Electronic Supplementary Information

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

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Contents:

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:[1]

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

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 μ_i, α_{ij}, and β_{ijk} terms are the dipole moment, polarizability, and the first hyperpolarizability, respectively, of which β_{ijk} is recognized as second-order nonlinear optical (NLO) response coefficient.[2] The mean dipole moment (μ_0), static polarizability (α_0), and the static first hyperpolarizability (β_{tot}) are defined as follows:

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (2)$$

$$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (3)$$

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (4)$$

where $\beta_i = (1/3)\sum_j (\beta_{ijj} + \beta_{jji} + \beta_{jij}) \qquad i, j = \{x, y, z\}$

The linear and nonlinear optical properties of these complexes, e.g., polarizability (α) and first hyperpolarizability (β), were calculated by using the long-range corrected CAM-B3LYP functional[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.[4]

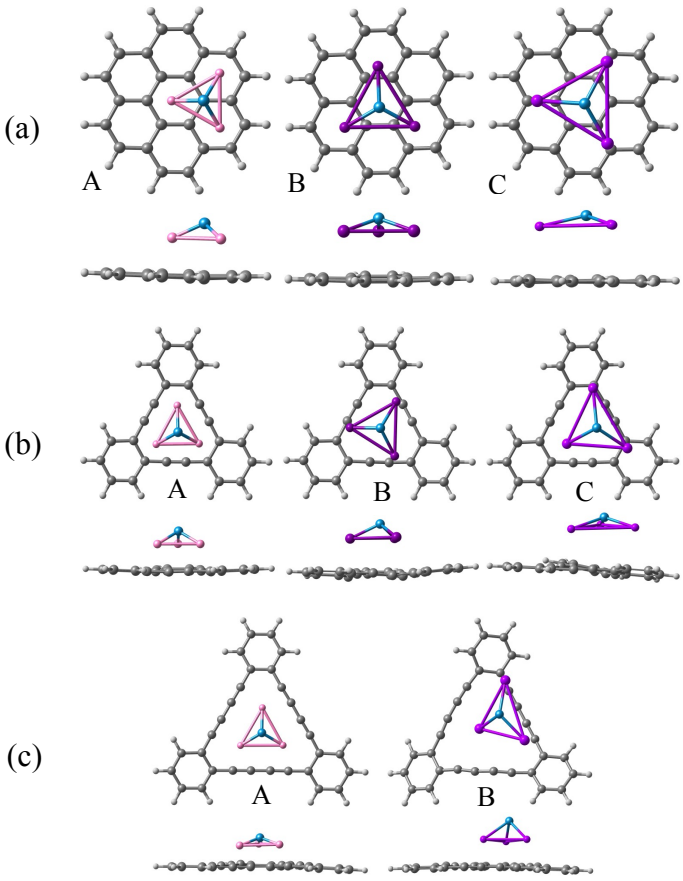

Figure S1. Optimized geometries of (a) $M_3F@GE^{0/+}$, (b) $M_3F@GY^{0/+}$, and (c) $M_3F@GDY^{0/+}$ (M = Li, Na, and K) complexes. The top and side views are labeled.

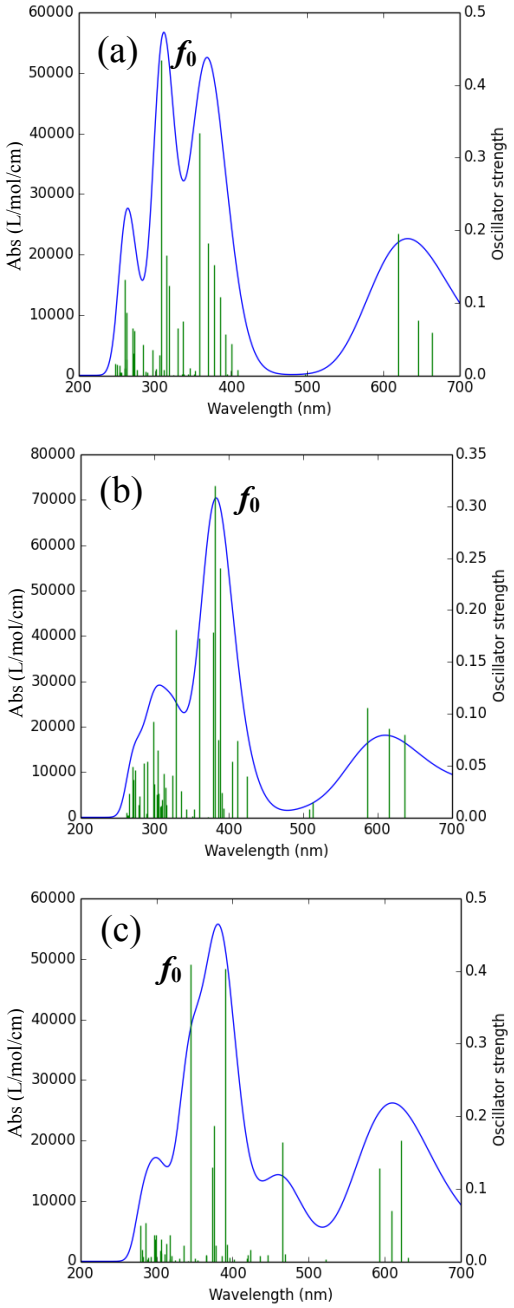

Figure S2. Simulated optical absorption spectra of neutral (a) Li_3F@GDY, (b) Na_3F@GDY, and (c) K_3F@GDY complexes using the CAM-B3LYP method. The oscillator strengths of them are inserted.

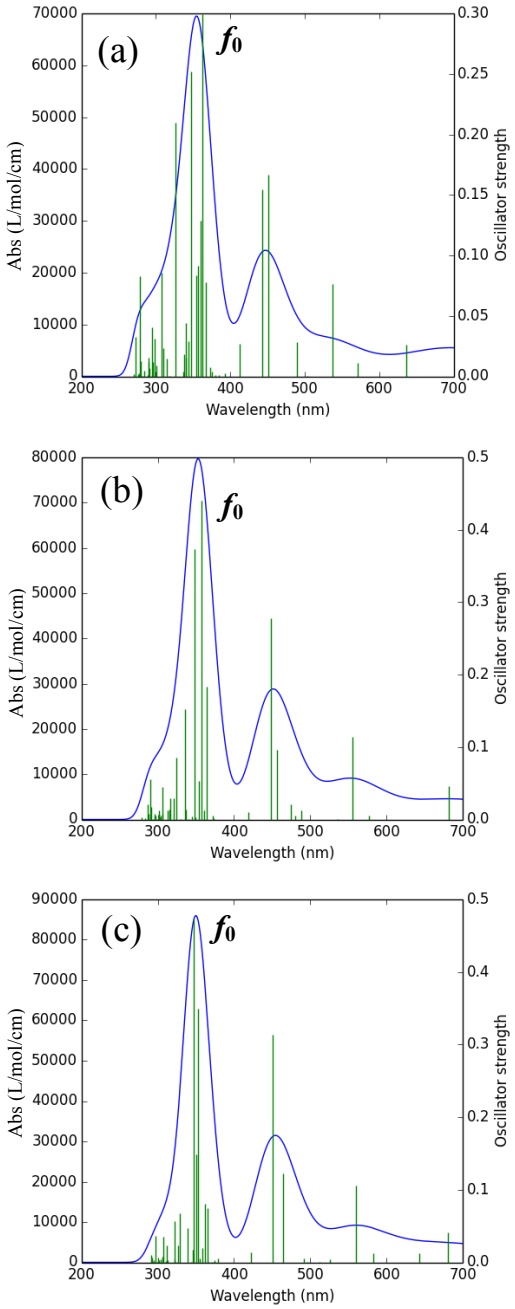

Figure S3. Simulated optical absorption spectra of the cationic (a) $Li_3F@GDY^+$, (b) $Na_3F@GDY^+$, and (c) $K_3F@GDY^+$ complexes using the CAM-B3LYP method. The oscillator strengths of them are inserted.

References

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