

Metal-to-ligand charge transfer absorption in a rhenium(I) complex that contains a π -conjugated bipyridine acceptor ligand

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Abstract

This Letter describes a study of the absorption and electroabsorption spectroscopy of a complex consisting of the $-\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}$ chromophore coordinated to the 4,4'-{bis-[2,5-(dimethoxyphenyl)ethynyl]}-2,2'-bipyridine ligand. The objective of the study is to explore whether $\text{Re} \rightarrow$ bipyridine metal-to-ligand charge transfer (MLCT) excitation leads to electron delocalization into the π -conjugated 2,5-(dimethoxyphenyl)ethynylene moieties. The results indicate that the two low-energy absorption bands observed for the complex have a strong degree of charge transfer character; however, the bands are dominated by intraligand (IL) π, π^* transitions. The spectroscopic data are consistent with possible configuration mixing between the lowest IL π, π^* and MLCT transitions. © 2001 Published by Elsevier Science B.V.

1. Introduction

There has been considerable recent interest in the optical properties of π -conjugated polymers and oligomers that contain transition metal-based metal-to-ligand charge transfer (MLCT) chromophores [1–4]. Our group has been particularly interested in the excited state properties of poly(phenylene ethynylene) (PPE)-based polymers and oligomers that contain the $(\text{bpy})\text{Re}(\text{CO})_3\text{Cl}$ MLCT chromophore ($\text{bpy} = 2,2'$ -bipyridine) [5–7]. In particular, we have characterized the photophysics of several series of oligomers in

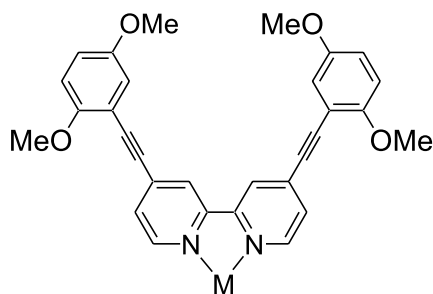
which the bpy unit (the electron acceptor in the $\text{Re} \rightarrow$ bpy MLCT transition) is an integral component of the PPE π -conjugated network [5–7]. In these systems an interesting question that arises concerns the extent to which the π -conjugated electron system in the PPE-substituted bpy acceptor ligand acts to delocalize the excited electron in the MLCT state.

One approach to address the question of electronic delocalization in a charge transfer excited state is to determine its dipole moment. Electroabsorption spectroscopy is particularly appropriate in this regard because it yields direct information concerning the difference in the dipole moments ($\Delta\mu$) of the ground state and the Franck–Condon excited state that is produced by optical absorption [8–11]. Thus, in the present

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Letter we describe the results of an electroabsorption spectroscopy study of **1a**, which contains the $-\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}$ metal complex coordinated to a bpy acceptor ligand that is substituted with a pair of dimethoxyphenylene ethynylene ($-\text{C}\equiv\text{C}-\text{DMP}$) units at the 4,4'-positions. This complex serves as a model to allow us to explore whether MLCT excitation leads to electron delocalization into the $-\text{C}\equiv\text{C}-\text{DMP}$ π -conjugated system. Because the absorption spectrum of **1a** is complicated due to the close energetic proximity of the MLCT transition and two ligand-localized, π, π^* transitions, we have also carried out calculations based on Mulliken theory [12–14] to estimate the transition moment and oscillator strength for the MLCT transition. Taken together, the work presented herein provides considerable information concerning the nature of the lowest energy optical transitions for this π -conjugated, metal–organic system.



1a : $\text{M} = \text{Re}(\text{CO})_3\text{Cl}$

1b : $\text{M} = -$

2. Experimental

The synthesis of **1a** will be described in a forthcoming paper [15]. All solvents used for spectroscopic work were distilled according to standard laboratory practices. Steady-state absorption spectra were recorded on a Varian Cary 100 dual-beam spectrophotometer. Electroabsorption spectra were recorded on PMMA films doped with **1a** at room temperature and 77 K on a

previously described apparatus [16], so only a brief description is presented here. An Oriel 150 W xenon arc lamp coupled to a Spex monochromator and polarizer provided horizontally polarized excitation light. A Joe Rolfe high-voltage AC power supply was used to apply a field of approximately 3.0 kV at 440 Hz to the ≈ 100 μm thick film sample. Transmitted light was detected with a silicon photodiode, and the electroabsorption response was extracted from the signal with a Stanford Research Systems 850 lock-in amplifier. Three measurements at each temperature were recorded on two different polymer film samples, and each experiment returned nearly identical results, confirming their validity.

Semi-empirical calculations were performed with Hyperchem version 5.0 on **1a** and (4,4'-dimethyl-2,2'-bipyridine) $\text{Re}(\text{CO})_3\text{Cl}$ (**2**). Models were built within the Hyperchem program editor. The ligand structures were fixed in the all planar, syn (with respect to the bpy unit) conformation and then energy optimized using PM3. The $-\text{Re}(\text{CO})_3\text{Cl}$ unit was then constructed using the Hyperchem program editor and 'docked' with the geometry optimized ligand. In each case, the substituted bpy ligand was contained in the xy plane and the y -axis passed through Re and bisected the C2–C2' bond in the substituted bpy ligand. A single-point extended Hückel calculation was performed on each model (K factor = 1.75), and relevant information was extracted from the program output file.

3. Results

3.1. Absorption spectroscopy

The absorption spectra of **1a** and **1b** in THF are shown in Fig. 1. Ligand **1b** features two absorption bands with maxima at 33 780 and 28 900 cm^{-1} (296 and 346 nm, respectively). These two bands have large molar absorptivities (4.3×10^4 and $2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively) and therefore they are assigned to π, π^* transitions. Semi-empirical calculations suggest that the two bands are dominated by the HOMO \rightarrow LUMO and (HOMO – 1) \rightarrow LUMO transitions (in order of

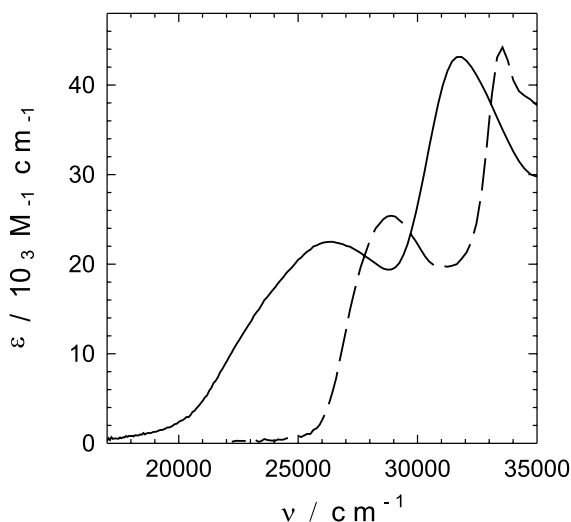


Fig. 1. Absorption spectra in THF at room temperature. (—) **1a**, (---) **1b**.

increasing energy). Metal complex **1a** also exhibits two bands, with maxima at 31 800 and 26 300 cm^{-1} (314 and 378 nm, respectively). Both peaks also have large absorptivity values ($\epsilon_{\text{max}} = 4.3 \times 10^4$ and $2.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively). There is a strong similarity in the spectra of the complex **1a** and ligand **1b**, with the exception that the absorption bands are red-shifted in the metal complex. This similarity suggests that the two absorption bands for the complex are also dominated by intraligand (IL) π, π^* transitions. The red-shift of the π, π^* absorptions in complex **1a** relative to their positions in **1b** is believed to arise because the electrophilic metal center decreases the HOMO–LUMO gap of the PPE oligomer. Recently published semi-empirical calculations suggest that metal complexation lowers both the HOMO and LUMO energies in bpy-containing π -conjugated oligomers, but the energy-lowering effect is larger for the LUMO resulting in the decreased bandgap [17].

Two features point to the fact that the low-energy absorption band in **1b** contains a contribution from an MLCT transition. First, the low-energy side of the band is noticeably asymmetric; indeed, a slight shoulder is apparent near 24 000 cm^{-1} . Second, the oscillator strength of the low-energy

band for complex **1a** is approximately 1.4 times larger than that for low-energy band in ligand **1b**. The increased oscillator strength for the band in the metal complex suggests that a transition other than π, π^* contributes to the band's total absorptivity¹.

Meyer and co-workers [18] reported the near-UV visible absorption spectrum of the 'model' complex, (4,4'-dimethyl-2,2'-bipyridine) $\text{Re}(\text{CO})_3\text{Cl}$ (**2**). This complex features a symmetric band with a maximum at 27 500 cm^{-1} (364 nm) which is assigned to the $d\pi\text{Re} \rightarrow \pi^*\text{bpy}$ MLCT transition. The MLCT band has a molar absorptivity of $3.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ and an oscillator strength of (f) ≈ 0.10 .

3.2. Electroabsorption spectroscopy

Electroabsorption spectroscopy has been used to investigate dipole moment changes associated with MLCT transitions in ruthenium complexes with a high degree of success [8–10,19]. The technique involves monitoring the change in the ground state absorption spectrum as the sample is subjected to an oscillating electric field. The resulting field-induced effects are modeled as a combination of the zeroth, first, and second derivatives of the original absorption spectrum using the fit equations specified in Eqs. (1a)–(1d) [10,16].

$$\Delta A(\tilde{\nu}) = \vec{F}^2 \left[a_z \left(A(\tilde{\nu}) \right) + b_z \frac{\tilde{\nu}}{15h} \frac{\partial}{\partial \tilde{\nu}} \left(\frac{A(\tilde{\nu})}{\tilde{\nu}} \right) + c_z \frac{\tilde{\nu}}{30h^2} \frac{\partial^2}{\partial \tilde{\nu}^2} \left(\frac{A(\tilde{\nu})}{\tilde{\nu}} \right) \right]. \quad (1a)$$

In (1a)–(1d), the $A(\tilde{\nu})$ term represents the unperturbed absorption as a function of wavenumber, $\tilde{\nu}$, and \vec{F} represents the field at the sample in V/cm. This effective field includes the enhancement of the

¹ The Zn^{II} complex of **1b** was generated in situ by titrating **1b** with $\text{Zn}(\text{OAc})_2$. The low-energy π, π^* band in the Zn^{II} (**1b**) complex is red-shifted to 27 300 cm^{-1} , but the band remains symmetrical and its oscillator strength is approximately the same as that of the free ligand. This further supports the notion that the asymmetry and increased oscillator strength of the low-energy band in **1a** are due to MLCT absorption.

applied field due to the cavity field of the matrix. The subscript χ represents the angle between the direction of the applied electric field and the electric field vector of the polarized light. Each of the coefficients in Eqs. (1a)–(1d), a_χ , b_χ , and c_χ , represents the magnitude of the contributions of the zeroth, first, and second derivatives of the absorption spectrum, respectively, to the electroabsorption spectrum. These are related to molecular parameters by the equations below at the magic angle ($\chi = 54.7^\circ$)

$$a_{54.7} = \frac{1}{30|\vec{m}|^2} \sum_{i,j} 10A_{ij}^2 + \frac{1}{15|\vec{m}|^2} \sum_{i,j} 10m_i B_{ijj}, \quad (1b)$$

$$b_{54.7} = \frac{1}{|\vec{m}|^2} \sum_{i,j} 10m_i A_{ij} \Delta\mu_j + \frac{5}{2} Tr\Delta\vec{\alpha}, \quad (1c)$$

$$c_{54.7} = 5|\Delta\vec{\mu}|^2. \quad (1d)$$

In Eqs. (1b)–(1d), the symbols $\vec{\alpha}$ (a second-order tensor) and $\vec{\mu}$ represent, respectively, the polarizability tensor and the dipole moment vector. The transition moment is represented by \vec{m} and the tensors \vec{A} and \vec{B} represent the transition moment polarizability and transition hyperpolarizability, respectively. Generally, \vec{A} and \vec{B} can be neglected for strongly allowed transitions. Information regarding $|\Delta\vec{\mu}|$ for the molecule is contained in the $c_{54.7}$ term (Eq. (1d)). To fit the electroabsorption data, the original absorption spectrum is modeled with combinations of Gaussian peaks that best reproduce the data and mathematically separate the different transitions of interest. After taking the zeroth, first, and second derivatives of the model, Eq. (1a) is used to yield the best fits for parameters a_χ , b_χ , and c_χ .

The analysis described above provides the following information for each optical transition considered in the fit.

1. The difference in polarizability between the ground and Franck–Condon excited states. This term is represented by $Tr\Delta\vec{\alpha}$, which is the trace of the difference in the second-order tensor $\vec{\alpha}$ that represents the polarizability.
2. The difference in the dipole moments of the ground and Franck–Condon excited states as represented by $|\Delta\vec{\mu}|$, where $\vec{\mu}$ is the dipole moment vector.

The electroabsorption spectrum for **1a** in a polymethylmethacrylate (PMMA) matrix at 77 K is shown in Fig. 2. Although three Gaussians were needed to properly model the absorption spectrum, the electric-field response is fit only to Gaussians 1 and 3 shown in Fig. 2a due to the small size of Gaussian 2. The use of Gaussian functions to model the two observed absorption bands in the spectrum allows the expansion of Eq. (1a) to a six-parameter fit and the extraction of $|\Delta\vec{\mu}|$ and $Tr\Delta\vec{\alpha}$ values for each transition [16]. For the low-energy band, four independent measurements at both 298 and 77 K produced an average $|Tr\Delta\vec{\mu}|$ of 8.6 ± 0.5 Debye and $Tr\Delta\vec{\alpha}$ of $174 \pm 9 \text{ \AA}^3$, while the higher-energy band returned an average $|\Delta\vec{\mu}|$ of 8.1 ± 0.5 Debye and $Tr\Delta\vec{\alpha}$ of $81 \pm 39 \text{ \AA}^3$.

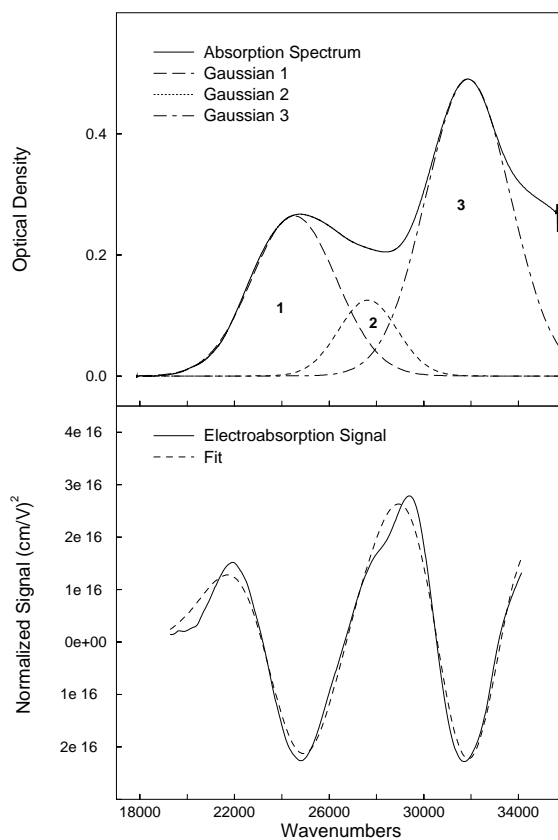


Fig. 2. Electroabsorption spectroscopy of **1a** in a PMMA matrix at 77 K. (a) Absorption spectrum illustrating Gaussians utilized in data fitting; (b) electroabsorption signal and fitting results using Eq. (1) and Gaussian 1 and 3 as the model.

(The results at 298 and 77 K were identical within experimental error.)

3.3. Mulliken theory calculations

To provide additional information concerning the nature of the MLCT transition in **1a**, calculations based on Mulliken theory were performed. These calculations were carried out in a manner similar to that described by Phifer and McMillin [13], who demonstrated that Mulliken theory works well for estimating the intensity of the MLCT transition in a series of Cu(I) phenanthroline complexes. Mulliken theory can be used to compute the transition moment (μ_{DA}) for an MLCT transition via Eqs. (2a)–(2c) [13,14,20].

$$\mu_{DA} = -e\lambda_{ad}R_{aa}, \quad (2a)$$

$$\lambda_{ad} = \frac{-\beta_{ad}}{E_{MLCT}}, \quad (2b)$$

$$R_{aa} = \sum_j C_{ja}^2 z_j + \sum_j \sum_{(j < k)} C_{ja} C_{ka} S_{jk} (z_j + z_k). \quad (2c)$$

In (2a), e is the charge of an electron (-1.60×10^{-19} C), λ_{ad} is the donor–acceptor mixing coefficient, β_{ad} is the off-diagonal interaction energy of the donor (Re d_{yz}) and acceptor (N p_z) molecular orbitals, E_{MLCT} is the energy of the charge transfer transition, C_{ja} is the LUMO π^* molecular orbital p_z orbital coefficient of atom j , z_j is the y -axis distance from the rhenium atom center to atom j , and S_{jk} is the overlap integral of the p_z orbitals on atoms j and k . All non-hydrogen atoms in the acceptor orbital ligand are considered when

calculating R_{aa} . The parameters needed for calculation of β_{ad} , S_{jk} , and C_{ja} were determined by an extended Hückel calculation performed on **1a**.

Mulliken Theory can also be applied to determine the integrated area under a charge transfer absorption band based on Eq. (3) [13].

$$v_{av} \int \epsilon(v) dv = KC_{Na}^2 S_{ReN}^2 R_{aa}^2. \quad (3)$$

In Eq. (3), v_{av} is the average transition energy, $\epsilon(v)$ is the molar absorptivity at frequency v , K is an experimental constant, C_{Na} is the LUMO molecular orbital coefficient of the nitrogen p_z orbitals, and S_{ReN} is the overlap integral between the nitrogen p_z and rhenium d_{yz} atomic orbitals. In order to determine K , extended Hückel calculations were performed on model complex **2** which has a known $v_{av} \int \epsilon(v) dv$ value [18]. The experimental $v_{av} \int \epsilon(v) dv$ for **2** is inserted into Eq. (3) along with the computed $C_{Na}(\mathbf{2})$, $S_{ReN}(\mathbf{2})$ and $R_{aa}(\mathbf{2})$ values to afford K (the number in parenthesis refers to complex **2**). The K factor computed using complex **2** is then used to determine $v_{av} \int \epsilon(v) dv$ for complex **1a** from the calculated parameters, $C_{Na}(\mathbf{1a})$, $S_{ReN}(\mathbf{1a})$ and $R_{aa}(\mathbf{1a})$. The relevant parameters used in the Mulliken theory calculations for **1a** and **2** are listed in Table 1.

4. Discussion

4.1. MLCT absorption in **1a**

Based on the findings of previous workers, we anticipate that the oscillator strength of the MLCT

Table 1
Mulliken calculation parameters and results^a

Complex	$R_{aa}/\text{\AA}$	β_{ad}/eV	λ_{ad}	μ_{DA}/Debye^c	Calculated values MLCT absorption ^b		Experimental values lowest energy absorption band	
					$v_{av} \int \epsilon(v) dv^d$	f^e	$v_{av} \int \epsilon(v) dv^d$	f^e
1a	2.53	−1.66	0.60	7.30	15×10^{32}	0.32	28.2×10^{32}	0.61
2	1.45	−1.67	0.49	3.40			4.79×10^{32}	0.10

^a Parameters obtained from Hyperchem calculations.

^b Calculated by using Mulliken theory, see text.

^c Calculated transition dipole moment.

^d Units: $\text{M}^{-1} \text{cm}^{-1} \text{s}^{-2}$.

^e Oscillator strength.

absorption in **1a** is enhanced (e.g., relative to **2**) due to the presence of the π -conjugated $-\text{C}\equiv\text{C}-\text{DMP}$ substituents on the bpy ligand. Specifically, McMillin and Phifer examined MLCT absorption in a series of Cu(I) phenanthroline complexes and observed that the MLCT oscillator strength is increased significantly when aryl groups are present in the 4- and 7-positions (in phenanthroline these positions are analogous to the 4,4'-positions in 2,2'-bipyridine). Similarly enhanced oscillator strength in the MLCT transition is seen in Ru(II) complexes that contain aryl-substituted bipyridine [21], phenanthroline [22] and terpyridine [23] ligands.

Unfortunately, the relatively intense low-energy IL π, π^* band obscures MLCT absorption in **1a**. However, the apparent oscillator strength of the low-energy band in **1a** ($f = 0.61$) is larger by approximately 40% relative to that in **1b** ($f = 0.45$). If the increased oscillator strength in **1a** is entirely due to the underlying MLCT absorption, then we estimate that approximately 25–30% of the total absorptivity in the low-energy band arises from this transition (i.e., the MLCT transition has $f \approx 0.15\text{--}0.20$). By comparison, for complex **2** the MLCT transition has $f \approx 0.10$ [18]. Thus, we conclude that the f value for the MLCT band in **1a** is 1.5–2 times larger than that for **2**. This enhancement is believed to arise due to the delocalization afforded by the π -conjugated $-\text{C}\equiv\text{C}-\text{DMP}$ substituents on the bpy acceptor ligand.

If the preceding argument concerning the oscillator strength of the MLCT transition in **1a** is correct (i.e., $f = 0.15\text{--}0.20$), then it is clear that the Mulliken theory calculation overestimates f by a factor of 1.5–2 (see Table 1). While there are a number of possible sources of error in this calculation, we believe that the most likely is the computed value of R_{aa} . Thus, this parameter may be overestimated due to the likelihood that under the experimental conditions the dimethoxyphenylene units are twisted out of the plane defined by the 2,2'-bipyridine ligand [24]. This would decrease the extent of conjugation in the acceptor ligand, in turn leading to a reduction in R_{aa} [21]. Alternatively, it is possible that there is configuration interaction between the π, π^* IL and MLCT

transitions which effectively decreases the extent of charge transfer that occurs concomitant to MLCT excitation (vide infra). This decrease in charge transfer character would lead to a reduction in the experimental value of f for the MLCT transition.

4.2. Electroabsorption spectroscopy

Electroabsorption studies have been previously carried out on MLCT absorption in Ru(II)-polypyridine complexes. Specifically, Oh and Boxer [9] reported $|\Delta\vec{\mu}| = 8.8$ Debye for the MLCT band in $\text{Ru}(\text{bpy})_3^{2+}$, while Hupp and co-workers [10] reported $|\Delta\vec{\mu}| = 6.7$ Debye for the MLCT band in $\text{Ru}(\text{phen})_3^{2+}$. Also relevant to the present work is a recent electroabsorption study of a Ru(II) complex that is coordinated to three bpy ligands that feature strongly electron donating *p*-(diethylamino)styryl-groups in the 4,4'-positions [25]. In direct analogy to **1a**, the absorption of the diethylaminostyryl-substituted complex is dominated by two π, π^* IL transitions and electroabsorption spectroscopy indicates that $|\Delta\vec{\mu}|$ for the two bands (in order of decreasing energy) is 7 and 16 Debye [25].

Analysis of the absorption spectrum of **1a** indicates that both of the low-energy bands are dominated by IL π, π^* transitions. Thus, the electroabsorption spectroscopy of **1a** is probably also dominated by the characteristics of these transitions. As shown in Fig. 3, we anticipate that the IL

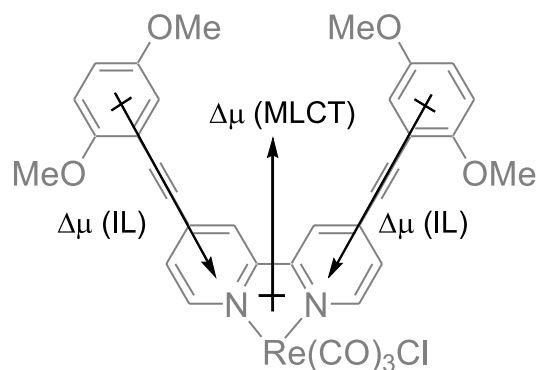


Fig. 3. Scheme illustrating approximate directions of permanent difference dipole moments ($\Delta\mu$) for the IL π, π^* and MLCT excited states.

π, π^* bands have a significant degree of charge transfer character (where the dimethoxyphenyl groups are donors and the pyridyl rings are the acceptors), which explains why comparatively large $|\Delta\vec{\mu}|$ values are observed for both of the absorption bands. The surprising feature is the fact that $|\Delta\vec{\mu}|$ for the low-energy band in **1a** is not larger than that of the high-energy band. Indeed, based on the results reported by Hupp and co-workers [25] on the diethylaminostyryl-substituted Ru(II) complex, one would expect that the low-energy band in **1a** would exhibit a larger $|\Delta\vec{\mu}|$ compared to the high-energy band.

The unexpectedly low $|\Delta\vec{\mu}|$ value may also arise due to configuration interaction between the IL π, π^* and MLCT transitions. Due to such configuration interaction, the low-energy transition will have characteristics that are a composite of the two transitions. Importantly, since the permanent difference dipole moments for the MLCT and IL excited states are largely opposing (see Fig. 3), there may be net destructive interference resulting in a partial cancellation of the $|\Delta\vec{\mu}|$ value for the low-energy absorption band.

5. Conclusion

This Letter presents an analysis of the near-UV visible absorption of rhenium complex **1a**, which contains a π -conjugated bipyridine acceptor ligand. The complex features two intense absorptions in the near-UV and visible. The low-energy absorption is believed to consist of two overlapping bands, with 70–75% of the oscillator strength contributed by an IL π, π^* transition and the remaining 25–30% of the intensity arising from an MLCT transition. The oscillator strength of the MLCT transition is enhanced approximately twofold relative to model complex **2**, and the enhancement is believed to arise due to the extended π -conjugation afforded by the $-\text{C}\equiv\text{C}-\text{DMP}$ substituents on the bpy acceptor ligand.

The electroabsorption spectroscopy of the complex is dominated by the IL π, π^* transitions. Both bands have appreciable $|\Delta\vec{\mu}|$ values, consistent with the fact that the transitions have a strong degree of charge transfer character. Unfortun-

nately, due to overlap (and possible configuration mixing) of the low-energy IL π, π^* and MLCT transitions, the electroabsorption spectroscopy does not provide direct information concerning the extent of delocalization in the MLCT excited state. However, the analysis of the oscillator strength of the low-energy band does reveal that the $-\text{C}\equiv\text{C}-\text{DMP}$ substituents increase the intensity of the MLCT absorption relative to the model complex **2**, which does not contain the π -conjugated substituents. This provides direct evidence that there is some charge delocalization into the $-\text{C}\equiv\text{C}-\text{DMP}$ units in the initially prepared MLCT state.

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