Structures and Properties of Anionic Acceptors and their Charge-Transfer Salts

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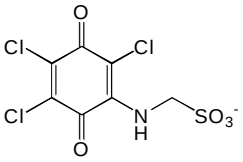
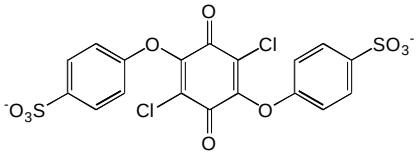
We have prepared several anionic weak acceptors (AA) that are both a weak acceptor and a monoanion. If we prepare a charge-transfer (CT) salt with organic donors (D), with stoichiometry $(D)_m(AA)_n$ where m, n = 1, 2, 3,⋯, the weak and strong CT interactions can coexist in the salt. Through the weak CT interaction, the weak acceptor part can receive a fraction (x << 1) of an electron from the donor molecule. The donor is therefore effectively doped by an amount equal to the partial charge x. To this end, we have prepared several anionic weak acceptors (figure) that combine the *p*-haloanil moiety (chloranil and bromanil) with the sulfonate ($-SO_3^-$) group. We have already reported two ET salts of **1** [1], in both of which no doping effect appears in the physical properties. Our conclusion is that the reduction potential of **1** may be too low compared with the oxidation potential of ET so not electrons are transferred for the salts to show a doping effect.

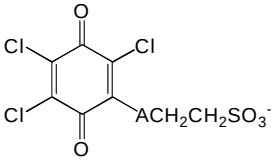
In this presentation, we will introduce seven new AA molecules (**2**-**7**). The first reduction potential of **1**-**7**, as determined by cyclic voltammetry vs SCE in CH_3CN, are -0.42, -0.17, -0.23, -0.26, -0.36, -0.45, -0.45, and -0.46 V, respectively. Unfortunately, stronger acceptors than **1** (**2**-**4**) did not provide any ET salts. On the other hand, each of the weaker acceptors (**5**-**7**) provided two types of isomorphous ET salts, β-$(ET)_5(AA)$·dichloroethane·H_2O and λ-$(ET)_2(AA)$·methanol. All ET salts show semiconducting behaviour. The AA **3** and **4** have also provided the TTF salts, the structures and properties of which will be reported. In addition, all salts did not show a doping effect on the physical properties at present.



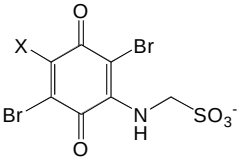
1



2



3 (A = S)
4 (A = $N(CH_3)$)



5 (X = Br)
6 (X = $Br_{0.5}Cl_{0.5}$)
7 (X = Cl)

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[1] H. Akutsu *et al.*, Solid State Commun. 144 (2007) 144.