(TD-)DFT-Supported Analysis of Triarylamine Vinyl Ruthenium Conjugates: Spin- and Charge-Delocalization

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Density Functional (DFT) and Time-Dependent Theory (TD-DFT) quantum chemical calculations were performed in order to gain deeper insight into the electronic structures of alkenylruthenium-triarylamine conjugates in their various accessible oxidation states. These compounds were experimentally scrutinized in their neutral, mono- and dicationic states by infrared, UV/Vis/near-infrared and electron paramagnetic resonance (EPR) spectroscopy. Our combined experimental and computational data provide detailed information on the impact of the triarylamine substituents on the charge and spin density distributions in the mixed-valent radical cations.

1 Introduction

Electron-rich triarylamines exhibit similar (electronic) properties as alkenylruthenium compounds of the type [aryl-CH=CH-Ru(CO)Cl(PiPr$_3$)$_2$], such as reversible one-electron oxidations at low potentials, electrochromism with intense NIR absorption in the oxidized state, and resolved hyperfine splittings in EPR experiments [1]. This raises the question as to how the charge and spin densities are (de)localized in oxidized forms of alkenylruthenium-triarylamine conjugates, in particular in their mixed-valent radical cations. In previous work [2, 1], the radical cation of the di(p-anisyl)amine derivative has been shown to exhibit full delocalization despite the presence of two chemically equivalent redox sites. We here explore the effect of introducing electron withdrawing substituents at the triarylamine entity.

2 Computational Method and Comparison to experimental data

The structures of the neutral complexes and their mono- and dioxidized forms were DFT-optimized with the Gaussian09 [3] program using the PBE1PBE basis sets (6-31G(d), Ru: MWB28) [4], pseudo-potentials and the polarizable continuum model (PCM) [5] to account for solvation effects. Calculated IR data for the neutral (blue) and the mono-oxidized states (red) of the complexes, using the charge-sensitive CO stretch of the ruthenium-bonded carbonyl

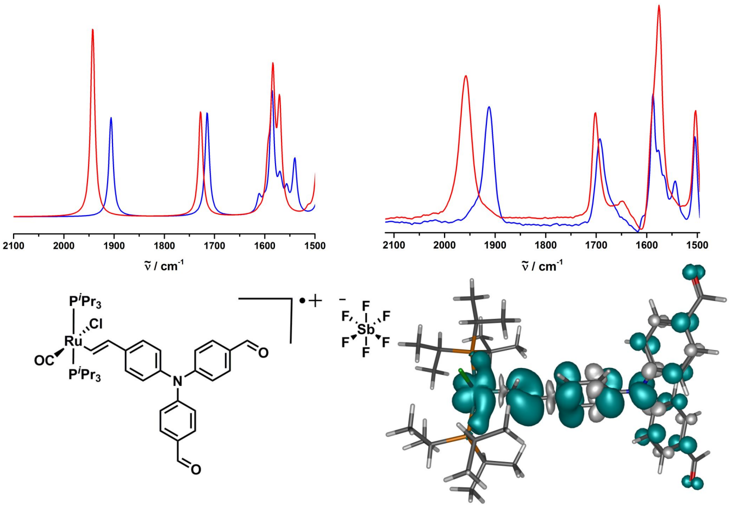

Figure 1: Comparison between exp. and calc. IR spectra (top), calculated spin density (bottom).

ligand and the amine bonded formyl groups, were compared with experimental data and display good levels of agreement, which confirms computational reliability (Figure 1).

DFT calculations also provide insight into spin density distributions in the different oxidized states (green and white colors). Computational data compare well with the experimentally observed EPR hyperfine splitting constants, which were extracted by simulation with the MATLAB Easyspin program suite. TD-DFT calculations provide insight into the underlying electronic transitions observed in the vis/NIR. Introducing electron withdrawing substituents has the consequence of changing the electronic structures of the radical cations from fully to partially delocalized with higher contributions from the alkenyl ruthenium moiety.

3 Conclusions

Calculated IR, EPR and UV/vis/NIR data on neutral and oxidized alkenylruthenium triarylamine conjugates agree well with experimental results. In particular, they show how electron-withdrawing substituents at the triarylamine site shift the charge and spin density of the associated radical cations onto the alkenylruthenium site. This allows us to study the spectroscopic consequences of tuning the radical cations from fully to partially delocalized mixed-valent systems.

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