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Characterization of ion-radical π-bonding and electron transfer using cation-radical salts with weakly coordinating anions

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The goals of the project are to elucidate the nature and energetics of the multicenter bonding of cation-radicals (frequently referred to as pancake bonding). In order to achieve these goals, we study structures of dimers of cation radicals in the solid state and thermodynamics of their formation in solution. Specifically, we studied cation-radicals of tetrathiafulvalene derivatives of (tetramethyltetratiafulvalene (TMTTF), tetrametlyltetraselenafulvalene (TMTSF) and bis(ethylenedithio)tetrathiafulvalene (BEDTTTF)), as well as octamethylbiphenylene (OMB) and octamethylanthracene OMA). In order to establish intrinsic ability of cation-radicals to form multicenter bonds, it is essential to minimize and to evaluate counter-ion and solvent effects in this bonding. Therefore, we prepared cation-radical salts with weakly coordinating anions, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, BArF$^-$, and closo-dodecamethylcarborane, CAR$^-$. We studied thermodynamics of the cation-radical dimer formation via UV-Vis measurements of the solutions of these salts in various solvents. To establish structures of the dimers, we prepared single crystals and carried out X-ray structural analysis of these salts. These experimental studies were accompanied by quantum-mechanical (DFT) computations which helps to analyze electronic and molecular structures of π-bonded dimers. Student training also represented a significant part of the project.

Spectral studies of formation of π-bonded complexes. The formation of the dimers was studied using the variable-temperature UV-Vis measurements of the solution of cation-radicals in various organic solvents. These measurements showed that decrease of temperature resulted in gradual conversion of the spectra of the cation-radicals into the spectra of their dimers. At room temperature, UV-Vis-NIR spectra 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 propionitrile is shown in Figure 1.

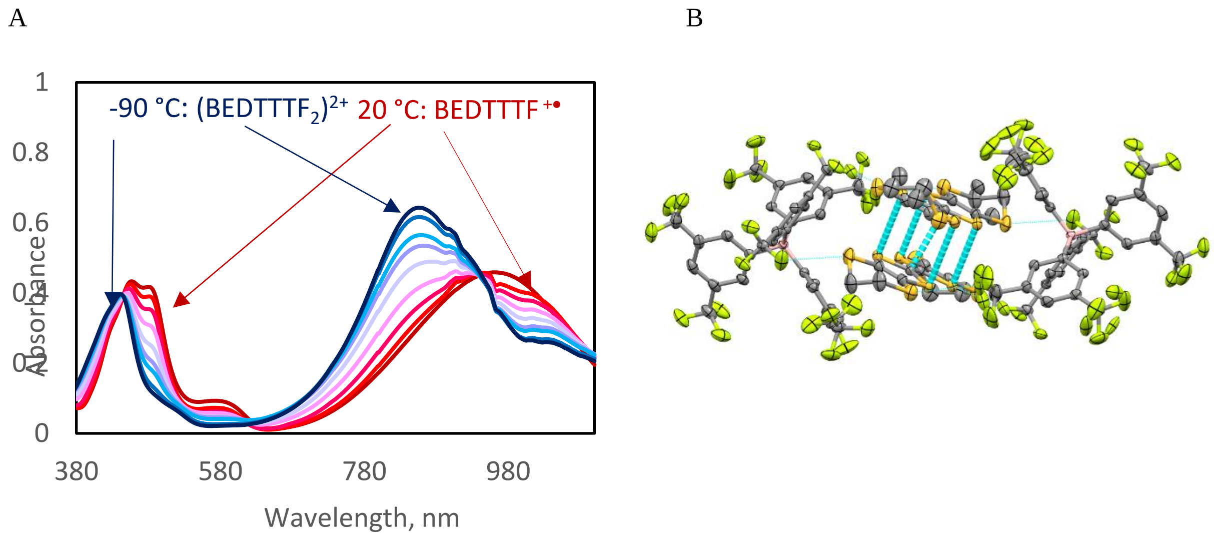

Figure 1. A) Temperature-dependent spectra of solutions of BEDTTTF$^{+•}$ BArF$^-$ salt in propionitrile showing reversible conversion of monomer into dimer with lowering temperature. B) Crystal structure of BEDTTTF$^{+•}$ BArF$^-$ salt showing π-bonded dimer. Blue line show contacts shorter than van der Waals separations.

Treatments of temperature and concentration dependencies of absorption band intensities confirmed that they are related to the formation of the dimers (D)$_2^{2+}$ (eq 1) and produced ΔH and ΔS values.

$$D^{+\bullet} + D^{+\bullet} \rightleftarrows (D)_2^{2+} \qquad (1)$$

Temperature-dependent studies in the other organic solvents showed similar monomer-dimer interconversions. Spectral and thermodynamic characteristics of the monomers and dimers of cation-radicals are listed in comparison with the earlier reported data for the tetrathiafulvalene, TTF, in Table 1.

Table 1. Spectral and thermodynamic characteristic of π-bonded dimers $(D)_2^{2+}$ in various organic solvents.

D	Solvent^{a}	λ^{D}, nm	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1}K^{-1}	K(293), M^{-1}
TMTSF	PN	820 645	30.9	72	150
	AN	820 645	45.0	118	230
	DCM	825 650	44.2	200	0.01
BEDTTTF	PN	965 485	41.8	98	20
TMTTF	PN	769 460	51.5	187	1.4
TTF	PN	730 396	36.5	132	1.2
OMA	PN	807 513	45.1	135	27
OMB	PN	788 510	48.2	143	54
	AN	788 510	52.9	157	82
	DCM	788 510	37.5	163	0.05

a) PN – propionitrile, AN – acetonitrile, DCM – dichloromethane .

X-ray structural studies. Crystallization of cation-radical salts with weakly-coordinating BArF^{-} and CAR^{-} anions afforded three 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 BEDTTTF dimer (in salt with BArF^{-}, Figure 1B). Crystals of OMA$^{+\bullet}$CAR^{-} salt and BEDTTTF$^{+\bullet}$CAR^{-} salt showed mixed valence stacks. These crystal structures complemented earlier measured structures of the other cation-radicals with these counter-ions and will be used in two manuscripts which are in preparation now.

*Computational studies***.** The DFT (M062X/def2tzvpp and wB97XD) computations of the dimeric species were carried out using various solvents as media with PCM solvation model. All cation radicals pairs under study produced minima in which cation-radical moieties were arrange at short interplanar separations with multiple interatomic contact shorter than the van der Waals radii. The interaction energies varied from 15 to 60 kJ mol^{-1}. Most importantly, their dependence on cation-radical structure and solvent followed, in general, experimental data. Spectral properties (from TD DFT calculations) of π-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 π-associates and can be used for the detailed analysis of their molecular and electronic structures, as well as main driving forces of intermolecular π-bonding.

Student training. During 2nd year, three 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 learned how to treat 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. One of the students presented results of the cation-radical dimer formation at the National Meeting of the American Chemical Society in San Diego (August, 2019).

In summary, the spectral and thermodynamic characteristics of dimers of cation-radicals of tetrathiafulvalene derivatives as well as octamethylanthracene and octamethylbiphenylene were established in various organic solvents, and their molecular and electronic structures were scrutinized via quantum mechanical computations and X-ray analysis. These results are used in preparations of two manuscripts which are currently under way. One of these articles is focusing on the crystal structures of the mixed-valence cation-radical salts with weakly-coordinating anions. Another article describes the thermodynamics of cation-radical dimer formation in solutions.

The results obtain during this period contributed to the fulfilment of the 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, such as electron transfer reactions.