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Molecular excitons in a copper azadipyrrin complex

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Exciton coupling is investigated in a copper azadipyrrin complex, Cu(L-aza) 2. Exciton coupling in Cu(L-aza) 2, assuming a single π-π* state on the L-aza ligand fails to account for the electronic structure of Cu(L-aza) 2, which displays two almost equal intensity transitions at 15 600 cm −1 and 17 690 cm −1. TD-UB3LYP/6-31G(d) calculations suggest multiple π-π* transitions for the L-aza ligands and simple vector addition of the transition dipoles predicts two nearly orthogonal co-planar excitonic transitions that correctly reproduce the absorption band profile. Empirical modelling of absolute resonance Raman intensities using wavepacket dynamics confirms Cu(L-aza) 2 has two equal intensity orthogonal exciton transitions. The phenyl substituents at the α- and γ-positions of the pyrrole rings play a central role in determining the orientation of the transition dipoles. Consequently the π-π* transitions for the L-aza ligands are oriented towards the substituent groups and are not in the plane of the pyrrole rings. Mode displacements in the Franck-Condon (FC) region obtained from the wavepacket model suggest that pyrrole ring and phenyl modes control the exciton FC dynamics. Our results suggest that Cu(L-aza) 2 is an ideal model for theoretical, computational and experimental investigations of molecular excitons in molecular systems.

Introduction

The combination of desirable spectroscopic properties and versatile synthetic chemistry has generated considerable interest in dipyrrins and their aza-analogues in recent years. 1,2 The core dipyromethene structure provides π-π* transitions with very large molar absorption cross-section in the visible wavelength range which leads to excellent scattering cross-sections; derivatives with coordinated pyrrole rings, such as BODIPY TM have excellent emission quantum yields, 3,4 whilst the neutral uncoordinated dipyrrin has very strongly enhanced resonance Raman cross-sections. 5 Azadipyromethene complexes have attracted interest due to low energy transitions generating strong absorption and emission in the near infrared, 6−10 and as potential n-type charge-carrier materials. 7,11 (Aza)dipyrrins exhibit rich coordination chemistry with a wide variety of transition metal species. 7,12−19 In transition metal species with multiple (aza)dipyrrin ligands, the large transition dipole moment of the π-π* generates coupling between the π-π* states which leads to the formation of excitonic states in metalloidipyrrin species. 20−22

Exciton theory assumes dipole-dipole coupling between the π-π* states of the chromophores. 23 The relative orientation (Figure 1) of the chromophores determines the energies and oscillator strengths of the excitonic states. However, if the coupling strongly perturbs the electronic structure of the chromophores then the electronic structure is more generally described as a manifold of delocalized π-π* states. These delocalized states will resemble exciton states but the simple dependence of the energies and oscillator strengths on the geometrical parameters is lost.

In this work we consider the electronic structure of a copper tetraphenylazadipyrrin compound (Cu(L-aza) 2, Figure 1). The electronic absorption spectrum of Cu(L-aza) 2 has been reported previously, 12,17,24 and appears anomalous compared to other M(L-aza) 2 species, with two intense bands with nearly identical oscillator strength. Furthermore, applying exciton coupling theory using structural parameters (such as dihedral angle) to calculate energy splittings and intensities fails to account for the equal intensities observed in the Cu(L-aza) 2 spectrum. To the best of our knowledge, a satisfactory explanation of the electronic structure of Cu(L-aza) 2 has not appeared and in general the nature of excitonic interactions in azadipyromethene compounds has not been examined. The aim of this work is to determine if the electronic states of Cu(L-aza) 2 are properly described as excitonic or as delocalized π-π* states.

We use electronic structure calculations and resonance Raman spectroscopy to characterize the exciton states in Cu(L-aza) 2, and examine the cause of the apparent failure of the exciton theory for the copper azadipyrrin system. There are two simple possibilities; the wrong parameters are being used within the exciton coupling model and/or strong coupling may be present, in which case the electronic structure is more correctly described as a manifold of π-π*
excited states, rather than excitonic states. To proceed we employ electronic structure calculations to identify the components of the transition dipole moment vectors and apply exciton coupling theory using these components.

**Figure 1.** Top. Definition of $\theta$ and $\tau$ for non-planar dipoles, following ref. 7. The “line of ligand centres” (dashed arrow) and the dipole vector define the dihedral planes and $\tau$ is the dihedral angle between these planes. Middle. The calculated structure of Cu(L-aza)$_2$ (with hydrogen atoms omitted for clarity). The z-axis is the line of ligand centres. Bottom, $\theta$ and $\alpha$ for co-planar dipoles. The line of ligand centres (shifted for clarity) still defines $\theta$ and $\alpha$ is the angle between the dipoles.

We use resonance Raman spectroscopy as a detailed probe of the nature of the excitonic states. The resonant enhancement of the Raman mode intensities depends strongly on the nature of electronic states. Interference between Raman scattering from multiple excitonic states allows the orientation of the exciton transition dipoles to be determined by fitting an empirical model of wavepacket dynamics to experimental absolute resonance Raman cross-sections.

The wavepacket model also provides a description of the nuclear dynamics in the Franck-Condon state. Previous resonance Raman studies of metallopyrrin compounds have shown that Franck-Condon dynamics directly influence excited-state lifetime and emission properties and the substituent at the meso-position plays a critical role in determining Franck-Condon dynamics in dipyrrin compounds. In this work we identify the key structural features that control Franck-Condon dynamics in Cu(L-aza)$_2$. The quantitative resonance Raman cross-sections presented here will also provide valuable experimental data for validating recently introduced ab initio and DFT methods for the calculation of resonance Raman intensities in complex molecules.

**Results and discussion**

**Exciton Splitting Energy**

![Figure 2](image)

Figure 2. Experimental absorption spectrum (black trace) for Cu(L-aza)$_2$ in CH$_2$Cl$_2$. The red trace shows the absorption spectrum simulated using wavepacket dynamics.

The absorption spectrum is shown in Figure 2 (using an energy scale) and in Figure 3 (using a wavelength scale). The exciton splitting energy is 2140 cm$^{-1}$ for Cu(L-aza)$_2$. If we assume the transition dipole lies within the plane of the dipyromethene core then the two-fold ligand symmetry requires $\theta = 90^\circ$. We calculate the exciton splitting energy using

$$\Delta E = \frac{2|\langle M_\tau \rangle|^2}{r^3}\left(\cos \tau - 3\cos^2 \theta\right).$$

For $\tau \neq 0$ the dipoles are non-planar, and the exciton splitting energy is determined by the dihedral angle, $\tau$. We compare the
previously reported zinc complex of L-aza,\textsuperscript{31} for which $\tau = 63.5^{\circ}$, with Cu(L-aza)\textsubscript{2}. The dihedral angle of Cu(L-aza)\textsubscript{2} is $48^{\circ}$,\textsuperscript{17} this difference in dihedral angle increases the exciton splitting energy in Cu(L-aza)\textsubscript{2} by a factor of 1.58 (assuming the transition dipole moment, $M$, and distance between chromophores, $r$, are approximately equal for the copper and zinc complexes). The zinc complex shows a strong peak at 16900 cm$^{-1}$ and a weak shoulder at 15625 cm$^{-1}$, giving a splitting of 1290 cm$^{-1}$. The ratio of observed splitting energies, 2140 cm$^{-1}$/1290 cm$^{-1}$ = 1.65, is not dissimilar from that predicted using the geometrical dihedral angle. Although this analysis approximately accounts for the energy splitting (for the wrong reasons) it fails entirely to predict the intensities of the bands for Cu(L-aza)\textsubscript{2}, as the oscillator strength can only be carried by one of the exciton transitions for non-planar transition dipoles.\textsuperscript{23}

Table 1. Experimental and calculated transition energies, oscillator strengths ($f$) and transition dipole moment coordinates ($x$, $y$, $z$).

<table>
<thead>
<tr>
<th>Experimental</th>
<th>Calculated</th>
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<tbody>
<tr>
<td>$\nu$ / cm$^{-1}$</td>
<td>$f$</td>
</tr>
<tr>
<td>15 600</td>
<td>0.143</td>
</tr>
<tr>
<td>17 690</td>
<td>0.204</td>
</tr>
<tr>
<td>18 020</td>
<td>0.49</td>
</tr>
<tr>
<td>18 520</td>
<td>0.10</td>
</tr>
<tr>
<td>18 550</td>
<td>0.64</td>
</tr>
</tbody>
</table>

TD-DFT Results and Exciton Transition Intensities

For non-planar dipoles ($\theta = 90^{\circ}$, $\tau \neq 0$), the exciton coupling theory predicts only one of the exciton transitions is allowed.\textsuperscript{22, 23} The copper complex shows two exciton bands with equal intensity and it is the origin of these intensities that must be established. Implicit in the exciton model is the excited state manifold of each chromophore (or each ligand for Cu(L-aza)\textsubscript{2}) is dominated by a single excited state. For the azadipyrrins, our computational results suggest a more complicated picture. Calculated excited-state energies, transition dipole coordinates and oscillator strengths are presented in Table 1, and shown in Figure 3. Structural parameters, and calculated frequencies (supplementary information) show good agreement with experimental data. Due to the $D_2$ symmetry of Cu(L-aza)\textsubscript{2}, $\pi$-$\pi^*$ transitions for the individual ligands cannot be identified. There are five states with sufficient oscillator strength to exhibit dipole-dipole coupling. The transition dipoles for these states are oriented along the $C_2$ symmetry axes (which coincide with the Cartesian axes), shown in Figure 4. There are two transition dipoles oriented along the $C_2(z)$ and $C_2(y)$ axes, and one dipole along the $C_2(x)$ axis with sufficient magnitude for dipole-dipole coupling. The $C_2(y)$ dipoles have a larger magnitude ($f \approx 0.5$) than the $C_2(z)$ dipoles ($f \approx 0.1$) and the $C_2(x)$ dipole has an intermediate magnitude ($f \approx 0.3$). Note the $C_2(z)$ dipoles have the same magnitude and direction.

Figure 3. Top, transition energies and oscillator strengths from TDDFT-UB3LYP/6-31G(d) calculation. Bottom, experimental absorption spectrum.

Figure 4. Calculated structures for Cu(L-aza)\textsubscript{2}. Hydrogen atoms have been omitted for clarity. Views are shown looking down the $x$ (left) and $y$ (right) axes. The calculated dihedral angle, $\tau$, is 56$^{\circ}$.

We now demonstrate that vector addition of the transition dipoles shown in Table 1 creates two resultant dipoles that are co-planar but not parallel. In this case the relevant expressions for the exciton splitting energy and transition dipole magnitude are

$$\Delta E = \frac{2|M|^2}{r^3}(\cos \alpha + 3\cos^2 \theta)$$

$$M' = \sqrt{2M} \cos \theta$$

$$M'' = \sqrt{2M} \sin \theta$$

For simplicity, the addition of the $C_2(y)$ and $C_2(z)$ dipoles is described first. $\theta$ is defined using the “line that joins the ligand centres”. Considering only the $y$- and $z$- components this line is the $z$-axis. Vector addition using the values in Table 1 gives two co-planar resultant dipoles in the $yz$-plane with $\theta \approx 67.5^{\circ}$ and $\alpha \approx 45^{\circ}$. Extending this analysis to include the $C_2(x)$ dipole, note that the
line of ligand centres† must lie in the \(xz\)-plane, and also in the plane of the final resultant dipoles. The plane containing the final exciton dipoles makes an angle of approx. 60.7° with the \(yz\)-plane, and we find \(\theta \approx 48°\) and \(\alpha \approx 86°\) for the final exciton dipoles. The calculated dipole magnitudes are approximately equal and our analysis shows there are two exciton transitions with approximately equal intensity \((M''/M' = 1.1)\). We conclude from this analysis that exciton coupling theory does hold for the Cu(L-aza)\(_2\) system, but the transition dipoles are not simply related to structural elements. In Cu(L-aza)\(_2\), dipole-dipole coupling generates co-planar dipoles in an orientation that distributes intensity almost equally to both exciton states. The plane of the exciton transition dipoles no longer coincides with the plane of the pyrrole rings. Considering the analysis of the exciton splitting energies above, it is merely good fortune that the parameters obtained from the structural data provide an exciton splitting energy in good agreement with the experimental data. The TD-DFT calculations provide the relative orientation (and magnitude) of the transitions dipoles, which allows \(M''/M'\) to be determined, but not the separation, \(r\), between the dipoles. The exciton energy splitting cannot therefore be determined from the TD-DFT output alone.

Although Cu(L-aza)\(_2\) appears somewhat anomalous compared to other homoleptic L-aza complexes,\(^{13, 16, 17, 31}\) there are examples of excitonically coupled dipyrrin chromophores that exhibit a clearly defined doublet in their electronic absorption spectra.\(^{32-34}\) Broring et al have synthesized covalently coupled BODIPY dimers with absorption spectra that resemble the Cu(L-aza)\(_2\) spectrum and the dipyrrin chromophores are also co-planar in these systems. The co-planar orientation of the dipyrrin transition dipoles leads to a similar intensity distribution as the co-planar exciton dipoles for Cu(L-aza)\(_2\).

The calculated excited state transitions are described by multiple configurations which complicates the interpretation, but a qualitative description of the transitions can be obtained from the Kohn-Sham (KS) orbitals (supporting information); the \(z\)-polarised transitions originate on orbitals localized on the \(\gamma\)-phenyl substituents and terminate on orbitals including the pyrrole ring atoms and bridging nitrogen atoms; the \(x\)-polarised transition originates on orbitals involving pyrrole atoms and terminates on the orbitals of the phenyl groups at the \(\alpha\)-positions; the \(y\)-polarised transitions also originate on orbitals localized on the \(\gamma\)-phenyl substituents and terminate on orbitals including the pyrrole ring atoms and bridging nitrogen atoms. It is clear that the phenyl substituents strongly influence the electronic transitions in Cu(L-aza)\(_2\). In Cu(L-aza)\(_2\), at least, the exciton transition dipoles, whose coordinates are shown in Figure 5, are oriented toward the phenyl rings and away from the plane of the pyrrole rings.

B3LYP is known to have difficulties predicting spectroscopic properties of systems with extended \(\pi\)-systems and charge-transfer transitions.\(^{35-37}\) The TD-B3LYP transitions calculated for Cu(L-aza)\(_2\) are the result of the short-range correlation effects included in the B3LYP model. It is therefore not surprising that the TD-B3LYP method does not completely account for the observed excitonic interactions.\(^{38, 39}\) By taking the TD-B3LYP transition dipoles and semi-quantitatively accounting for long-range dipole-dipole coupling ex post facto we obtain excellent agreement with the experimental data. We believe the excitonic states in Cu(L-aza)\(_2\) provide an ideal proving ground for more sophisticated ab initio treatments of azadipyrrin excited states\(^{40-42}\) that were beyond the scope of the current work.

The alternative explanation, i.e. strong coupling or delocalization across the azadipyrrin ligands, would be mediated by orbital overlap. There is minimal amplitude on the copper atom in the frontier orbitals in Cu(L-aza)\(_2\) which suggests that delocalisation is not responsible for the electronic structure in Cu(L-aza)\(_2\). \(\pi\)-\(\pi\) interactions between the phenyl substituents may also mediate coupling between the ligands. Using a recent study of the magnitude of \(\pi\)-\(\pi\) interactions in benzene dimers\(^{43}\) we estimate the interaction energy between the phenyl substituents of Cu(L-aza)\(_2\) to be \(< 400\) cm\(^{-1}\), well below the experimentally observed splitting energy. It is likely that \(\pi\)-\(\pi\) interactions are present but do not dominate the coupling between the ligands in Cu(L-aza)\(_2\).

**Resonance Raman spectra and wavepacket modelling**

The resonance Raman spectra of Cu(L-aza)\(_2\) are shown in Figure 6. Variations in band intensities are observed as excitation is moved across the exciton states. These variations are shown more clearly in the Raman excitation profiles (data points) in Figure 7.

Wavepacket dynamics were used to simulate the resonance Raman intensities and absorption spectrum.\(^{44}\) The excited-state structure was modelled with two excited states, \(X_1\) and \(X_2\); the parameters for each state included excited-state energy, \(E_{00}\), transition dipole length, \(\mu\), and relative orientation of the transition dipoles, \(\alpha\) (as defined in Figure 1), along with parameters to describe the solvent interaction.\(^{30}\) These empirical parameters are varied to obtain resonance excitation profiles and an absorption spectrum that best fit the experimental data. The best fit absorption spectrum is shown in Figure 2. Figure 7 shows simulated Raman excitation profiles and the absolute differential Raman cross-sections used to fit the excitation profiles. Selected optimized parameters are shown in Table 2 and Table 3. The Raman profiles were simulated for a range of \(\alpha\) values. For resonant Raman scattering from two states,
Figure 6. Resonance Raman spectra of Cu(L-aza)$_2$ in CH$_2$Cl$_2$ solution. A. 514 nm excitation, B. 568 nm excitation C. 633 nm excitation D. Calculated Raman spectrum. Solvent bands are marked with ‘S’.

For these modes the simulated profile for $\alpha = 85^\circ$ shows a much better fit to the experimental data than for $\alpha = 15^\circ$ or $\alpha = 45^\circ$. The resonance Raman data therefore supports two excited states with nearly orthogonal transition dipoles, as suggested by the analysis of the TD-DFT output presented above. The same model for the electronic states is used to generate the absorption spectrum and resonance Raman profiles (the essential difference for the Raman profiles is the wavepacket motion is projected onto the individual vibrational wavefunctions). The absorption spectrum and the resonance Raman data then provide independent experimental verification of the exciton coupling model for Cu(L-aza)$_2$.

Table 2. Electronic parameters for Cu(L-aza)$_2$, obtained from simulation of absorption and Raman profiles. $X_1$ = low energy exciton state, $X_2$ = high energy exciton state. $\lambda$ = outer-sphere (solvent) reorganization energy.

<table>
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<tr>
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<th>$X_1$</th>
<th>$X_2$</th>
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<tbody>
<tr>
<td>$E_{00}$ / cm$^{-1}$</td>
<td>14 425</td>
<td>16 725</td>
</tr>
<tr>
<td>$\mu$ / Å</td>
<td>0.918</td>
<td>1.03</td>
</tr>
<tr>
<td>$\lambda$ / eV</td>
<td>0.086</td>
<td>0.117</td>
</tr>
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</table>

and 1509 cm$^{-1}$ profiles are particularly sensitive to the value of $\alpha$, with the dip around 18 000 cm$^{-1}$ increasing as the transition dipoles become orthogonal.

The mode displacements map the dynamics of the excited-state wavepacket in the Franck-Condon region, i.e. within the first few fs following photoexcitation, and as such the resonance Raman spectra provide complementary information to ultrafast studies of photodynamics. Although ultrafast studies of azadipyrrins have been reported, these studies focus on donor-acceptor photoinduced electron transfer and utilize systems with single azadipyrrin chromophores.$^{45-47}$ We are not aware of any ultrafast studies of...
Reorganization Energies

Azadipyrrin complexes have been identified as potential n-type charge-carrier materials due to their low reorganization energies. A recent theoretical study calculated internal (inner-sphere) reorganization energies for oxidation and reduction of Zn(L-aza)_2 and other complexes. The inner-sphere reorganization energy (in cm⁻¹ units) for exciton generation for Cu(L-aza)_2 can also be calculated directly from the vibrational mode displacements (Table 3 and supporting information), determined by the resonance Raman intensity analysis, using

\[ \lambda_{\text{inner}} = \sum_i v_i \Delta_i^2 \]

where \( v_i \) is the vibrational mode wavenumber (in cm⁻¹) and \( \Delta_i \) is the dimensionless mode displacement. We obtain 0.294 eV and 0.249 eV for the low and high energy exciton states respectively. Our analysis also provides the outer-sphere reorganization energy for exciton generation (Table 2), with 0.086 eV and 0.117 eV for the low and high energy states respectively. For hole transfer, the theoretical method of Seneviratha et al. calculates the reorganisation energy using

\[ ^4\lambda = E_0(Q_+) - E_0(Q_0) + E_+(Q_0) - E_+(Q_+) \]

Conclusion.

The absorption spectrum and resonance Raman excitation profiles strongly support two excited-states with equal oscillator strengths for Cu(L-aza)_2. Analysis of the absorption and resonance Raman spectra of Cu(L-aza)_2 using TD-DFT and wavepacket dynamics has shown that the excited-states of Cu(L-aza)_2 are exciton states, with approximately orthogonal and co-planar transition dipole moments. The phenyl substituents play a key role in determining the electronic structure in Cu(L-aza)_2. We are currently applying this model to other homoleptic L-aza and dipyrrin complexes to determine if our simple model holds generally for dipyrrins and their aza analogues.

Acknowledgements

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Notes and references


Electronic Supplementary Information (ESI) available: TD-UB3LYP output including structural parameters and electronic transition data, plots of atomic displacements for selected vibrational modes, images of selected KS orbitals, table of mode displacements used for wavepacket analysis. See DOI: 10.1039/b000000x/

A comment on the definition of “line of ligand centres” is required. If θ, α or τ are determined using structural parameters then it is appropriate to define the line of ligand (or molecule or chromophore) centres using structural elements (i.e. the ligand centres). However our analysis suggests that the transition dipoles themselves should define the line of ligand centres, and in this case “line of transition centres” is perhaps a more appropriate description. In some cases e.g. J-aggregates, the transition dipole moment and line of molecule centre coincides and there is no need for the distinction.


Exciton coupling is applied for the first time to successfully explain the excited-state structure of metalloazadipyrrins.