Photoinduced charge shift in Li^+ doped giant nested fullerenes

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Abstract

Carbon nano-onions (CNOs) and their functionalized analogues find numerous applications in material sciences. At the same time lithium-ion doped fullerenes provide long lifetimes of charge-separated (CS) states and significantly improve air stability in perovskite solar cells. In the present work, we have performed a systematic computational study of structural and electronic properties in a series of double-layered CNOs – $C_{60}@C_{240}$, $C_{60}@C_{540}$, $C_{60}@C_{960}$, $C_{240}@C_{540}$, $C_{240}@C_{960}$, and $C_{540}@C_{960}$, and their Li^+ doped derivatives. Our study is performed using the TD-DFT method for the first time in CNOs. We find that TD-DFT results differ substantially from those of previous studies that used semiempirical methodologies. Moreover, TD-DFT results reproduce experimental results more accurately than semiempirical methods. On the basis of TD-DFT calculations, we show that long-wave absorption by the Li^+ doped species leads to charge shift between the shells. The charge-shift energy depends strongly on the size of the concentric fullerenes. Depending on the structure, two types of charge separated (CS) states are generated (1) with alternating charges like $Li^+@C_{60}^-@C_{240}^+$, and (2) with a positive charge on the outer shell as in $Li@C_{240}@C_{540}^+$. We have suggested a simple expression to roughly estimate the energy difference of denoted excited states in nested fullerenes Me@X@Y $\Delta = IP(Me) - 0.475(\ln N_X + 67N_X^{-\frac{1}{2}} - 0.42)$ and thus to predict the type of the lowest CS state.