

Assignment of the Optical Transitions in 1,3-Diethynylcyclobutadiene(cyclopentadienyl)cobalt Oligomers

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The nature of the visible optical transitions in 1,3-diethynylcyclobutadiene(cyclopentadienyl)cobalt oligomers has been studied by polarized optical absorption and resonance Raman spectroscopy. The transition at 360 nm (the band exhibiting the largest bathochromic shift in the solution spectra of the oligomer series) as well as the feature at 450 nm, which does not show a bathochromic shift, were examined. Both have their transition dipole moment parallel along the π -conjugated electron system. Based on Raman studies this long wavelength transition was assigned as being localized on the butadiene bridges.

Organometallic materials offer properties not known in purely organic systems. Organometallic materials and polymers have thus attracted considerable interest in the past few years.^{1–3} Our group has a long standing interest in chemistry and materials science properties of multiply ethynylated cyclobutadiene complexes of cobalt and iron. We described the synthesis and characterization of a series of oligomers/polymers containing the 1,3-diethynyl(cyclobutadiene)cyclopentadienylcobalt unit **1** (Scheme 1).³ The oligomers and the polymer obtained from **1** by a Hay-type coupling show unusual features in their UV–vis spectra, insofar as, despite the increasing length of the oligomers, the spectral position of the longest wavelength absorption does not change appreciably, while other bands observed in the spectra of the oligomers show a distinct bathochromic shift. The existence of a localized ligand-to-metal charge-transfer transition (LMCT) was proposed. The interpretation of these data obtained from solution was difficult, because no information existed about the orientation of the corresponding transition dipole moments with respect to the molecular axes.

Molecular orientation of a model such as **5** should allow polarized absorption spectroscopy. It will help to identify and assign the observed transitions in the oligomers and in the corresponding polymer. The Langmuir–Blodgett (LB) technique enables the controlled preparation of mono- and multilayers of organic compounds.^{4,5} It has been shown that rigid rod polymers carrying alkoxy substituents are polar enough to form stable monolayers.^{6–8} In the Langmuir–Blodgett assembly the molecules are oriented parallel to the substrate surface. Due to the inhomogeneous flow of the polymer chains toward the substrate during transfer, they possess a preferential alignment parallel to the dipping direction.

Quite surprisingly, nonamer **5** formed stable Langmuir layers on water within which one molecule of **5** occupies 1.28 nm² at a surface pressure of 12 mN m^{−1}. This area is far below the

prediction of surface area = 6.7 nm² for molecules deposited flat onto the water surface (assuming a length of **5** of 7.4 nm and a diameter of 0.9 nm), indicating an inclined orientation. Transfer of the layers onto solid substrates was possible at 5 °C at a pressure of 12 mN m^{−1} and a dipping speed of 1.0 cm/min with a transfer ratio close to one. However, no in-plane alignment was induced by the transfer.

To enforce the desired in-plane orientation of **5** to a higher extent, the material was co-spread with butyl cellulose (ratio 40% **5**, 60% butylcellulose).⁹ The mixed system forms well-defined LB films in accordance with the results obtained by Schaub and Wegner for pure butyl cellulose¹⁰ and for the mixture of isopentylcellulose and PcPs by Wu et al.¹¹ The observed maximum optical polarization, the $S_{360\text{ nm}}$ -value ($S = (A_{||} - A_{\perp})/(A_{||} + A_{\perp})$) is 0.23, similar to that obtained by polarized IR spectroscopy (vide infra).

Polarized UV–vis spectra (recorded using a Perkin–Elmer Lambda-9 spectrophotometer equipped with calcite polarizers, Figure 1) display an anisotropy over the whole spectral region (220–600 nm), indicating the (desired) in-plane orientation of **5** dispersed in the mixed multilayer, forced by the butylcellulose. The absorption spectrum shows absorption peaks at $\lambda = 270$, 360, and 450 nm, identical to the positions of the optical transitions recorded in chloroform or dichloromethane solution. In addition, unpolarized absorption spectra recorded from the solid film on a fused silica substrate reveals a band at $\lambda = 220$ nm. The above experiments strongly suggest that electronic coupling between the transition dipole moments of adjacent molecules is negligible, probably due to the steric bulk exerted by the TMS as well by the CpCo groups. This is an important prerequisite for the assignment of molecular optical properties based on the optical spectroscopy of the LB layers. To corroborate the results obtained from the optical spectroscopy, an IR study was conducted upon the oriented films on silicon substrates. Dienes show a weak but easily detectable IR absorption in an area of the spectrum where no other functional groups are observed (2182, 2126 cm^{−1}). In polarized TIR spectra (not shown here) the absorption of this vibration for parallel polarization $A_{||}$ is considerably larger than the absorption A_{\perp}

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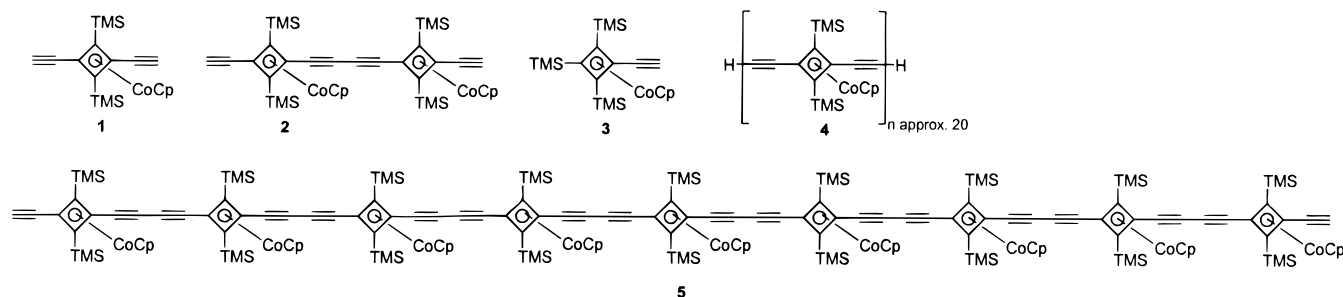
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SCHEME 1

TABLE 1: Frequencies for the Observed Totally-Symmetric Vibrations^a

sample	peak (cm ⁻¹)	vibration
3	2152	carbon triple bond stretch
	2905	C-H stretch (TMS group)
2	2181	carbon triple bond stretch
	2850	C-H stretch (TMS group)
4	2181	carbon triple bond stretch
	2843	C-H stretch (TMS group)

^a Spectra were taken by setting the monochromator to 472 and 510 nm, respectively.

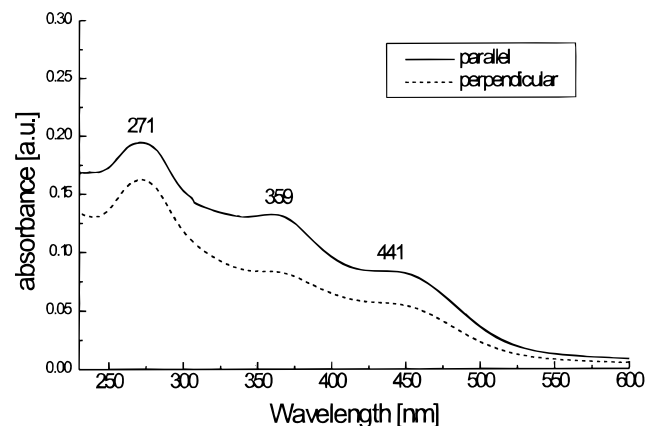


Figure 1. Polarized UV-vis spectra of a 5/butylcellulose mixed multilayer assembly (60 monolayers) for light being polarized parallel (—) and perpendicular (---) to the dipping direction.

Resonance Raman Spectra

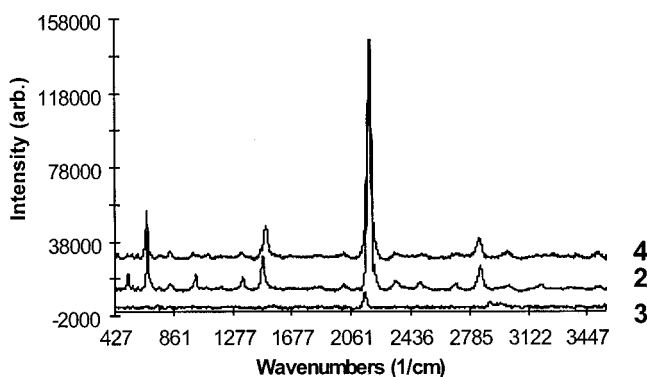


Figure 2. Resonance Raman spectra of 4, 2, and 3 excited at 457.9 nm.

with $S = 0.25 \pm 0.03$ ($S = (A_{||} - A_{\perp}) / (A_{||} + A_{\perp})$). In the grazing incidence infrared spectroscopy (GIR), the bands at 2182 and 2126 cm⁻¹ are absent, reinforcing our interpretation that the molecules are oriented parallel to the substrate surface in the mixed layers.

The polarized UV-vis absorption shows the largest anisotropy with $S = 0.23$ for the feature at 360 nm which is also the band exhibiting the largest bathochromic shift in the solution spectra of the oligomer series. This value for S is in excellent agreement with the value determined by IR measurement, which we accord to a transition along the diyne chromophore, parallel to the backbone. Surprisingly, the feature at 450 nm, which does not show a bathochromic shift in the solution spectra of the oligomer series, has a similar value of the order parameter (0.22). An order parameter of $S = 0.10$ and 0.13, roughly half of the value of the order parameter for the band at 360 nm, is observed in the vicinity of the high-energy absorption located at 270 nm. This band does not experience any bathochromic shift in the oligomer series. All transitions show a polarization parallel to the dipping direction and thus we assume that MLCT contributions, which are probably responsible for the deep color of the complexes, must be strongly coupled to a transition polarized along the conjugated π -system.

To better understand the nature of the longest wavelength transition at 435 nm, we undertook a resonance Raman study. The principle of resonance Raman enhancement allows the connection of optical transitions to the corresponding involved vibrational features. It is possible to determine the location or delocalization of optical transitions into or onto a specific functional group (such as a butadiyne unit or the whole hydrocarbon ligand) of the molecule under consideration. Solutions of 2–4 were obtained by dissolving in carbon tetrachloride. Concentrations of the samples were chosen to give the maximum intensity of the peaks of interest. The organometallic materials were excited at the 457.9 nm line by a Coherent Innova 300 argon ion laser. Laser power at the fluid sample surface was measured to be 90 mW. The laser light was focused onto the top of the solution to avoid passing through a window. Raman-scattered light was collected at 180° to reduce sample reabsorption of the scattered intensity. Light was collected and focused into a Chromex 250IS imaging spectrograph equipped with an 1800-gr/mm grating blazed at 500 nm. A Princeton Instruments Inc. TE/CCD-1100-PF 1100 × 330 element CCD array thermoelectrically cooled to -50 °C was used for detection. The detector was controlled with Win Spec version 1.6.2 software from Princeton Instruments. The entrance slit width of the spectrograph was set at 0.125 mm giving resolution between 8 and 9.4 cm⁻¹ across the total range over which the spectrum was measured. For depolarization measurements, the scattered light was passed through an Ealing 23-5671 polarizer, and a Coherent 43-8655 depolarizer before reaching the spectrograph. The depolarizer was used to negate any polarization dependence of the spectrograph. *Despite the intense excitation into the lowest energy visible absorbance of the compounds, no evidence for photodecomposition of the samples by the laser was observed.* Spectral waveforms were independent of laser power, and remained unchanged with

exposure to the laser for 2–5 min. The only circulation of the sample was through convective mixing.

Spectral corrections to subtract out solvent peaks and polynomial-fitted fluorescence baselines were made using Wavemetrics Igor Pro. This program was also used to calibrate the wavenumber scale for each of the spectra based on a toluene standard. The standard was EM Science reagent grade toluene used as received from the company. The wavenumber scale values for toluene frequencies were obtained from the 50/50 toluene/acetonitrile ASTM Raman Shift Standard supplemented with values taken from an FT Raman spectrum of toluene (Perkin–Elmer 1700X NIR FT-Raman spectrometer).

Laser-irradiation into λ_{\max} of **2** and **4** results in a dramatic enhancement of the butadiyne vibrational band at 2181 cm^{-1} while the monomer **3** has only modest enhancements due to the lack of a strong absorbance in the visible. The resonance Raman enhancement is determined to be approximately 10^6 – 10^7 for the butadiyne groups in **2** and **4**, with other enhancements an order of magnitude less. The presented results are consistent with an assignment of the lowest energy visible absorbance as being completely localized on the butadiyne bridge.¹² The findings do not only agree very well with all the other data we have gathered by optical spectroscopy but also explain the observed polarization in **5** without any constraints or additional assumptions.

A semiquantitative relationship between resonance Raman enhancements and relative displacement from the ground-state equilibrium positions for the normal vibrational modes, however, can be derived from Raman transform theory as¹³

$$I_1/I_2 = (\Delta_1\omega_2/\Delta_2\omega_1)^2 \quad (1)$$

where I_1 and I_2 are the intensities of two observed Raman modes and Δ_1 and Δ_2 are dimensionless displacements of the vibrational normal modes at frequencies ω_1 and ω_2 , respectively. On the basis of this approximation and the observed intensities, we find that vibrations other than the alkyne stretching modes are significantly distorted. In particular, the displacements of the symmetric breathing mode in the Cp rings and the Si–C and C–H vibrations of the TMS groups are comparable to those observed in the butadiene group. These observations are consistent with a MLCT or LMCT nature to the lowest excited state. The available evidence from resonance Raman suggests an electron promotion between a molecular orbital of the butydyne group and one strongly associated with the cobalt ions. This causes a large perturbation of the butadiyne equilibrium vibrational position and distorts all of the π -bonding ligands of the metals through a π -backbonding interaction. In contrast, if the lowest energy absorbance were localized on the linear butadiyne group, one would expect a spectrum dominated by the 2181 cm^{-1} butadiyne vibration (as is observed), but with negligible intensities for the remote ligands of the metal ions.

In conclusion, oligomers of 1,3-diethynylcyclobutadiene-(cyclopentadienyl)cobalt exhibit unusual optical properties, so far not observed for one-dimensional π -conjugated systems.

Polarized optical absorption spectra performed on oriented Langmuir–Blodgett layers of the nonamer **5** co-spread with butyl cellulose proved that optical transitions are polarized parallel to the dipping direction. There was no feature polarized perpendicular to the backbone. Results from resonance Raman spectroscopy on **3**, a dimer and the polymer are consistent with the assignment of the lowest energy visible absorbance as being completely localized on the butadiyne bridge and one organometallic fragment. This finding implies that the transition is not a property of the extended π -system but of only a subunit. This is the first case of a conjugated system, in which the transition at the lowest energy is not a property of the extended π -system but of only a subunit, in this case the isolated butadiyne chromophore coupled to CpCo fragment. It will be of interest if this behavior is only observable in this specific organometallic environment or if purely organic examples with similar behavior will be found soon.

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