

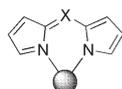
Controlling Molecular Excitons with Coordination Chemistry

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Introduction

The conjugated π system of dipyrrens illustrated by **1** is analogous to that of porphyrins and endows dipyrren and dipyrrenato complexes with interesting and useful light absorption, light emission,¹ and optical properties.² BF_2 complexes of dipyrren ligands (or BODIPYs) have been well studied.³



1, dipyrren ligand,
X = CR or N

A defining feature of dipyrrens is that they possess a large transition dipole moment across the pyrrolic rings. When two or more dipyrren units come into close proximity, *e.g.* by coordinating to a metal centre, the transition dipole moments interact strongly, owing to the strength and close spatial proximity of the chromophores (see Fig. 1). This leads to new electronic states that are delocalized across the dipyrren units,^{2,4} described as molecular excitons.

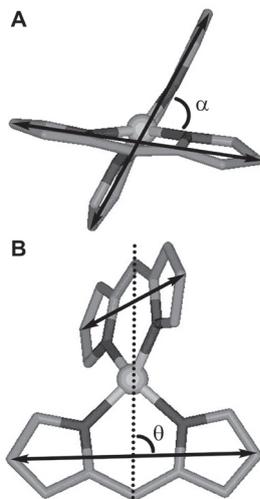
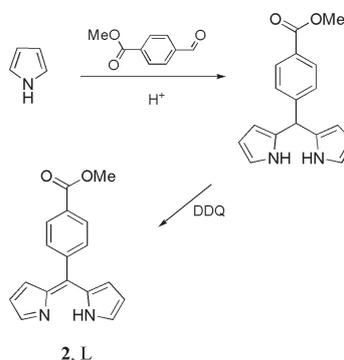


Fig. 1. Tetrahedral $[\text{ML}_2]$ with the transition dipoles shown with double headed arrows; α is the dihedral angle with respect to a vector that connects the transition dipoles (A). The line of molecular centres, shown with the broken vertical line, makes an angle θ with the transition dipole, which is 90° for all $[\text{ML}_2]$ dipyrren complexes (B).

Synthesis of Dipyrrens and Azadipyrrens

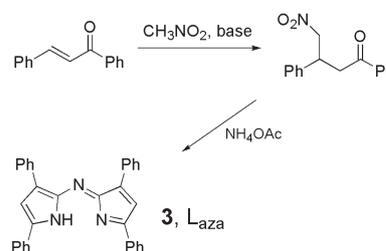
meso-Substituted dipyrrens **2** are easily accessible from arylaldehydes via an acid-catalyzed condensation with pyrrole, followed by oxidation (Scheme 1).^{1,5,6}

There are two general methods for preparing azadipyrrens (Scheme 2) of which the first involves a Michael addition across an α,β -unsaturated ketone with nitromethane, followed by a reaction with an ammonia source, such as ammonium acetate or carbamate (Route A).⁷ Route B involves the condensation of a diarylpyrrole bearing a ni-

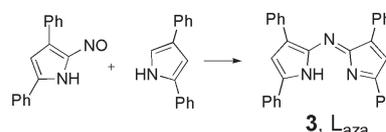


Scheme 1. Classic synthesis of dipyrrens.

Route A



Route B



Scheme 2. The two general syntheses of azadipyrrens.

troso group at the 5-position with a second molecule of pyrrole.⁸

Dipyrren Complexes

Dipyrrens chelate to metal ions in a monoanionic fashion following deprotonation and are known to form homoleptic and heteroleptic complexes with a variety of metal ions.¹ Preparation of these complexes often involves a reaction with the appropriate metal acetate in an alcoholic solvent. If the complex is neutral then the complex can be conveniently isolated by filtration and purified by recrystallization. Other metal salts are also commonly used in conjunction with a base. Various functional groups may be incorporated on the periphery of complexes of dipyrrenato ligands by substitution on the aryl and/or pyrrole rings. On kinetically inert complexes, these functional groups can be interconverted using standard synthetic methodologies.⁹

The mutual orientation of two or more dipyrren ligands in a ML_2 or ML_3 complex is governed largely by the coordination geometry preferred by the metal ion. For example the coordination geometry of d^6 Co(III) is octahedral (see Fig. 2A). Four coordinate CoL_2 dipyrren complexes are

reported to oxidise to the octahedral CoL_3 complex in air.⁹ A further example is the coordination geometry of a PdL_2 complex (see Fig. 2B).¹⁰ The coordination geometry of d^8 Pd(II) is strictly square planar. However, to accommodate the preferred coordination geometry of Pd the two dipyrin ligands cannot remain coplanar due to the steric interactions between the α hydrogen atoms. As a consequence the ligands cannot get away from the PdN_4 plane and the bispyrrolic core of the ligand contains significant curvature.¹⁰ The coordination geometry of d^9 Cu(II) can be manipulated by substituents in the α positions. In the case of $\text{Cu}(\text{L}_{\text{aza}})_2$ the coordination geometry is distorted tetrahedral to accommodate the bulky phenyl substituents (Fig. 2C).⁴

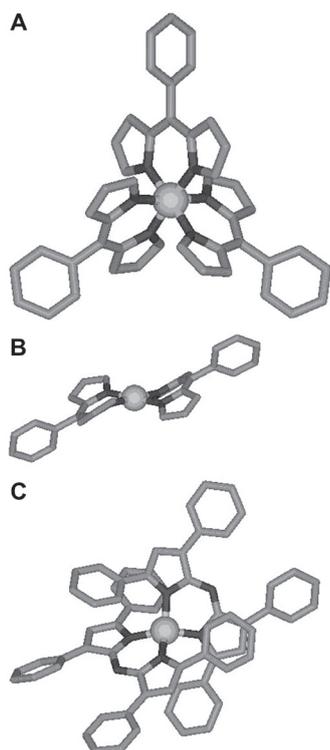


Fig. 2. Coordination geometries of A - CoL_3 (ref. 9), B - PdL_2 (ref. 10), and C - $\text{Cu}(\text{L}_{\text{aza}})_2$ (ref. 4).

Interactions between $\pi-\pi^*$ excited-states of dipyrin ligands (see below) lead to large electronic energy level shifts which are reflected in the electronic absorption spectra. Chelation of the dipyrin unit to a metal centre also gives rise to shifts in the absorption spectra of dipyrins. Fig. 3 shows electronic absorption spectra of a free dipyrin ligand and a single dipyrin ligand coordinated to a palladium centre. In the free ligand, protonation of only one pyrrole ring introduces an asymmetry that reduces the degree of delocalization across the pyrrole rings. Upon coordination (and deprotonation), the pyrrole rings become equivalent, and delocalization reduces the gap between the ground and $\pi-\pi^*$ electronic state. This results in a red-shift and substantial increase in the oscillator strength. Similar effects are observed in weak acid solution where protonation of the second pyrrole rings also removes the asymmetry.¹¹ The strong σ -donor properties of the dipyrin also contribute to the red-shift.

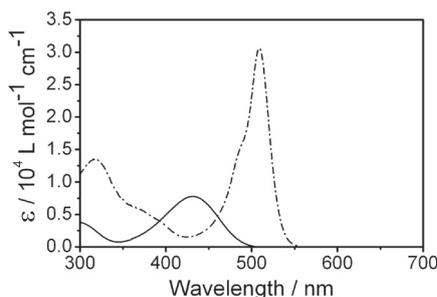


Fig. 3. Electronic absorption spectra of free dipyrin ligand (L) and $[\text{PdLdppe}]^+$ where dppe = 1,2-bis(diphenylphosphino)ethane.

Exciton Interactions with Two States

Exciton effects are well-established in molecular aggregates^{12,13} and composite molecules¹⁴ such as the light-harvesting complexes in green plants and some bacteria.¹⁵ They may be observed if there are sufficiently strong interactions between electronic states. Consider the system shown in Fig. 2 which shows a tetrahedral complex: dipolar coupling interactions between the $\pi-\pi^*$ states of each ligand result in a resonance splitting of the excited state energy levels which are degenerate or near-degenerate in the absence of interactions. The excited-state coupling leads to a new set of electronic states (the excitonic states), and this results in strong spectral shifts or splitting of the absorption bands in absorption spectroscopy¹⁴ or as positive and negative bands in circular dichroism spectroscopy.

The exciton concept originates in solid-state physics (and semiconductor materials in particular) where it describes a *correlated* electron-hole pair that results from excitation of an electron across the band gap between the valence and conduction bands.¹⁶ The hole describes the absence of an electron in the valence band. In molecular systems, generation of an excited-state arises from promotion of an electron into an unoccupied orbital and the creation of a hole in the originally occupied orbital. The exciton concept is useful in chemistry because it focuses attention on the dynamics that result from correlation of the photo-excited electron in the previously unoccupied orbital and the hole in the occupied orbitals.

A simple state interaction theory accounts for the electronic structure of the interacting system, using the framework of perturbation theory.¹⁴ The nature of the perturbation is dipolar coupling between the transition dipole moments of the unperturbed states. A necessary assumption is that the perturbation is sufficiently strong to generate new electronic states and these new states can be accurately described using the unperturbed (diabatic) states as a basis. For the case of interacting dipyrin units, the diabatic states in this theory are the $\pi-\pi^*$ excited-states of the individual dipyrin chromophores. Fig. 4 illustrates the simple case of only two interacting units. If the transition dipoles are parallel (Fig. 4A), then for one of the new excitonic states, \mathbf{E}'' , there will be a Coulombic interaction resulting in an energy lowering; and in the other, \mathbf{E}' , an energy rise relative to the original energy \mathbf{E} . Furthermore, the transition moment is given by the vector sum of the individual

transition dipole moments of the ligand component of the complex. Therefore, transitions from the ground state (**G**) to **E'** are forbidden while transitions from the **G** to **E''** are allowed. The physical consequence of this is that the dipole-allowed electronic transition for the system will be *blue shifted* with respect to the uncoupled π - π^* dipyririn states. If the transition dipoles are co-linear (see Fig. 4B), a similar splitting is observed but the vector coupling of the transition dipole moments leads to transitions from the **G** to **E'** being allowed while transitions from **G** to **E''** are forbidden. In this case the physical consequence is that the dipole-allowed electronic transition for the system will be *red shifted* with respect to the uncoupled π - π^* dipyririn states.

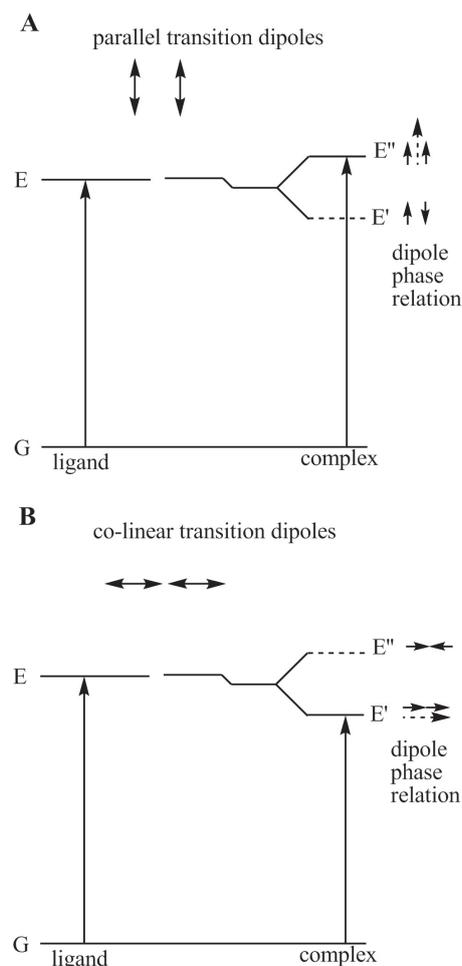


Fig. 4. Exciton energy diagram for a complex with components with A) parallel transition dipoles and B) co-linear transition dipoles.

These effects are well-known in the case of aggregated cyanine dyes where the parallel and co-linear arrangements are known as J- and H-aggregates respectively.¹⁷ Signatures of J- and H- aggregation have also been observed in weakly interacting quantum dot systems, *e.g.* GaSe.¹⁸ In the case of transition metal dipyririn complexes, the specific requirements of the transition metal coordination geometry allow precise control over the exciton interaction and provide a route to a variety of new electronic states. In general, the transition dipole moments need not be coplanar and the dihedral angle (α) between ligand planes which contain the transition dipole may take any value from 0° to 90° . The relationship between the

uncoupled π - π^* states and the exciton states is shown in Fig. 5, which illustrates the general expression given by Eq. 1 below. Note that for $\alpha = 90^\circ$ the exciton states are degenerate (but will have twice the intensity of a single π - π^* transition).

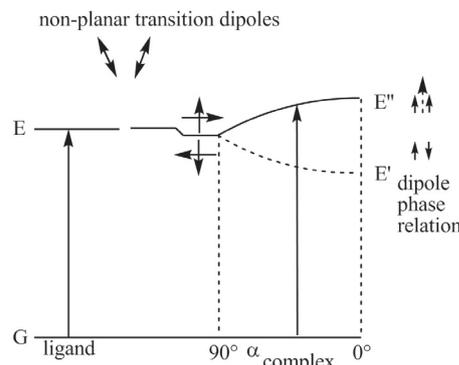


Fig. 5. Exciton energy diagram for a complex with ligand components with non-planar transition dipoles.

The exciton splitting energy is given by:

$$E'' - E' = \frac{2|\mathbf{M}|^2}{r_{ab}^3} (\cos \alpha - 3\cos^2 \theta) \dots \text{(Eq. 1)}$$

where \mathbf{M} is the transition dipole, r_{ab}^3 is the centre to centre distance between ligands a and b, α is the angle between the molecular planes of the ligands, and θ is the dihedral angle with respect to a vector that connects the transition dipoles (see Fig. 1).

The transition moments from the ground state to the exciton states **E'** and **E''** vary with the angle α . Equation 1 also explains why strong exciton interactions are rarely observed in the visible region for transition metal complexes. The difference in energy between the excitonic states depends on the square of the transition dipole moment (\mathbf{M}), which is very large ($\epsilon \sim 50\,000$ mol/L/cm) for π - π^* transitions in dipyririns. Weak ligand field transitions do not have sufficient oscillator strength to generate substantial coupling between the electronic states. For moderate intensity metal-to-ligand charge-transfer transitions, strong coupling with fluctuations in the solvent bath destroys the coherence of the excitonic state and the individual MLCT chromophores behave as individual units.¹⁹ For the dipyririn complexes, the small separation between the units provided by the coordination geometry of the metal further enhances the exciton coupling due to the $1/r^3$ dependence.

The absorption spectra of a variety of dipyririn species, including uncoordinated dipyririn are shown in Fig. 6. The first of these (Fig. 6A) shows the large shift in the position and width of the absorption bands as exciton coupling effects increase in magnitude. Particularly striking is the copper complex of **3**, $\text{Cu}(\text{L}_{\text{aza}})_2$ (Fig. 6B) which, in particular, illustrates the potential of these materials as solar energy sensitizers, as efficient solar energy sensitizers should absorb a significant fraction of the solar spectrum. Biological systems adopt a similar strategy to extend the sensitizing properties of chlorophyll, for instance in the light-harvesting complexes of *Rhodobacter sp.*^{20,21}

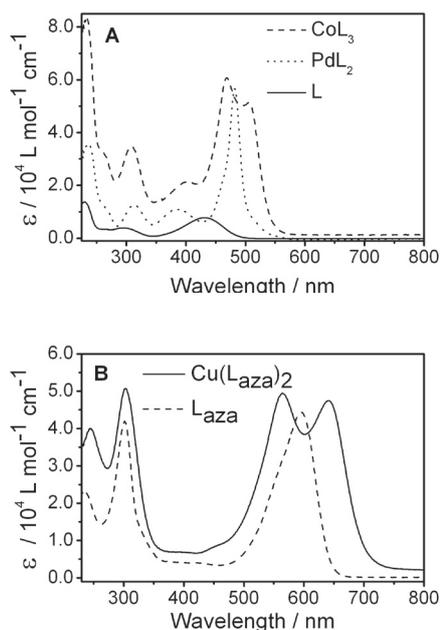


Fig. 6. Absorbance spectra of metallodipyrrin complexes of A - 2, and B - L_{aza} (3).

Three (or more) π - π^* States

The treatment of the coupling of two dipyrrin π - π^* states to generate two excitonic states resembles a molecular orbital theory treatment of two-level systems.²² In molecular orbital theory, group theory provides an efficient platform for extracting the essential features of a problem with minimal effort.²³ Group theoretical arguments can be applied to assemblies with three (or more) dipyrrin units. For instance, the case of a linear trimer of π - π^* dipyrrin states is formally equivalent to the Huckel treatment of the π bonding in the allyl radical. For the Huckel treatment of the allyl radical it is assumed that only nearest neighbour interactions are non-zero and that these interactions are characterised by a single coupling, J . The resulting energy levels of the allyl radical are then $-\sqrt{2}J$, 0 and $+\sqrt{2}J$. For C_3H_3 , the three-fold rotational axis generates energy levels $-2J$ and J , with symmetries A + E.²³ For the excitonic states of dipyrrin complexes, it is now the π - π^* states that play the role of the uncoupled levels. Coupling parameters (as determined by the symmetry of the problem) are required to complete the description of the system. The CoL_3 species possesses a three-fold rotational axis which, by analogy to the C_3H_3 system, immediately indicates that the excitonic states will be split into a single, non-degenerate level and two degenerate levels, *i.e.* A + E. The absorption spectrum of CoL_3 confirms this simple analysis with two peaks being observed at 469 nm and 505 nm, *cf.* Fig. 6A.

By analogy with the treatment of delocalized π systems, group theory arguments provide only a qualitative description of the number and types of energy levels. To obtain the energies of the excitonic states and the coupling strengths, the electronic absorption spectrum can be simulated using a time-dependent wavepacket model.^{24,25} In this model $|\psi_g\rangle$ is the ground vibrational eigenstate, *i.e.* a Gaussian. The transition dipole moment operator, μ , induces a Franck-Condon transition into the excitonic

state(s). By virtue of the Franck-Condon process, the vibrational wavefunction retains its Gaussian form and becomes a wavepacket in the excitonic state and executes dynamics according to the requirements of the propagator, $[-(i/\hbar)H_{ex}t]$ on the excitonic state potential surface. A time-dependent correlation function between the excited-state wavepacket and the ground-state wavefunction records the excited-state dynamics. The correlation function also contains all the spectral information about the electronic transition and this information is extracted in the form of the absorption cross-section by a Fourier Transform of the correlation function. The connection with the electronic structure of the excitonic states is made through the excitonic state Hamiltonian, H_{ex} . The CoL_3 system described above has three unperturbed π - π^* states, each of which may be modelled as a simple displaced harmonic oscillator, x_i . This approach effectively replaces the large number of active vibrational modes in the Franck-Condon transition with one effective mode. Assuming only nearest neighbour interactions, H_{ex} is a 3 x 3 matrix of the form:

$$H_{ex} = \begin{pmatrix} H_1(x_1, x_2, x_3) & J_{12} & J_{13} \\ J_{21} & H_2(x_1, x_2, x_3) & J_{23} \\ J_{31} & J_{32} & H_3(x_1, x_2, x_3) \end{pmatrix}$$

Symmetry determines the form of the Hamiltonian, for instance, a linear trimer will have $J_{13} = J_{31} = 0$ (because the terminal states do not couple under the nearest neighbour approximation).²⁴ Simulation of the three-state CoL_3 presents some technical challenges;²⁶ however, a simulation of the two-state $Cu(L_{aza})_2$ system is shown in Fig. 7. For the purposes of the simulation, the single *effective mode* has a dimensionless displacement of 0.5, the energies of the perturbed states were 14 600 cm^{-1} and 16 800 cm^{-1} respectively.

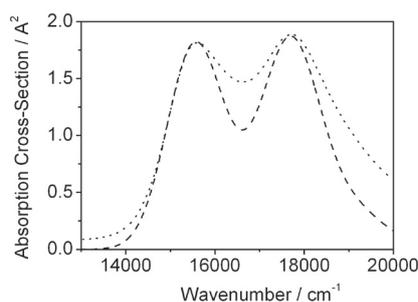


Fig. 7. Experimental (solid) and simulated (broken line) absorption spectrum of $Cu(L_{aza})_2$.

Summary

Metallodipyrrin complexes display a wide variety of exciton coupling effects that may enhance their utility in solar energy conversion and other optical applications. Their synthesis is relatively facile and simple quantum mechanical models explain their electronic structure. Beyond the basic spectroscopy and electronic structure lie interesting challenges in determining the dynamics in the excitonic states. Ultrafast spectroscopy and resonance Raman spectroscopy are currently being used by our group to investigate these aspects.

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