Electronic Supplementary Information

Design of Novel Graphdiyne-based Materials with Large Second-Order Nonlinear Optical Properties

Xiaojun Li,a

aThe Key Laboratory for Surface Engineering and Remanufacturing in Shaanxi Province, School of Chemical Engineering, Xi’an University, Xi’an 710065, Shaanxi, P. R. China

Contents:

- Simulated infrared spectrum of the GDY cluster, Fig. S1;
- Electrostatic potential maps of the GDY and AM3@GDY clusters, Fig. S2;
- The crucial transitions of crucial excited energies for the AM3@GDY clusters, Table S1
Fig. S1. Simulated infrared spectrum of the GDY cluster, obtained at the B3LYP/6-31+G(d) level of theory. The scaling factor of 0.953 was applied to correct all calculated vibrational frequencies. The vibrations for the C≡C stretching modes are specially labeled.
Fig. S2. Electrostatic potential maps of the (a) GDY, (b) Li₃@GDY, (c) Na₃@GDY, and (d) K₃@GDY clusters.
Table S1 Mean dipole moment ($\mu_0$, in a.u.), static polarizability ($\alpha_0$, in a.u.), the static first hyperpolarizability ($\beta_{tot}$, in a.u.), transition energy ($\Delta E$, in eV), maximum oscillator strength ($f_0$, in a.u.), the change in dipole moment ($\Delta \mu$, in a.u.), and crucial transitions of crucial excited energies for the AM$_3$@GDY (AM = Li, Na, K) clusters.

<table>
<thead>
<tr>
<th>Clusters</th>
<th>$\mu_0$</th>
<th>$\alpha_0$</th>
<th>$\beta_{tot}$</th>
<th>$\Delta E$</th>
<th>$f_0$</th>
<th>$\Delta \mu$</th>
<th>Crucial Transitions*</th>
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</table>
| Li$_3$@GDY | 0.84    | 671.19     | 9208.88       | 3.32       | 0.178 | 2.186       | $\beta$(H $\rightarrow$ L+16) (35%),  
|           |         |            |               |            |       |             | $\beta$(H $\rightarrow$ L+20) (19%)         |
| Na$_3$@GDY | 1.62    | 786.44     | 69788.24      | 2.75       | 0.232 | 3.444       | $\alpha$(H $\rightarrow$ L+10) (26%),  
|           |         |            |               |            |       |             | $\alpha$(H $\rightarrow$ L+5) (11%)         |
| K$_3$@GDY  | 3.32    | 1065.49    | 161201.31     | I: 2.98    | 0.777 | 10.650      | $\beta$(H-2 $\rightarrow$ L) (14%),  
|           |         |            |               |            |       |             | $\beta$(H-1 $\rightarrow$ L+1) (13%)         |
|           |         |            |               | II: 1.91   | 0.315 | 6.735       | $\alpha$(H $\rightarrow$ L+4) (34%),  
|           |         |            |               |            |       |             | $\beta$(H $\rightarrow$ L+2) (22%)         |

*H = HOMO, L = LUMO.