Supplementary data

Large static first and second hyperpolarizabilities dominated by excess electron transitions for radical ion pair salts $M_2{\cdot}^{+}TCNQ{\cdot}^{-}$ (M=Li, Na, K)

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Basis set effect on the molecular geometry

The choice of suitable basis set to calculate geometry is important. For the $Li_2{\cdot}^{+}TCNQ{\cdot}^{-}$ with C_{2v} symmetry, effects of basis sets on calculations of stable structures are studied at the UB3LYP level of theory with the 6-31G, 6-31G(d), 6-31++G, 6-31+G(d), 6-311+G(d), 6-311+G(d, p), 6-311++G(2d, 2p) basis sets. The results obtained with the medium-sized 6-31+G(d) basis set agrees well to those of the largest 6-311++G(2d, 2p) basis set for all calculated parameters of the geometries. In brief, smooth convergences of the UB3LYP results are observed for R(N-Li), R(N-N), R(Li-Li) in following Table S1. Thus, the 6-31+G(d) basis set is suitable and employed in discussions of present article. The structure of $Li_2{\cdot}^{+}TCNQ{\cdot}^{-}$ is shown in Fig. S1.

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TABLE S1. Selected geometrical parameters (Å) of $Li_2{\cdot}^{+}TCNQ{\cdot}^{-}$ at the UB3LYP level.

	6-31G	6-31G(d)	6-31++G	6-31+G(d)	6-311+G(d)	6-311+G(d, p)	6-311++G(2d,2p)
N-Li	1.906	1.933	1.897	1.928	1.925	1.925	1.921
N-N	3.742	3.943	3.718	3.897	3.883	3.883	3.886
Li-Li	3.378	3.180	3.405	3.213	3.207	3.208	3.211

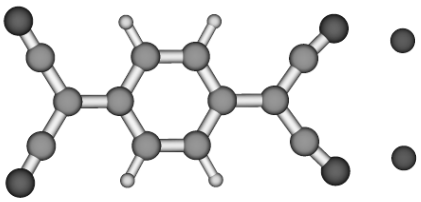

FIG S1. Geometrical structure of $Li_2{\cdot}^{+}TCNQ{\cdot}^{-}$ by DFT/UB3LYP method.

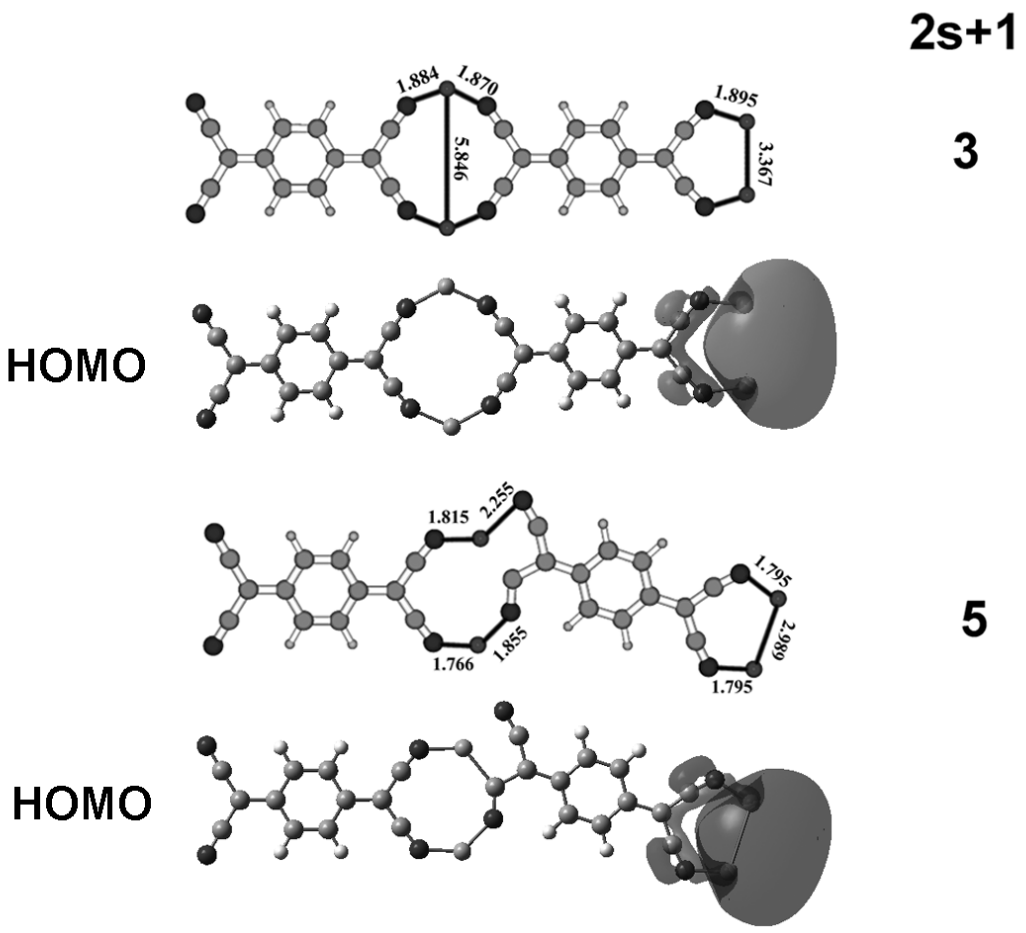

FIG S2. Geometrical structure and frontier molecular orbitals of the $Li_2{\cdot}^{+}TCNQ{\cdot}^{-}$ dimers.

TABLE S2: Basis set effect of β_0 at the MP2 level, for Li atom 6-311++G(3df, 3pd) is employed.

Basis Set for C, N and H	6-311++G 366(100%)	6-311++G(d) 446(122%)	6-311++G(d, p) 458(125%)	6-311++G(2d, 2p) 550(152%)
β_0	19203(100%)	18523(96.5%)	18244(95%)	18460(96.1%)