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## Characterization of ion-radical $\pi$ -bonding and electron transfer using cation-radical salts with weakly coordinating anions

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The goals of the project are to quantify intrinsic energetics of the cation-radicals  $\pi$ -bonding (which will clarify the nature of this intermolecular interaction) and to establish the effect of these interactions in the electron-transfer processes. In accord with the Experimental plan, we were focusing during 2<sup>nd</sup> year on the spectral studies of formation of  $\pi$ -bonded complexes, as well as on the intermolecular interactions in solid state using X-ray structural analysis of cation-radical and mixed-valence salts. Substantial part of time was spent on the synthesis of cation-radical salts with weakly-coordinating anions (tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, BArF<sup>-</sup>, and closo-dodecamethylcarborane, CAR<sup>-</sup>, as well as their precursors required the solution-phase and solid-state studies. In addition, quantum-mechanical (DFT) computations were carried out to analyze electronic and molecular structures of  $\pi$ -bonded dimeric species. Student training also represented a significant part of the project.

*Spectral studies of formation of  $\pi$ -bonded complexes.* The dimerization of the cation-radicals in the presence of the weakly-coordinating anions was tested via the variable-temperature UV-Vis measurements of the solution of D<sup>+•</sup>BArF<sup>-</sup> salts in organic solvents (Figure 3A). At room temperature, UV-Vis-NIR measurements of solutions of these salts showed intense absorption band of monomeric cation-radicals. At lower temperatures, the intensities of these bands were decreasing, and new absorption bands appeared. An example of such spectral changes taking place in 1 mM solution of tetramethyltetraselenafulvalene in acetone is shown in Figure 1.

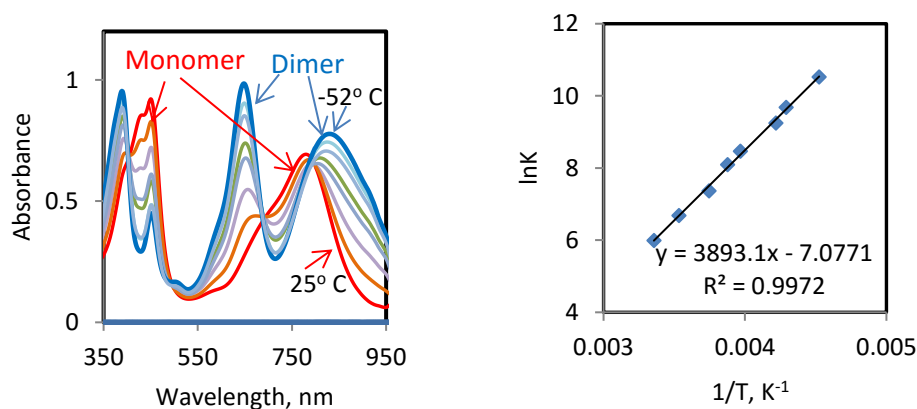
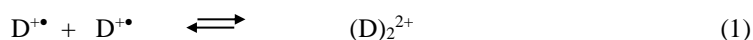


Figure 1. A) Spectra of the TMTSF<sup>+•</sup> BArF<sup>-</sup> salt in acetone showing reversible monomer to dimer conversion with lowering temperature. B) Temperature dependence of equilibrium constant of TMTSF cation-radicals' dimerization.

Quantitative treatment of temperature and concentration dependencies of absorption band intensities confirmed that these changes are related to formation of the dimeric species (D)<sub>2</sub><sup>2+</sup> (eq 1) and afforded thermodynamic parameters  $\Delta H$  and  $\Delta S$  of dimerization.



Spectral and thermodynamic characteristics of the dimers of cation-radicals of tetramethyltetraiafulvalene (TMTTF), tetramethyltetraselenafulvalene (TMTSF) and bis(ethylenedithio)tetrathiafulvalene (BEDTTTF) which were established for the first time in the current work. They are listed (in comparison with the earlier reported data for the tetrathiafulvalene, TTF, in Table 1.

Table 1. Experimental and calculated spectral and thermodynamic characteristic of  $\pi$ -bonded dimers

Donor	Experimental values				Calculated values	
	$\lambda^D$ , nm (log $\epsilon$ )	$\Delta H$ , kJ mol <sup>-1</sup>	$\Delta S$ , J mol <sup>-1</sup> K <sup>-1</sup>	$\lambda^D$ , nm (log $\epsilon$ )	$\Delta H$ , kJ mol <sup>-1</sup>	
TMTTF	773(4.0) 570(3.9)	-39.2	-118	874(4.0) 468(4.1)	-36.5	
TMTSF	830 (3.9) 648 (4.1)	-32.4	-59	897 (4.0) 545(4.1)	-53.1	
BEDTTTF	850(4.4) 440 (4.2)	-28.3	-65	1100(3.9) 686(4.3)712	-53.1	
TTF	730(4.3) 520 (4.1)	-33.5	-117	712(4.1) 438(3.8)	-14.4	

*X-ray structural studies.* Crystallization of cation-radical salts with weakly-coordinating  $\text{CAR}^-$  anions afforded six new structures (X-ray analysis of the crystals prepared by the PI and his students were carried out by Dr. Mathias Zeller at Purdue University). The new salts showed isolated cation-radicals, dimers or mixed valence stacks and they complemented earlier measured structures of cation-radicals with  $\text{BArF}^-$  counter-ions. Specifically, structure of 1:1  $\text{BEDTTTF}^+\text{CAR}^-$  salt showed cation-radical dimers (illustrated in Figure 2, left) separated by  $\text{CAR}^-$  anions. Several intermolecular S...S and C...C distances between BEDTTTF moieties were shorter than the sums of their van der Waals radii, which suggest substantial attractive interaction between these cation-radical species.

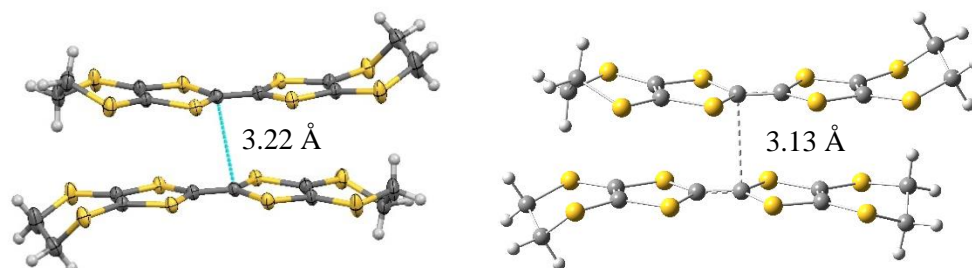


Figure 2. Structure of  $[(\text{BEDTTTF})_2]^{2+}$  dimer from X-ray analysis (left) and DFT computations (right).

Crystallization of  $\text{TMTTF}^+\text{CAR}^-$  salt produced crystals with 3:1 TMTTF to  $\text{CAR}^-$  ratio. The partially oxidized TMTTF moieties formed mixed-valence stacks separated by  $\text{CAR}^-$  anions. Interestingly, crystallization of  $\text{TMTTF}^+\text{CAR}^-$  salt from the mixture of dichloromethane and toluene resulted in formation of heteromolecular stacks of alternating  $\text{TMTTF}^+$  and TOL moieties. Similar crystallization of octamethylbiphenylene (OMB) cation-radicals salts with  $\text{CAR}^-$  anions afforded homomolecular mixed-valence OMB stacks. These crystals comprise two OMB per one  $\text{CAR}^-$  moiety, and molecules of toluene. Finally, crystals of tetramethyl-p-phenylenediamine and dodecahydro-3a,9a-diazaperylene cation-radical salts with  $\text{CAR}^-$  anion comprised isolated monomeric radicals. All these data provided valuable information about structural features of  $\pi$ -bonded solid-state associates involving cation-radicals. Also, the salts showing mixed-valence stacks are interesting for further studies of their conducting properties.

*Computational studies.* The DFT (M062X/def2tzvpp) computations of the dimeric species (using PCM solvation model) produced minima with energies about  $30 \text{ kJ mol}^{-1}$  lower than that of two isolated monomers. The enthalpies of dimer formation (Table 1) and their structural features (Figure 2) were in reasonable agreement with the experimental values. Spectral properties (from TD DFT calculations) of  $\pi$ -bonded associates were also reasonably close to the experimental values obtained from the spectral (solution-phase) studies. These agreements suggest that calculated dimers represent good models of the experimental  $\pi$ -associates and can be used for the detailed analysis of their molecular and electronic structures, as well as main driving forces of intermolecular  $\pi$ -bonding.

*Student training.* During 2<sup>nd</sup> year, six undergraduate students participated in the project. They were trained by the PI and subsequently carried out syntheses of organic donors and cation-radical salts, performed UV-Vis measurements or assisted with computations. Students were involved in the analysis of literature data and their own results. They also learned how to analyze results of the spectral measurements and how to obtain spectral and thermodynamic characteristics of the intermolecular complexes. Besides learning various spectral measurements, this work enhanced students' knowledge of thermodynamics. All students also learned basics of the X-ray structural analysis. They were trained in preparation of single crystals for X-ray structural analysis and their crystals resulted in ten new structures. Importantly, students improved their team-work and presentation skill.

*In summary,* the spectral and thermodynamic characteristics of dimers of cation-radicals of tetrathiafulvalene derivatives were established, and their molecular and electronic structures were scrutinized via quantum mechanical computations and X-ray analysis during 2<sup>nd</sup> year of the project. These results created solid basis for the further studies and assured successful completion of the project. They also represented a significant step towards long-term goals of the PI: to contribute to the elucidation of the nature and properties of supramolecular interactions and their role in chemical reactivity.