Coordination Chemistry Reviews 282–283 (2015) 33–49

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Substituent effects on the electronic properties of complexes with dipyridophenazine and triazole ligands: Electronically connected and disconnected ligands

Holly van der Salm, Anastasia B.S. Elliott, Keith C. Gordon*

Department of Chemistry and MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Otago, PO Box 56, Dunedin 9054, New Zealand

Contents

ARTICLE INFO

Article history:
Received 11 December 2013
Received in revised form 14 April 2014
Accepted 2 May 2014
Available online 12 May 2014

Keywords:
Dipyridophenazine
Triazole
Spectroscopy
Photophysics
Electrochemistry

ABSTRACT

Substituent effects may tune and alter the optical and electronic properties of ligands and the complexes which they comprise. We review the effect of electron-withdrawing and -donating groups on the dipyridophenazine (dppz) framework. The observation of selected modulation of the properties associated with the phenazine or phenanthroline MOs is observed and reflected in the electrochemical and optical properties. The effect of donor groups that can give rise to ligand-centred charge-transfer optical transitions is also discussed. The effect of substituents on complexes with triazole ligands is examined; in stark contrast to the findings for dppz systems, and virtually regardless of the type of triazole ligand, substituents have only a muted effect on optical and electrochemical properties.

1. Introduction

The use of substituents on ligands to imbue changes in electronic or steric properties has been used advantageously for decades. An example of this is the use of phenyl groups at the 4,7 positions of 1,10-phenanthroline (bathophenanthroline) to redshift the metal-to-ligand charge transfer (MLCT) transition of iron(II) complexes from 510 nm for $[Fe(phen)_3]^{2+}$ to 533 nm for $[Fe(4,7\text{-}Ph_2phen)_3]^{2+}$ [1]. Using appropriate substituents it is possible to reprogram the 1,10-phenanthroline ligand to bind copper(I) in preference to iron(II). Substitution at the 2,9 positions inhibits octahedral coordination and favours a tetrahedral geometry. Using phenyl groups it is possible to alter the intensity of the MLCT transitions associated

* Corresponding author. Tel.: +64 34797599.
E-mail addresses: keith.gordon@otago.ac.nz, kgordon@chemistry.otago.ac.nz (K.C. Gordon).

http://dx.doi.org/10.1016/j.ccr.2014.05.003
0010-8545/

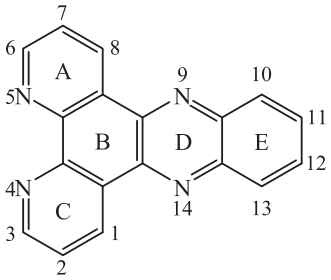

Fig. 1. Numbering scheme and ring labelling for dppz.

with the $[Cu(L)_2]^+$ by extending or diminishing the charge-transfer length [2]. All of these effects are predicated upon the electronic connectivity of the parent ligand framework. A number of physical properties can inform on substituent effects. The lowest energy absorption gives a convenient method of observing substituent effects by modulation of the HOMO and LUMO energies [3]. These may also be probed using electrochemistry [4]. The alteration of MO energies can result in distinct changes to excited state properties; notably quantum yields and excited state lifetimes [5]. These methods allow for analysis of the effect of substituent groups. In this review we discuss the effect of electron donor and acceptor moieties on the electronic properties for two classes of ligand. The first of these is dipyrido[3,2-a:2′,3′-c]phenazine (dppz) which has a level of electronic connectivity imbued by its distinct electronic structure in which the unoccupied molecular orbitals are partitioned over different sections of the ligand. In the second section we review triazole-based ligands in which electronic connectivity is rather poor and thus substituent effects can be subtle.

2. Substituents on dppz ligands

The effect of substituents on the optical properties of both a ligand and various metal complexes can be exemplified in dppz. The nature of the molecular orbitals in this ligand means the position of substituents can lead to quite different effects. There are a number of positions in which the dppz ligand can be substituted, see Fig. 1, and substituents can be broadly separated into electron-withdrawing and electron-donating groups. The nature and position of substituents affect the optical and electronic properties of dppz ligands, as well as metal complexes which contain them, and this has been investigated in a number of contexts [6]. Ru complexes of dppz are well known for switchable emission behaviour, in that strong emission is observed in aprotic solvents, but this is quenched in the presence of protic solvents or DNA. The origin of this 'light-switch' effect, which is caused by an interplay between emissive MLCT(phen) and dark MLCT(phz) states was originally thought to be due to a change in energy of the MLCT(phz), stabilised by coordination of protic solvents to the phenazine nitrogens [7]. However, variable temperature emission spectroscopy revealed that $[Ru(bpy)_2(dppz)]^{2+}$ in nitrile solvents and alcohols exhibits a 'roll-over' effect, in which *increasing* the temperature *increased* the emissive lifetime up to a certain temperature, and then decreased it again (see Fig. 2) [8]. This behaviour differs significantly from that of $[Ru(bpy)_3]^{2+}$. The explanation for 'roll-over' behaviour was that there is an equilibrium between the lower energy MLCT(phz) state and the higher energy MLCT(phen) state, in which the dark state is enthalpically favoured, and the bright state entropically favoured. Thus at low temperatures the MLCT(phz) state is populated and no emission is observed; with increasing temperature the bright MLCT(phen) state begins to be populated, and the 'roll-over' effect occurs because at sufficiently high temperatures the MLCT(phen) state is depopulated via

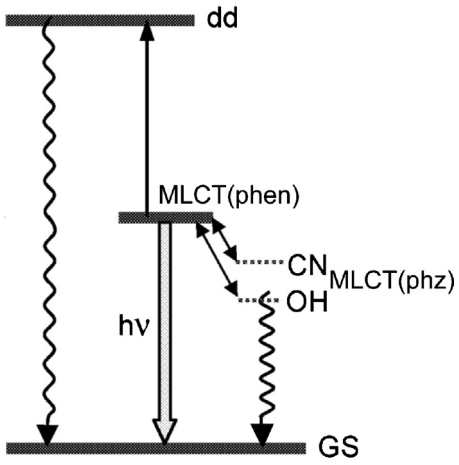

Fig. 2. Energy level diagram depicting excited states of $[Ru(bpy)_2(dppz)]^{2+}$, where CN and OH refer to nitrile and alcohol solvents respectively.
Figure modified from Brennaman et al. [8].

thermal population of metal-based d-d states, well-known in Ru compounds [8].

Substituent effects are also very interesting because they can alter relative MO energies and hence the equilibrium between excited states. $[Ru(bpy)_2(dppzMe)]^{2+}$ showed similar behaviour to the unsubstituted compound in alcohol solvents, but in nitrile solvents the bright state was populated at all temperatures, attributed to either a sufficiently small energy gap between the two states that thermal population is always possible, or a reverse in the state order causing MLCT(phen) to be entropically and enthalpically favoured [8]. This study exemplifies the effect substituents can have on the electronic structure of dppz, and also the environmental sensitivity of dppz compounds.

2.1. Electron-withdrawing substituents

Electron withdrawing substituents on the phenazine section (on the E-ring at 11 and/or 12 positions, see Fig. 1) have been widely utilised, and these include symmetrical and unsymmetrical substitution patterns with groups such as Cl, CN, NO_2, COOH/COOR, CF_3, F and Br. The dppz ligand shows electronic absorption bands in the UV region, with lowest energy bands (340–380 nm, $\epsilon \sim 1 \times 10^4\,M^{-1}\,cm^{-1}$) n,π* in nature and higher energy bands (270–290 nm, $\epsilon \sim 2.5 \times 10^4\,M^{-1}\,cm^{-1}$) π, π* in nature [9–11]. Metal complexation causes a red-shift in absorption bands and in most cases the lowest energy absorption then becomes MLCT in nature; this may be a tail or a distinct band depending on the metal, but tends to have lower oscillator strength than ligand-centred transitions (Fig. 3).

The first reduction (E_{red}) of dppz to be phenazine-based [11,27], and hence this value is significant in order to assess how the phenazine orbital is altered by substitution. The E_{red} for unsubstituted dppz and its Cu and Re complexes in DCM have values of −1.28, −1.25 and −1.01 V vs SCE respectively. This suggests that Re affects the phz MO energy but Cu does not [12]. In DMF, dppz emits at 535 nm (400 nm excitation) with a quantum yield of 12.3×10^{-3} [13], in DCM emission is observed at 502 nm [28].

Electron-withdrawing substituents at the phz MO (see Fig. 1, positions 10 to 13) lower the LUMO energy which is manifested as a red-shift in absorption spectra. The LUMO is predominantly phz-based, although it can delocalise across the substituent [15]. Using DFT calculations for dirhodium complexes it was found that the LUMO had a higher % phz contribution the more electron-withdrawing the substituents, which also corresponded to a more