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### COMMUNICATION

# Induction of E/Z isomerization in a pendant metal-bound azobenzene: a synthetic, spectroscopic and theoretical study

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**Re(CO)$_3$ conjugates 1 and 2 that incorporate azobenzenes can be readily generated via one-pot reactions using Schiff base reaction forming conditions. Excitation of the MLCT bands in 1 and 2 results in isomerization of the azobenzene moiety, and this process has been investigated via time-resolved photophysics and TDDFT calculations.**

Light energy can be used to drive a wide variety of molecular processes, ranging from energy and electron transfer to both homolytic and heterolytic bond lysis. Photons may also be used to induce molecular motion, most typically seen in isomerization reactions. The photoinduced isomerization of azobenzene is a well-studied example of such a light driven process.[1-4] Azobenzene has been appended to a number of chromophores, including transition metal complexes, in an attempt to couple the E/Z isomerization process to an external electronic transition.[5-13] Transition metal compounds that exhibit metal to ligand charge transfer transitions (MLCT), as seen in many d$^6$ metal complexes, are ideal for transferring energy to an external group.[14-18] In this report, we present a study of two Re(CO)$_3$ diimine complexes with a pendant azobenzene group. These compounds can be readily generated in one step via metal-mediated Schiff base formation.[19] Time-resolved photophysical characterization has revealed that excitation of the MLCT bands of the Re(CO)$_3$ diimine fragments results in isomerization of the azo bonds in
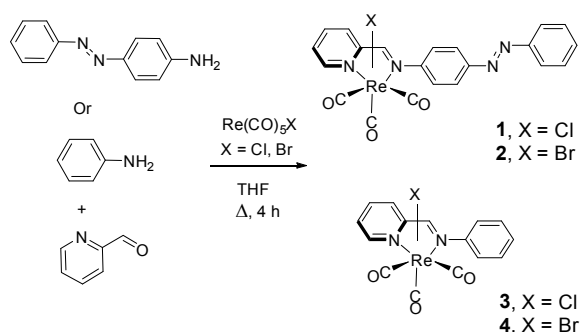


Scheme 1. Synthesis of compounds 1-4.

the pendant groups. TDDFT calculations reveal that these energy transfer processes occur due to partial diazo antibonding character of the LUMO orbital, allowing the MLCT band to induce isomerization.

Re(CO)$_3$ diimine complexes exhibit MLCT bands in their UV-visible spectra,[20-23] and these compounds have been frequently employed in energy transfer[24-30] and light harvesting[31,32] applications. There are several examples of Re(CO)$_3$ compounds with pendant azo benzene units either directly bound to the metal or pendant to chelates that exhibit photoinduced isomerization activity.[14-18,33] Excitation of the MLCT bands has been shown to induce isomerization of the E/Z state in pendant azobenzenes as well as modify the mechanism of isomerization, as seen in 4-phenylazopyridine systems. In other cases, the azobenzene has been linked directly to the diimine containing group, but in these instances the nature of the photophysical processes have not been extensively probed via time-resolved or theoretical methods.

We employed a simple one-pot method for the generation of an azobenzene-appended Re(CO)$_3$ diimine via the reaction shown in Scheme 1. This method has been useful in generating complexes with a wide variety of groups, ranging from peptides to aromatic rings, substituted at the imine nitrogen. The desired azobenzene conjugates **1** and **2** were produced in high yields, and were fully characterized, including

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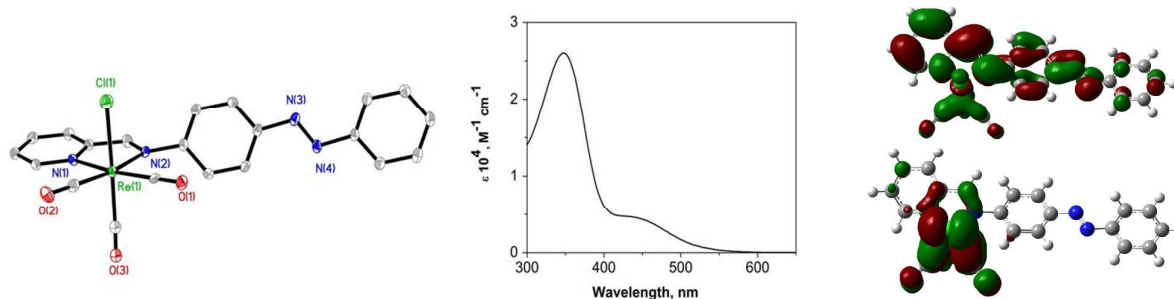
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Fig. 1.  Left: The structure of **1** with 35% thermal ellipsoids.  Hydrogen atoms have been omitted for clarity. Center: The UV-visible spectrum of **1** in THF.  Right: Structures of the HOMO (bottom) and LUMO (top) calculated using TDDFT methods for compound **1**.

by X-ray crystallography.  All methods of characterization are consistent with the structure shown in the figure, including NMR, IR, elemental analysis and mass spectrometry.  Figure 1 shows the structure of the chloride analogue **1**; the bromide is isostructural except for the identity of the halide. There is some isomerization along the halide-carbonyl bond ordinate; this is frequently observed in $Re(CO)_3X$  with asymmetric bidentate chelates The coordination geometry about the metal is typical for $Re(CO)_3$ complexes, with a facial arrangement of the carbonyls, and the pyridine imine coordination is as expected.   In the two structures, both the metal diimine and the azobenzene units are planar, but these two units are not coplanar. However, as seen in the $^1$H NMR spectrum, the single nitrogen-carbon bond that connects these two units can rotate, allowing for coplanar conformations and thus overlap of the π systems of these two units. The UV-visible spectrum of compound **1** is shown in Figure 1. The spectra for the two compounds are very similar and comprised of two bands: a higher energy, higher intensity band that corresponds to an azobenzene-based transition, and a lower energy, lower intensity band that corresponds to primarily a MLCT transition.

Bulk photolysis of **1** or **2** with either 365 or 450 nm light results in changes in the electronic spectra that are consistent with trans→cis (E→Z) isomerization (Figures S9-12). These data include a loss of absorbance at 316 nm with a concomitant growth at 450 nm and are in accord with absorption changes associated with isomerization in azobenzene. Quantum yield measurements demonstrate that the geometric isomerization of **1** or **2** is inefficient at either wavelength (Φ < 0.01). Thus, not only can isomerization be induced from direct excitation of the appended azobenzene, but the results from 450 nm irradiation indicate that MLCT excitation (Re dπ → iminopyridine π*) prompts isomerization in the distal azobenzene chromophore.

In an effort to better understand the electronic properties and excited state reactivity of these complexes, we utilized time-resolved pump-probe spectroscopy. In order to make a comprehensive study, we investigated the rhenium azo
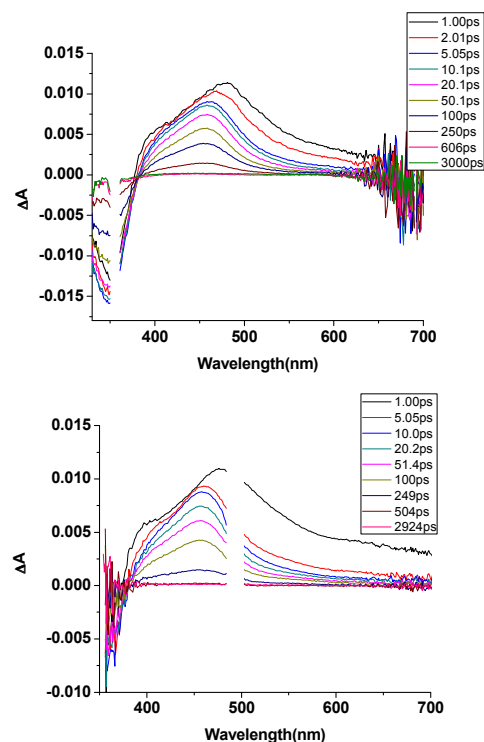


Fig. 2: Transient absorption spectra for compound **1** in DCM at 360 (top) and 490 (bottom) nm.

complexes **1** and **2** as well as the rhenium complex without the azobenzene unit (compounds **3** and **4**) and the azobenzene (**5**)

separately. Compounds **3** and **4** have been prepared and characterized previously[34-36] and can be synthesized via one-pot methods[19] identical to those used to prepare **1** and **2**. Excitation of *trans*-azobenzene at 355 nm corresponding to the $S_0 \rightarrow S_2$ ($\pi\pi^*$) transition resulted in the formation of three narrow excited state absorption (ESA) transitions centered at ~405, 485, and 600 nm (See supplemental information). These features decayed rapidly to nearly zero within 20 ps. However, the two lowest energy ESA bands (485 and 600 nm) relaxed more rapidly than did the feature at 405 nm. These results are consistent with recent literature reports investigating azobenzene, and are assigned to vibrational cooling on the ground state potential energy surface as isomerization is essentially complete on a sub-picosecond timescale.[37,38]

Excitation of our control rhenium complex **3** (absent azobenzene) at 490 nm yielded pump probe data that were similar to those observed for [Re(bpy)(CO)$_3$Cl] (bpy is 2,2′-bipyridine) by a variety of researchers.[39-41] This wavelength coincides with the red-edge of the MLCT transition, where the excited state is characterized as Re$^{II}$ and reduced diimine (see supplemental information). The time-resolved features are consistent with this formulation as we observe growth of an ESA at 390 nm that is attributed to a $\pi \rightarrow \pi^*$ transition for reduced diimine. Importantly, we do not observe any new features in the visible portion of the spectrum. The state giving rise to the 390 nm ESA decays with a time constant of 1433 ps, in accord with previous literature reports.[40]

With these results in hand, we investigated the excited state characteristics of **1** and **2** with two separate pump wavelengths of 360 nm and 490 nm, shown in Figure 2. The UV excitation wavelength will excite both the azo unit directly and the MLCT transition, whereas the lower energy excitation (490 nm) will prompt only the MLCT transition, and not directly excite the azo unit. The data obtained at these two wavelengths are remarkably similar regardless of the excitation energy. The first traces reveal an ESA near 480 nm, which is not found in the pump-probe data of the Re complex absent the azo unit. This feature must be associated with the azobenzene unit, as is suggested by the DFT results (see below). Thus, it is clear that even upon excitation at the red edge of the Re $d\pi \rightarrow$ iminopyridine p$\pi^*$ MLCT, the LUMO manifold of the azobenzene unit is populated on a femtosecond timescale. The temporal evolution of the spectral traces is nearly identical for the two separate excitation wavelengths. The ESA maximum blue-shifts to nearly 450 nm and the state exhibiting a 450 nm ESA relaxes nearly to zero by 3000 ps. Both sets of spectra show evidence of the *cis*-isomer in the 3000 ps transient spectra, again commensurate with literature results.[37,38]

To probe the origin of this MLCT-induced isomerization process, we used TDDFT methods to investigate the electronic structure of compounds **1** and **2**. The MLCT band results from a HOMO to LUMO transition, and both orbitals for the coplanar configuration of the ligand in compound **1** are shown in Figure 1. The HOMO is primarily d orbital in character, whereas the LUMO is ligand based. As shown in Figure 1, when the ligand is in the planar configuration, the LUMO

extends onto the azobenzene unit and exhibits diaza antibonding character. Although the crystal structures shows that the two planes of the ligand are not co-planar in the solid state, the single C-N bond between the imine and the pendant phenyl of the azobenzene unit is free to rotate. This would result in at least partial overlap between the pyridine imine orbitals and the azobenzene antibonding orbitals. Full details of the TDDFT methods can be found in the supplementary information.

The data displayed here do not permit us to comment on the nature of the azobenzene isomerization (i.e., rotation vs inversion). However, a tri-exponential fit of the data ($\lambda_{exc}$ 490 nm; $\lambda_{obs}$ 520 nm) returns lifetimes of $0.7 \pm 0.1$ ps, $3.2 \pm 0.2$ ps, and $109 \pm 6.3$ ps. We assign the longest lifetime of 109 ps to $^3$MLCT relaxation to the ground state. We are less certain of the assignments of the shorter time constants. In both sets of data, there are ESA maxima shifts to shorter wavelengths during the first 5 ps, suggestive of azobenzene isomerization. These shifts are especially pronounced in the 360 nm excitation data. However, $^3$MLCT formation and solvent cooling are also expected on this timescale.[40] The shortest two time constants then must represent all of these processes. However, in order to form the planar iminopyridine-azobenzene structure (DFT) from the non-planar form (X-ray data), it is clear that azobenzene must rotate on a femtosecond timescale in order for isomerization to occur. If these two units remain non-planar, then the excited state remains localized on the Re-diimine portion and isomerization does not occur. The driving force for this rapid structural reorganization is electron delocalization in the planar structure.

In conclusion, we synthesized via one-pot methods two Re(CO)$_3$–azobenzene conjugate compounds that differ in the identity of the halide. These compounds were fully characterized and show UV-visible absorption bands that result from both the azobenzene unit and the Re(CO)$_3$ diimine unit. Excitation of each compound results in isomerization of the azobenzene bond, which we observed by time-resolved methods. Our calculations indicate that the coplanar conformation of the diimine-azobenzene unit has diaza antibonding character, and thus a MLCT HOMO-LUMO transition can result in E/Z isomerization via population of this antibonding state. We are continuing our work on photochemically active Re(CO)$_3$ complexes and materials.
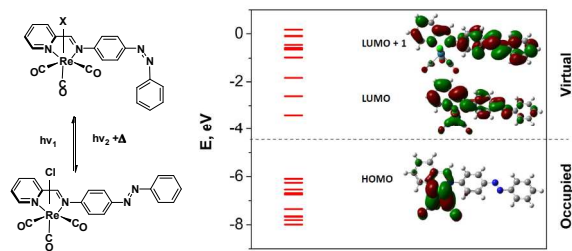
## Notes and references

1   H. M. D. Bandara, S. C. Burdette, *Chem. Soc. Rev.,* 2012, **41**, 1809–1825.
2   T. Schultz, J. Quenneville, B. Levine, A. Toniolo, T. J. Martínez, S. Lochbrunner, M. Schmitt, J. P. Shaffer, M. Z. Zgierski, A. Stolow, *J. Am. Chem. Soc.,* 2003, **125**, 8098–8099.

3   A. Cembran, F. Bernardi, M. Garavelli, L. Gagliardi, G. Orlandi, *J. Am. Chem. Soc.,* 2004, **126**, 3234–3243.
4   G. Tiberio, L. Muccioli, R. Berardi, C. Zannoni, *ChemPhysChem,* 2010, **11**, 1018–1028.
5   T. Yutaka, I. Mori, M. Kurihara, J. Mizutani, N. Tamai, T; Kawai, M. Irie, H. Nishihara, *Inorg. Chem.,* 2002, **41**, 7143–7150.
6   K. Yamaguchi, S. Kume, K. Namiki, M. Murata, N. Tamai, H. Nishihara, *Inorg. Chem.,* 2005, **44**, 9056–9067.
7   T. Yutaka, I. Mori, M. Kurihara, N. Tamai, H. Nishihara, *Inorg. Chem.,* 2003, **42**, 6306–6313.
8   S. Kume, M. Kurihara, H. Nishihara, *Chem. Commun.* 2001, 1656–1657.
9   M. Kurihara, H. Nishihara, *Coord. Chem. Rev.,* 2002; **226**, 125–135.
10  C. J. Lin, Y. H. Liu, S. M. Peng, J. S. Yang, *J. Phys. Chem. B*, 2012, **116**, 8222–8232.
11  R. Sakamoto, S. Kume, M. Sugimoto, H. Nishihara, *Chem. Eur. J.,* 2009, **15**, 1429–1439.
12  M. E. Moustafa, M. S. McCready, R. J. Puddephatt, *Organometallics,* 2012, **31**, 6262–6269.
13  T. Yutaka, I. Mori, M. Kurihara, J. Mizutani, K. Kubo, S. Furusho, K. Matsumura, N. Tamai, H. Nishihara, *Inorg. Chem.,* 2001, **40**, 4986–4995.
14  V. W. Yam, V. C. Y. Lau, L. X. Wu*, J. Chem. Soc., Dalton Trans.*, **1998**, 1461–1468.
15  M. Busby, P. Matousek, M. Towrie, A. Vlček, *Inorg. Chim. Acta,* 2007, **360**, 885–896.
16  V. W. Yam, V. C. Y. Lau, K. K. Cheung, *J. Chem. Soc., Chem. Commun.,* 1995, 259.
17  V. W. Yam, V. C. Lau, L. Wu, *J. Chem. Soc., Dalton Trans.,* 1998, 1461–1468.
18  V. W. Yam, Y. Yang, J. Zhang, B. W. K. Chu, N. Zhu, *Organometallics,* 2001, **20**, 4911–4918.
19  A. Hasheminasab, J. T. Engle, J. Bass, R. S. Herrick, C. J. Ziegler, *Eur. J. Inorg. Chem.,* 2014, **2014**, 2643–2652.
20  A. Juris, S. Campagna, I. Bidd, J. M. Lehn, R. Ziessel, *Inorg. Chem.*, 1988, **27**, 4007–4011.
21  K. S. Schanze, D. Brent MacQueen, T. A. Perkins, L. A. Cabana, *Coord. Chem. Rev.,* 1993, **122**, 63–89.
22  D. Stufkens, *Coord. Chem. Rev.,* 1998, **177**, 127–179.
23  D. J. Stufkens, *Comments Inorg. Chem.,* 1992, **13**, 359–385.
24  J. Bhuvaneswari, A. K. Fathima, S. J. Rajagopal, *Photochem. Photobiol.,* A Chem. 2012, **227**, 38–44.
25  R. L. Cleary, K. J. Byrom, D. A. Bardwell, J. C. Jeffery, M. D. Ward, G. Calogero, N. Armaroli, L. Flamigni, F. Barigelletti, *Inorg. Chem.,* 1997, **36**, 2601–2609.
26  E. Portenkirchner, D. Apaydin, G. Aufischer, M. Havlicek, M. White, M. C. Scharber, N. S. Sariciftci, *ChemPhysChem*, 2014, **15**, 3634–3638.
27  M. E. Walther, O. S. Wenger, *Dalton Trans.*, 2008, 6311–6318.
28  G. M. Hasselmann, G. J. Meyer, *J. Phys. Chem. B*, 1999, **103**, 7671–7675.
29  G. Tapolsky, R. Duesing, T. J. Meyer, *Inorg. Chem.* 1990, **29**, 2285–2297.
30  V. W. Yam, C. C. Ko, N. Zhu, *J. Am. Chem. Soc.*, 2004, 126, 12734–12735.
31  H. Takeda, M. Ohashi, T. Tani, O. Ishitani, S. Inagaki, *Inorg. Chem.,* 2010, **49**, 4554–4559.
32  X. Yi, J. Zhao, W. Wu, D. Huang, S. Ji, J. Sun, *Dalton Trans.,* 2012, 41, 8931–8940.
33  E. Gindensperger, H. Köppel, C. Daniel, *Chem. Commun.*, 2010, **46**, 8225–8227.
34  R. N. Dominey, B. Hauser, J. Hubbard, J. Dunham, *Inorg. Chem.,* 1991, **30**, 4754–4758.
35  V. W. Yam, K. M. Wong, V. W. Lee, K. K. Lo, K. Cheung, *Organometallics,* 1995, **14**, 4034–4036.

36  W. Wang, B. Spingler, R. Alberto, *Inorg. Chim. Acta*, 2003, 355, 386–393.
37  H. Satzger, C. Root, M. Braun, *J. Phys. Chem. A*, 2004, **108**, 6265-6171.
38  C.W.; Chang, Y. C. Lu, T, T. Wang, E.W.G. Diau, *J. Am. Chem. Soc.*, 2004, **126**, 10109-10118
39  B. D. Rossenaar, D. J. Stufkens, A. Vlček*, Inorg. Chem.,* 1996, **35**, 2902–2909.
40  A. El Nahhas, A. Cannizzo, F. van Mourik, A. M. Blanco-Rodríguez, S. Záliš, A. Vlček, M. Chergui, *J. Phys. Chem. A*, 2010, **114**, 6361–6369.
41  S. Záliš, C. Consani, A. El Nahhas, A. Cannizzo, M. Chergui, F. Hartl, A. Vlček, *Inorg. Chim. Acta,* 2011, **374**, 578–585.

Graphical Abstract



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