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UV-visible spectral data for cation-radicals and dications of quaterpyrrole and dimethylquaterpyrrole.

Cyclic voltammetry of a solution of quaterpyrrole displays two reversible waves corresponding to the formation of the cation-radical ($E^\circ = 0.16_0$ V/SCE) and the dication ($E^\circ = 0.43_5$ V/SCE)¹. Oxidation of a solution of quaterpyrrole by 2 eq FeCl_3 ² gives a large increase of absorbance in the visible (518 nm) and in the near IR (945nm) due to the formation of the cation-radical. At room temperature, this cation radical is not completely stable and disappears in 3-5 minutes to give a broad absorption around 600nm. After addition of two more equivalents of FeCl_3 , new peaks develop at 360 nm and 658 nm that can be ascribed to the dication. (Figure 1a). If the solution containing the cation-radical of the quaterpyrrole is cooled down fast enough to avoid chemical degradation, the peak at 518 decreases and two new peaks appear at lower wavelengths, at (440-450) nm and 740 nm. This new absorption disappears when the solution is returned to room temperature. From Meijer's results concerning stable cation-radicals from oligopyrrole, these new absorptions are ascribed to π -dimers^{10c}. Using the molar absorptivity, ϵ , at room temperature for the cation-radical (determined from the oxidation by FeCl_3 and assuming a stoichiometry $\frac{1}{2}$ for this oxidant in aprotic solvent²), we can estimate the equilibrium constant of π -dimerization³. We found $K = 70$ and $K = 1.5 \cdot 10^4 \text{ L.mol}^{-1}$ at 20°C and -35°C, respectively (Figure 1b). To obtain the spectra for the dimethylquaterpyrrole, we oxidized a solution of monomethylbipyrrrole with FeCl_3 . Upon adding several quantities of the oxidant, the solution first develops absorbances very similar to those found for the cation-radical of the quaterpyrrole and then absorbances similar to those of the dication of the quaterpyrrole. The spectral characteristics for the quaterpyrroles with their cation-radicals and dications are summarized in Table 1.

Table 1. Spectral Characteristics of Quaterpyrroles.

λ_{max} (nm)	Neutral	Cation-radical	Dication	π -dimer
quaterpyrrole	344	518, 945	360, 660	445, 740
dimethylquaterpyrrole	349	532, 980	360, 685	

References

- (1) Andrieux, C. P.; Hapiot, P.; Audebert, P.; Guyard L.; Nguyen Dinh An, M.; Groenendaal, L.; Meijer, E.W. *Chem. Mater.*, **1997**, 9,723.
- (2) (a) The half reaction for the $\text{FeCl}_3/\text{FeCl}_2$ couple is reported to be in CH_2Cl_2 : $2 \text{FeCl}_3 + e^- \rightarrow \text{FeCl}_2 + \text{FeCl}_4^-$ ^{2b}. (b) Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F. *Synth. Met.* **1990**, 39, 243.
- (3) Miller, L.L.; Mann, K.R. *Acc. Chem. Res.* **1996**, 29; 417.

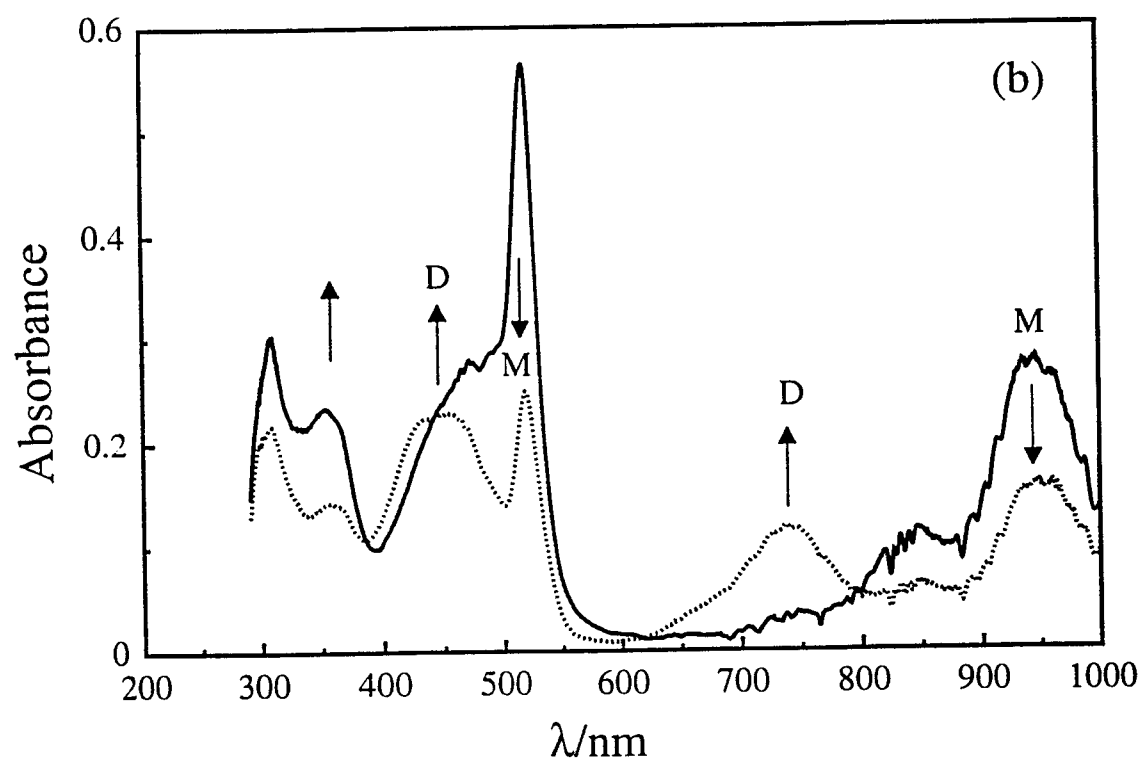
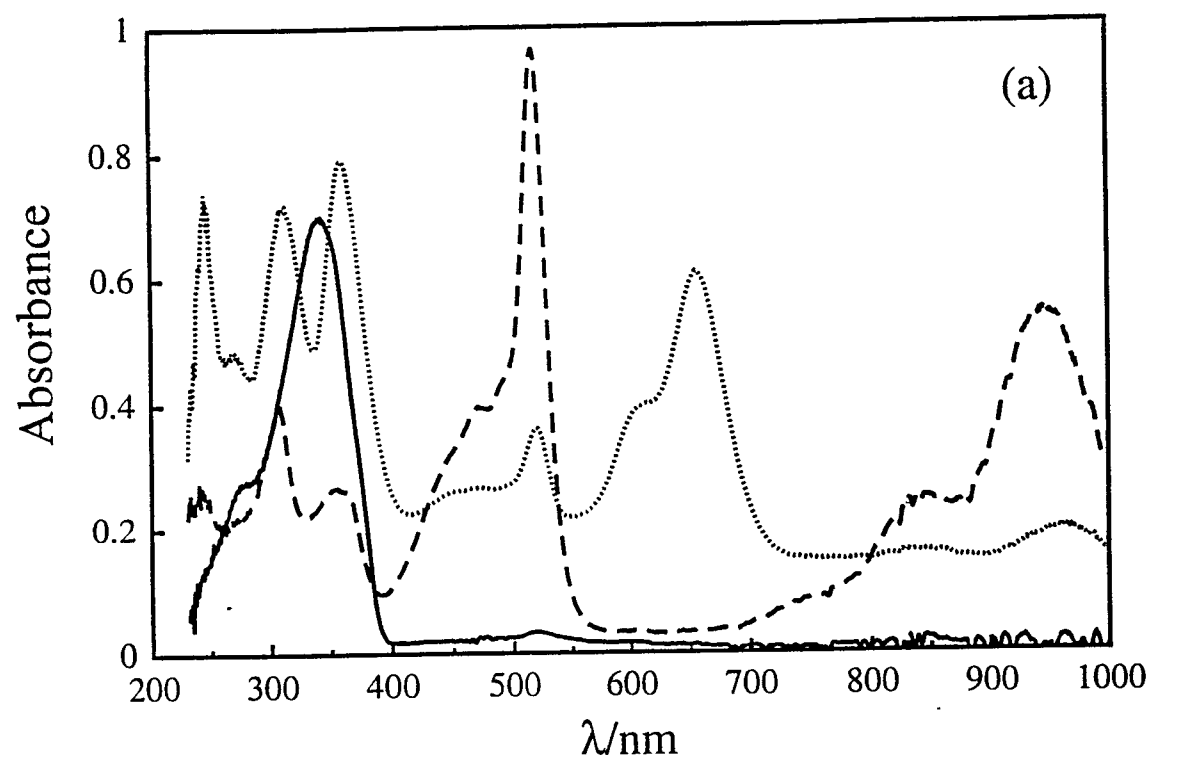


Figure 1. Chemical oxidation of quaterpyrrole by FeCl_3 . (a) (—) neutral quaterpyrrole, (---) cation-radical, (...) dication, $T=20^\circ\text{C}$. (b) (—) cation radical at 20°C , (...) formation of the π -dimer (D) at -35°C .