

Review

Benzoquinonediimine ligands: Synthesis, coordination chemistry and properties



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ABSTRACT

This review covers the synthesis and properties of 2,5-diamino-1,4-benzoquinonediimines (DABQDI), and their use as ligand in coordination chemistry. Although reported more than a century ago, these molecules emerged as highly versatile ligands only from 1998, and are so far used for the synthesis of numerous complexes with remarkable properties. This exceptional versatility results from the possible tuning of the *N*-substituents and the observation of an isomerization process upon coordination depending on the metal center. As such, these DABQDI can be also considered as ligands that combine the structural elements of *ortho*- and *para*-benzoquinonediimines (*o*-BQDI and *p*-BQDI) which are bidentate monotopic and monodentate ditopic ligands, respectively. These two classes of BQDI ligands are also reviewed in order to parallel their properties to those of the complexes based on DABQDI.

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1. Introduction and scope

Quinoidal molecules have received particular attention from chemists, physicists and biochemists as building block in the fields of dyes chemistry, conducting organic materials, supramolecular chemistry and pharmacology [1–6]. Over the last three decades, they have also been strongly investigated as ligand, for the design of complexes that could be used in a wide range of applications ranging from catalysis and molecular electronics, to magnetism or optics [7–10]. Among these quinoidal ligands, *para*- and *ortho*-benzoquinonediimines (*p*- and *o*-BQDI) have a long history because of their easy access and their different coordination modes (monodentate vs bidentate) which allowed the preparation of numerous complexes (Chart 1). When 1,4-benzoquinonediimine (*p*-BQDI) is substituted in positions 2 and 5 by an amine function NH₂ (DABQDI), the coordination chemistry differs drastically and becomes much more versatile compared to *p*- and *o*-BQDI ligands because of the possible *p*→*o* isomerization of DABQDI. As a consequence, this latter can be considered as a ligand that combines the structural elements of these two BQDI which are bidentate monodentate ditopic ligands, respectively. Curiously, DABQDI can be considered as an emerging class of versatile ligands by comparison with its oxygenated analog (2,5-dihydroxy-1,4-benzoquinone DHBQ, see Chart 1) which has been extensively used in coordination chemistry for decades. The possible presence of *N*-substituents enlarges indeed the scope of these N₄ ligands for embracing new challenging areas. The present review is the first attempt that aims to summarize the coordination chemistry of these three types of benzoquinonediimine ligands.

In a first part, special attention will be devoted to the richness of the coordination chemistry of *para*- and *ortho*-benzoquinonediimines (*p*- and *o*-BQDI). While the position of the nitrogen atom within ditopic *p*-BQDI is ideal to develop conjugated complexes, the interest of *o*-BQDI isomer mainly lies in its bidentate character and multiple redox states. The second part will focus on the use of DABQDI (with or without *N*-substituents) as a versatile ditopic and bis-bidentate *N*-ligand for the design of coordination complexes featuring unique physico-chemical properties. These latter are relevant in several technological sectors, e.g. catalysis [11–13] or molecular materials (wires, switches, memories, ...) [14], by analogy with the well-known non-innocent ligands and mixed-valence complexes. The coordination and electronic assets let foresee a tremendous potential since this type of ligands can be employed to develop polynuclear

and conjugated complexes. Particular emphasis will be given to the optical and redox properties of the metal ligand complexes. Aside, the synthetic pathways to access these ligands and modify their substitution will be also described in order to highlight the versatility of this fascinating class of 12π-electrons quinones.

2. Coordination chemistry of *para*- and *ortho*-benzoquinonediimines

para- and *ortho*-Benzoquinonediimines (Chart 1) are respectively obtained from *p*- and *o*-phenylenediamine (PDA) following chemical, aerobic or metal-assisted oxidation of the species. Historically, these precursors are already well-known as oxidative hair colorants (for more than a century) [15,16] or as precursors for the synthesis of numerous dyes such as phenazines and azaacenes [17–22], which found several applications, notably as chemical and biological probes or in organic electronics [23–25]. Although the metalation of BQDI has been already reviewed, this section aims to exemplify their use as ligand in coordination chemistry and the diversity of the obtained complexes which will figure as basis for further description of DABQDI-based architectures (see Section 4).

2.1. *p*-Benzoquinonediimine ligands

Ludi and co-workers reported in 1975 the coordination of ruthenium(II)pentaamine with *p*-BQDI (Scheme 1) [26]. A tricationic complex **1·H⁺** was isolated as purple crystals, featuring intense visible absorption centered at 522 nm. The dramatic red-shift of absorption compared to the free diimine ligand (λ_{max} = 322 nm) is attributed to a ligand-to-metal charge transfer (LMCT) process. Disappearance of this transition is monitored upon two-electron reduction of complex **1·H⁺**, which presumably generates the aromatic form of the ligand (λ_{max} = 286 nm). Deprotonation of complex **1·H⁺** occurred in basic aqueous solution, generating the dicationic species **1**, featuring red-shifted absorption maximum at 562 nm, presumably due to increased LMCT. A pK_a of 10.6 was determined for this system, which underlines the higher basicity of the complex compared to the free *p*-BQDI ligand (pK_a = 5.75). Furthermore, the introduction of methyl groups at the iminium extremity (**2a**) and extension of conjugation using a central naphthalene ring (**3**) are efficient methods to further red-shift the absorption up to the orange spectral range (λ_{max} = 568 and 599 nm, respectively). Afterward, the same group reported in 1985 analogous complexes introducing osmium(II) (**2b**), and consequently evidenced the negligible effect of the transition metal on the absorption properties [27].

In 1981, Ludi et al. managed to prepare a dinuclear ruthenium complex incorporating a *p*-BQDI bridge (**4**, Fig. 1) by mixing *p*-PDA in an aqueous solution of [(NH₃)₅Ru(H₂O)]²⁺ [28]. Interestingly, the absorption spectrum of **4** exhibits three intense low energy bands in the red and near-infrared (NIR) ranges which were attributed to intervalence charge transfer (IVCT) transitions [29]. Cyclic voltammetry of **4** in acetonitrile/water reveals oxidation and reduction at 0.82 and 0.21 V vs. NHE, respectively, while the reduction of the *p*-BQDI ligand to *p*-PDA presumably occurs ca. –1 V. The comproportionation equilibrium was estimated to be

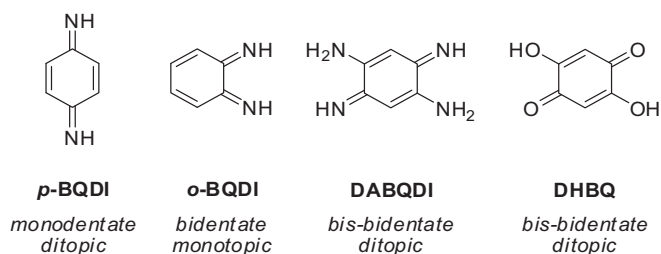


Chart 1. Benzoquinonediimines under the scope of this review and structure of dihydroxybenzoquinone.

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