complex, but peripheral metals may be added at outer quinone coordination sites. Prior research has included studies of a chelating salen [bis(salicylidene)diethylenetriamine] ligand containing naphthoquinone functionalities (1)⁵ and the octahydroxyphthalocyanine

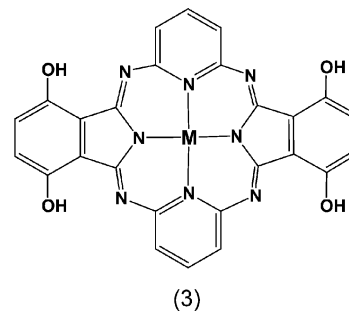


complex of Ni(II), $[Ni\{Pc(OH)_8\}]$ (2),⁶ as a conjugated tetra-catecholate ligand. In this case, tris(pyrazolyl)borate/zinc(II) units were observed to bond at the peripheral catecholate oxygens. In this Communication, we describe the synthesis of the conjugated bis(hydroquinone) ligand 1,4,14,17-tetrahydroxyhemiporphyrzine, $H_2hp(OH)_4$, and the unusually intense luminescence of its zinc complex.

Tetrahydroxyhemiporphyrzine (3) was prepared *via* the condensation of 2,3-dicyanohydroquinone with 2,6-diaminopyridine.¶ Dark red crystals of the ligand were obtained by sublimation of crude product obtained directly from the condensation reaction. Crystallographic characterization of $H_2hp(OH)_4$ [Fig. 1(a)] shows that the molecule is planar with a crystal structure consisting of canted columnar stacks of $H_2hp(OH)_4$ molecules. Inner-ring hydrogens bonded to N1 are 2.06 Å from one another across a



crystallographic center of inversion symmetry, and hydrogens bonded to the hydroquinone oxygens are hydrogen bonded with outer-ring nitrogens. The interplanar separation between molecules is 3.48 Å and relatively strong π interactions, with intermolecular hydrogen bonding, contribute to the low solubility of the ligand.† Oxidation of $H_2hp(OH)_4$ with Ag_2O was used to form the benzoquinone form of the ligand, $hp(=O)_4$ (4), obtained as an intensely colored solid of low solubility.



Transition metal complexes of $hp(OH)_4$ may be formed by refluxing a methanol suspension of the ligand with the salt of a metal ion. For example, zinc perchlorate was used to form $[Zn\{hp(OH)_4\}]$.¶ A sample of $[Zn\{hp(OH)_4\}]$ was dissolved in pyridine to give a bright red solution of $[Zn\{hp(OH)_4\}(py)]$. Slow evaporation of the solvent gave dark red crystals of $[Zn\{hp(OH)_4\}(py)]$ that were suitable for crystallographic analysis. The complex molecule has the square pyramidal geometry shown in Fig. 1(b), with the py ligand in the apical coordination site. The Zn atom is located 0.36 Å above the plane of the four coordinated $hp(OH)_4$ nitrogen atoms and the Zn–N bond lengths to the pyrrole nitrogens are significantly shorter than to the pyridine nitrogens due to the structural constraints of the ligand. Electrochemical characterization of $[Zn\{hp(OH)_4\}(py)]$ using cyclic voltammetry gave a pH-dependent irreversible couple that is similar in appearance to the couple reported for free hydroquinone,⁷ implying that the electronic coupling between the hydroquinone functionalities of the $hp(OH)_4$ ligand is weak.†

During characterization of $[Zn\{hp(OH)_4\}(py)]$, the complex was observed to exhibit intense fluorescence upon irradiation with long wavelength UV light. In contrast, the free $hp(OH)_4$ ligand fails to

† Electronic supplementary information (ESI) available: views showing intermolecular interactions in the crystal structure of $H_2hp(OH)_4$, a cyclic voltammogram of $[Zn\{hp(OH)_4\}(py)]$ in acetonitrile and the absorption spectrum of $[Zn\{hp(OH)_4\}(py)]$ in DMSO. See <http://www.rsc.org/suppdata/cc/b4/b401334d/>

‡ Present address: Bruker-AXS Inc., 5465 E. Cheryl Parkway, Madison, WI 53711, USA.

§ Present address: Department of Chemistry, Buffalo State College, 1300 Elmwood Avenue, Buffalo, NY 14222, USA.

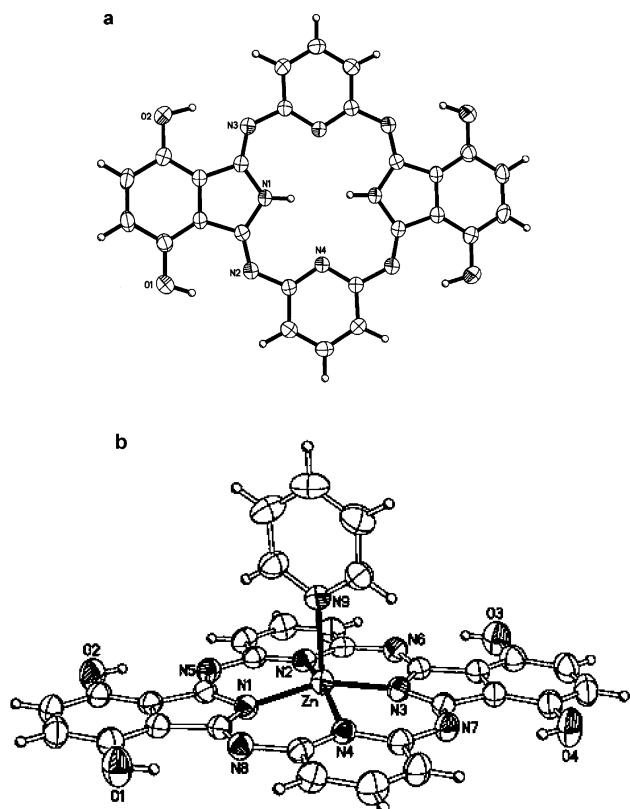
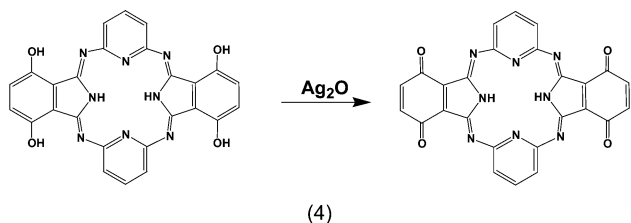


Fig. 1 Views showing the structures of the $\text{H}_2\text{hp}(\text{OH})_4$ (a) and $[\text{Zn}\{\text{hp}(\text{OH})_4\}(\text{py})]$ (b) molecules. Selected bond distances (Å) and angles ($^\circ$): Zn–N1 1.932(1), Zn–N2 2.265(1), Zn–N3 1.933(1), Zn–N4 2.276(1), Zn–N9 2.142(1); N1–Zn–N3 155.31(6), N2–Zn–N4 164.02(5).



fluoresce under similar conditions, possibly due to exciplex formation. Similar *chelation-enhanced* fluorescence has been observed earlier for a zinc complex of an anthracene containing TMEDA functionalities, 9,10-bis(TMEDA)anthracene.⁸ In DMSO, $[\text{Zn}\{\text{hp}(\text{OH})_4\}(\text{py})]$ was found to have an intense unsymmetrical absorption at 293 nm ($\epsilon = 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).[†] Excitation at 350 nm in either DMSO or pyridine solutions that were $4 \times 10^{-5} \text{ M}$ in $[\text{Zn}\{\text{hp}(\text{OH})_4\}(\text{py})]$ produced intense fluorescence at 535 nm. The emission obtained in DMSO, shown in Fig. 2, is unsymmetrical, with a shoulder on the low energy side of the spectrum. A comparative study with 9,10-dichloroanthracene ($\Phi_{\text{F}} = 0.58$)⁹ was used to obtain estimates of the fluorescence quantum yield for $[\text{Zn}\{\text{hp}(\text{OH})_4\}(\text{py})]$ of $\Phi_{\text{F}} = 0.68$ (DMSO) and 0.75 (pyridine).

Fluorescent sensors are important analytical probes for visualizing metal ions at low concentrations.¹⁰ The fluorescence intensity of $[\text{Zn}\{\text{hp}(\text{OH})_4\}(\text{py})]$ is of the order of the intensities obtained for fluorescent dyes functionalized with chelating agents for zinc coordination,¹¹ and the $\text{hp}(\text{OH})_4$ ligand may prove to be an accessible addition to the selection of probes that produce intense fluorescence upon metal ion coordination.

Notes and references

† *Synthesis of $\text{H}_2\text{hp}(\text{OH})_4$ (3)*: a suspension of 2,3-dicyanohydroquinone (4.00 g, 25.0 mmol) and 2,6-diaminopyridine (2.73 g, 25.0 mmol) was

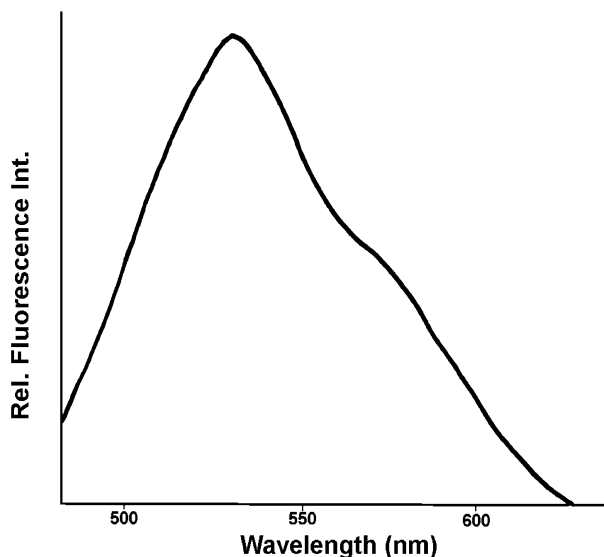


Fig. 2 The emission spectrum of $[\text{Zn}\{\text{hp}(\text{OH})_4\}(\text{py})]$ obtained in DMSO solution ($4 \times 10^{-5} \text{ M}$) upon excitation at 350 nm.

refluxed in 80 mL of ethylene glycol for 12 h. The colorless mixture turned red initially, then black. The mixture was cooled to room temperature and 100 mL of water was added. The resulting black precipitate was isolated by filtration, washed with 50 mL portions of hot methanol, and dried in air. The crude sample of $\text{H}_2\text{hp}(\text{OH})_4$ (4.13 g, 33% yield) was purified by sublimation (300°C , 20 mbar), yielding dark red crystals suitable for crystallographic characterization. IR (KBr): ν/cm^{-1} 3463 m, 1656 s, 1583 s, 1552 m. $[\text{Zn}\{\text{hp}(\text{OH})_4\}(\text{py})]$: $\text{H}_2\text{hp}(\text{OH})_4$ (1.00 g, 1.98 mmol) was added to $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.74 g, 1.98 mmol) dissolved in 30 mL of methanol. The mixture was refluxed for 2 h and cooled to room temperature. A black precipitate of the zinc complex was isolated by filtration. The precipitate was dissolved in 30 mL of pyridine. Dark red crystals suitable for crystallographic analysis (0.56 g, 44% yield) were obtained by slow evaporation of the pyridine solution. IR (KBr): ν/cm^{-1} 3414 m, 3111 m, 1604 s, 1491 s, 1452 s, 1145 s, 1100 s, 1073 s, 1045 m, 1017 m; $^1\text{H-NMR}$ [300 MHz, $\text{S}(\text{CD}_3)_2\text{O}$]: δ/ppm 8.56 (d), 7.78 (t), 7.38 (s), 7.36 (t).

Crystal data for $\text{H}_2\text{hp}(\text{OH})_4$: triclinic, $P\bar{1}$, $a = 4.6912(3)$, $b = 9.1062(5)$, $c = 12.4096(6)$ Å, $\alpha = 92.712(2)$, $\beta = 98.596(1)$, $\gamma = 91.648(2)^\circ$, $V = 523.24(5)$ Å³, $Z = 1$, $R(F) = 0.055$, $R_w(F^2) = 0.107$. For $[\text{Zn}\{\text{hp}(\text{OH})_4\}(\text{py})]$: triclinic, $P\bar{1}$, $a = 10.497(3)$, $b = 12.628(4)$, $c = 13.000(3)$ Å, $\alpha = 83.220(6)$, $\beta = 74.952(8)$, $\gamma = 66.869(7)^\circ$, $V = 1530.2(7)$ Å³, $Z = 2$, $R(F) = 0.030$, $R_w(F^2) = 0.082$. CCDC 229967 and 229968. See <http://www.rsc.org/suppdata/cc/b4/b401334d/> for crystallographic data in CIF or other electronic format.

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