Electronic Supplementary Information

Giant Enhancement of Electronic Polarizability and the First Hyperpolarizability of Fluorides-Decorated Graphene \textit{versus} Graphyne and Graphdiyne: Insights from Ab Initio Calculations

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Calculation of nonlinear optical properties

The energy of a system is a function of homogeneous electric field, and its Taylor expansion with respect to the field can be expressed as the following equation\(^\text{[1]}\):

\[
E(F) = E^0 - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l \cdots
\]

where \(E^0\) is the system energy in the absence of an electric field, \(F_i\) is the electric field component along the \(i\) direction. The \(\mu_i\), \(\alpha_{ij}\), and \(\beta_{ijk}\) terms are the dipole moment, polarizability, and the first hyperpolarizability, respectively, of which \(\beta_{ijk}\) is recognized as second-order nonlinear optical (NLO) response coefficient\(^\text{[2]}\). The mean dipole moment \(\langle \mu_0 \rangle\), static polarizability \(\langle \alpha_0 \rangle\), and the static first hyperpolarizability \(\langle \beta_{\text{tot}} \rangle\) are defined as follows:

\[
\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}
\]

\[
\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3
\]

\[
\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}
\]

where \(\beta_i = (1/3) \sum_j (\beta_{ij} + \beta_{ji} + \beta_{jj})\) \(\quad i, j = \{x, y, z\}\)

The linear and nonlinear optical properties of these complexes, e.g., polarizability \(\langle \alpha \rangle\) and first hyperpolarizability \(\langle \beta \rangle\), were calculated by using the long-range corrected CAM-B3LYP functional\(^\text{[3]}\) with the all-electron 6-311++G(2d, 2p) basis sets, because the method has been confirmed to be much reliable for the evaluation of various species\(^\text{[4]}\).
Figure S1. Optimized geometries of (a) $\text{M}_3\text{F}@\text{GE}^{0/\pm}$, (b) $\text{M}_3\text{F}@\text{GY}^{0/\pm}$, and (c) $\text{M}_3\text{F}@\text{GDY}^{0/\pm}$ ($\text{M} = \text{Li, Na, and K}$) complexes. The top and side views are labeled.
Figure S2. Simulated optical absorption spectra of neutral (a) Li$_3$F@GDY, (b) Na$_3$F@GDY, and (c) K$_3$F@GDY complexes using the CAM-B3LYP method. The oscillator strengths of them are inserted.
Figure S3. Simulated optical absorption spectra of the cationic (a) Li$_3$F@GDY$^+$, (b) Na$_3$F@GDY$^+$, and (c) K$_3$F@GDY$^+$ complexes using the CAM-B3LYP method. The oscillator strengths of them are inserted.
References


