

EPR-Spectroelectrochemical Analysis of Cation/Anion Radical of Cibalackrots – Potential Chromophores for Singlet Fission

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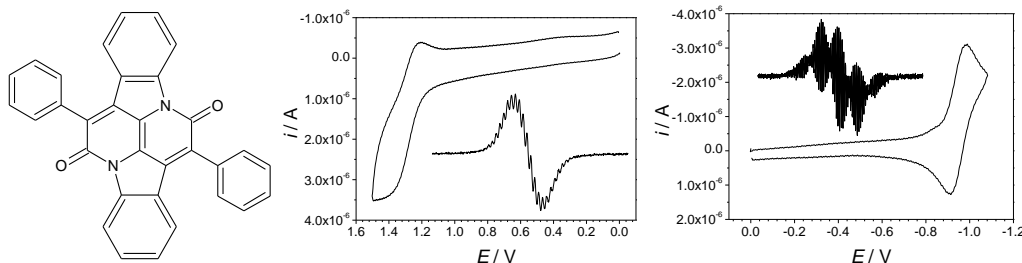
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Cibalackrots represent one type of chromophores studied for singlet fission. Singlet fission (SF) is a photophysical process in which an organic chromophore in excited singlet state shares its excitation energy with a neighbouring ground-state chromophore and both are converted into two triplet states. [1,2] The effect of singlet fission is very topical because of its use for increasing efficiency of solar cells. The study of redox properties is necessary for further development and application of singlet fission. Since substituents can influence electron excitation energies and other properties relevant to SF, a number of cibalackrot derivatives differing in structural aspects were synthesized with the aim to find the rule for designing the most promising chromophore for SF.

Reduction in two reversible steps by EE mechanism and, similarly, oxidation in two reversible steps is typical for all studied cibalackrot derivatives. The first oxidation/reduction step is associated with formation of stable radical/cation. The EPR spectrum of such radical is very narrow (around 10 G) and consists of a single broad Gaussian shape line with a peak-to-peak width of about 3.5 G. To observe a hyperfine structure was necessary to reduce modulation amplitude below 0.1 G, modulation frequency to 10 kHz and the microwave power to 0.2 mW. All attempts for analysis of spectra led to several combinations of splitting constants for which the simulated spectrum matches well with the measured spectrum. It is because of too many splitting constants in a narrow spectrum, where many of them are unresolved and hidden in the linewidth, which is in agreement with the Gaussian line shape.



Structure of cibalackrot. Cyclic voltammograms of the first oxidation/reduction step and corresponding cation/anion radical.

The measurement of selected deuterated cibalackrots significantly helped the analysis of EPR spectra. Replacing a proton with deuterium can only slightly alter the splitting constants in other positions. The splitting constant is affected by proton movements - especially by oscillations above and below the nodal plane of π -orbital. Thus, the change in the splitting constants of the unsubstituted protons on the phenyl is small, however the change in the splitting constants of the protons on the central (imidazole) part of the molecule is zero or negligible. Unlike hydrogen, deuterium splits ESR line into triplets due to different spin and splitting constants will be 6.6x lower due to the gyromagnetic ratio of deuterium. Thus, the whole spectrum will be predictably narrower.

Acknowledgements

The financial support of the grant 19-22806S (Czech Science Foundation - GAČR) and the institutional support RVO: 61388955 are highly appreciated.

References

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