

## Supporting Information

### **Diels-Alder Reactions of Graphene Oxides: Greatly Enhanced Chemical Reactivity by Oxygen-Containing Groups**

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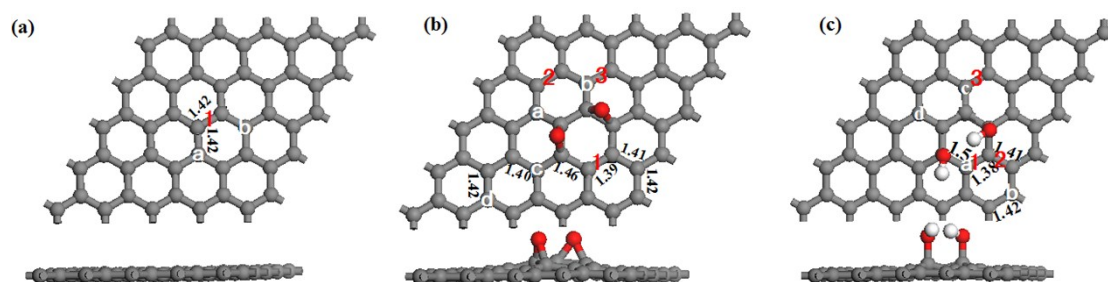
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## 1. Computational model.

When the oxygen groups are introduced to the graphene surface, the carbon atoms at different sites of graphene differ in reactivity for cycloaddition reactions. In order to investigate the site-dependent reaction activity, we constructed two atomic structures of GOs including two neighboring epoxides and 1,4-hydroxyl pair, denoted as **Ia** (Figure S1b) and **IIa** (Figure S1c), respectively. We examined two types of addition sites, (1) at two carbon atoms **ab**, **ac**, **cd**, and others, which are considered as the  $4\pi$  function component of GOs, and (2) at the bonds **1**, **2**, **3** and others, which represent the  $2\pi$  site.

Table S1 presents the relative energies for various addition sites. For the cycloaddition of TCNE, DMBD, and MA to these sites of GOs, the nearest-neighboring sites **ab** or **ac** in **Ia** and bonds **1** in **Ia** and **IIa** with respect to oxygen groups are most reactive. For example, the (4+2) adduct of DMBD at bonds **2** and **3** in **Ia** model are 32.3 and 4.6 kcal/mol higher in energy than that at bond **1**, respectively. Our computations also suggested that the dienophile character of **IIa** is far stronger than its behavior as diene, because the cycloaddition products of the three reactants under our investigation for the former are 25.2-30.4 kcal/mol lower in energy than the latter. Thus, we only select the carbon atoms **ab** and bond **1** around the oxygen groups as the cycloaddition sites in the 10 GO structures.



**Figure S1.** Side and top views of geometric structures of (a) pristine graphene and GOs including (b) two epoxides and (c) two hydroxyl groups (distance in Å). The carbon sites **ab**, **ac**, and **cd** in (a)-(c) represent that graphene functions as the  $4\pi$  component, while the bonds **1** to **3** are  $2\pi$  sites.

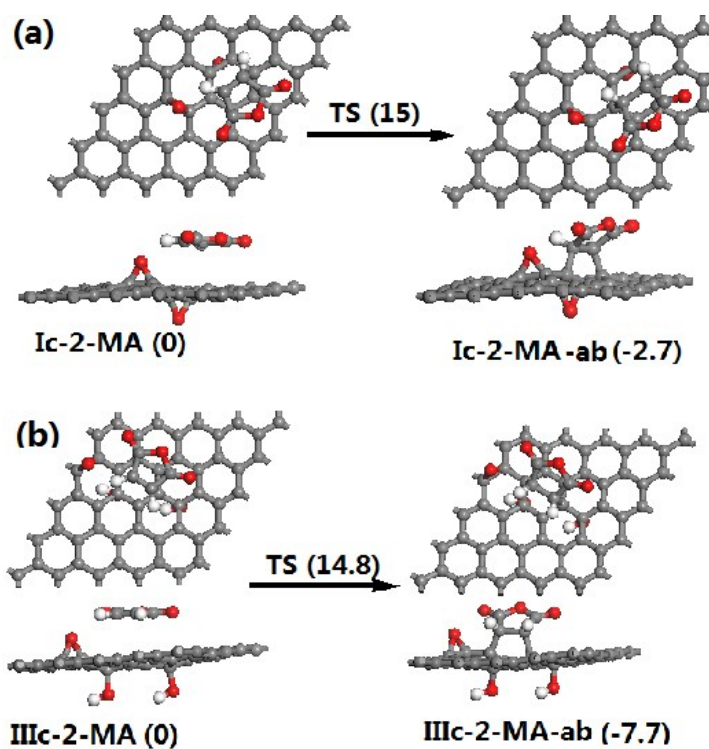
**Table S1.** Relative energies of various cycloaddition products of TCNE, MA and DMBD at different GO sites as shown in **Figure S1b** and **Figure S1c**.

				Ia						IIa	
	<b>1</b> <sup>Δ</sup>	<b>2</b>	<b>3</b>	<b>ab</b> <sup>Δ</sup>	<b>ac</b>	<b>cd</b>	<b>1</b> <sup>Δ</sup>	<b>2</b>	<b>3</b>	<b>ab</b> <sup>Δ</sup>	<b>cd</b>
TCNE				0	*	*				0	*
MA				0	-1	*				0	*
DMBD	0	32.3	4.6				0	20.1	*		

<sup>Δ</sup>The energies for cycloaddition products at all sites are relative to that of the adduct at site **1** or **ab**.

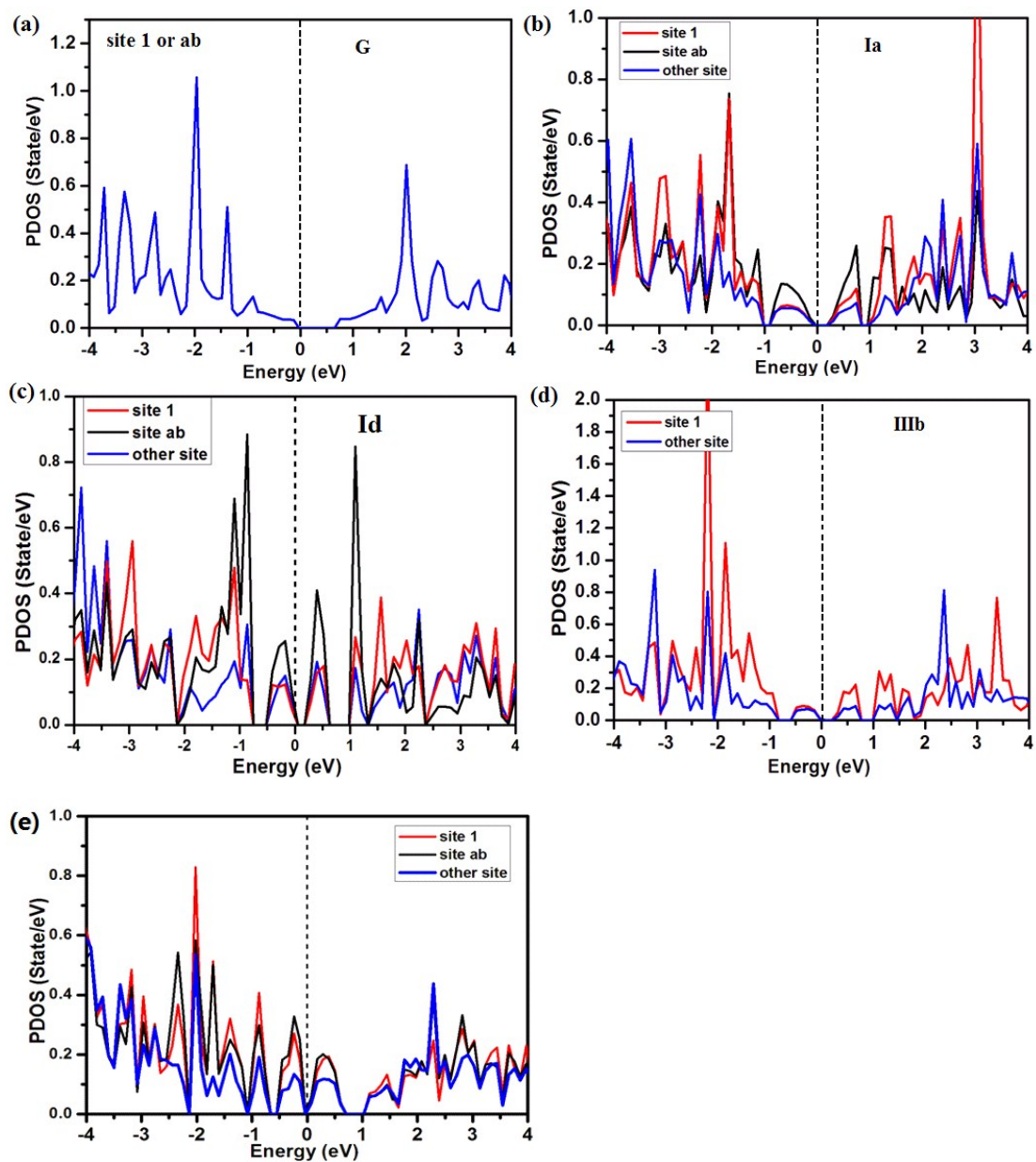
\* No local minimum for cycloaddition product at this site is found.

## 2. Effect of the oxygen functional group at the opposite side on DA reaction.



**Figure S2.** Side and top views of the geometric structures and the relative energies (in kcal/mol) for transformation from non-covalent complex to (2+4) product of MA on GO. TS represents transition state for reaction, and the activation energies are given in the parentheses. All the energies are relative to the non-covalent complex.

### 3. Density of states of GOs.



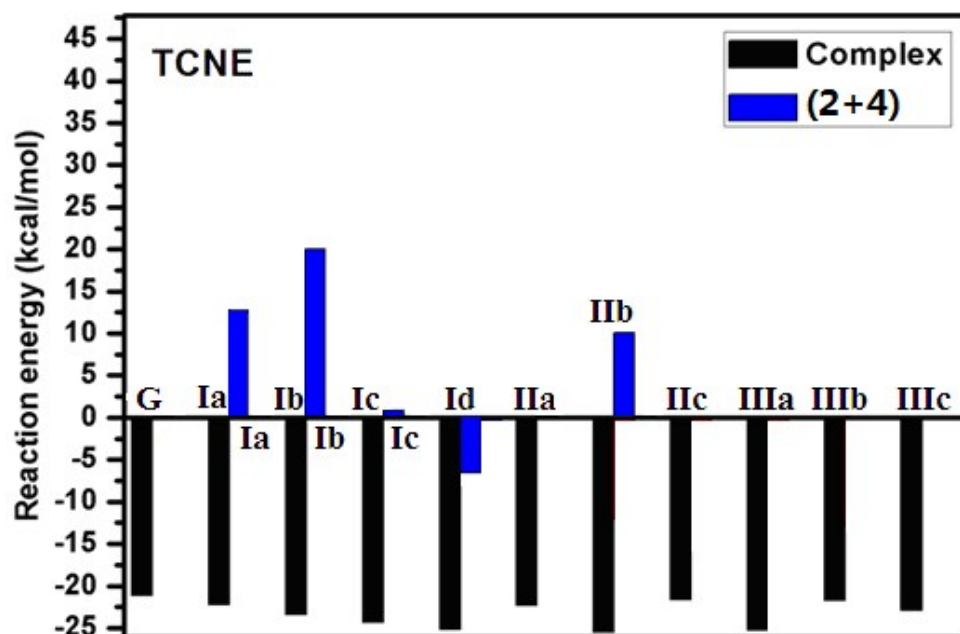
**Figure S3.** The projected density of states (PDOS) of two carbon atoms at different addition sites in (a) graphene, and (b) **Ia**, (c) **Id**, (d) **IIIb**, and (e) **IIb** models, where the sites **1** and **ab** are shown in Figure 1, while the other sites are the two carbon atoms away from the oxygen groups. The Fermi level is set to 0.

#### 4. Charge transfers between organic molecules and GOs in the non-covalent complexes.

**Table S2.** Charge Transfers (in  $e$ ) from the MA, TCNE, and DMBD Molecules to GOs in Their Non-Covalent Complex

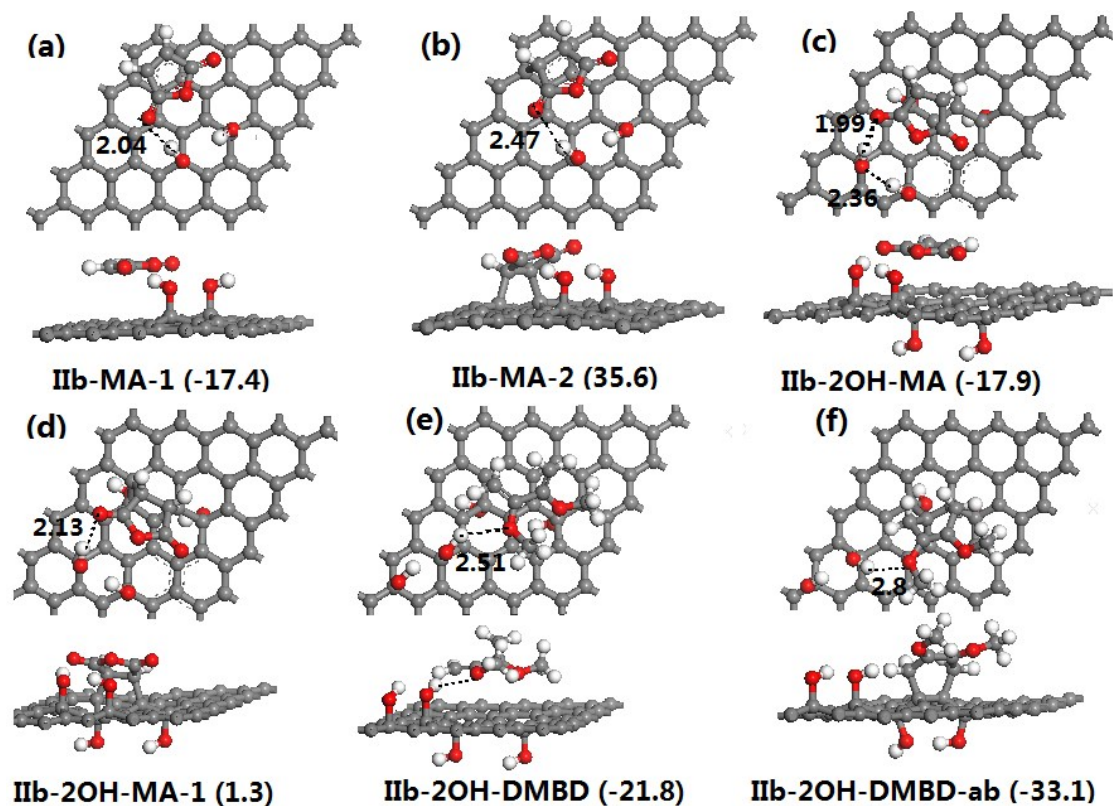
Molecule	G	Ia	Ib	Ic	Id	IIa	IIb	IIc	IIIa	IIIb	IIIc
MA	-0.002	-0.017	-0.046	-0.03	-0.05	-0.015	-0.05	-0.08	-0.07	-0.04	-0.05
TCNE	-0.24	-0.28	-0.28	-0.3	-0.31	-0.23	-0.31	-0.32	-0.31	-0.23	-0.26
DMBD	0.06	0.076	0.08	0.09	0.09	0.09	0.124	0.15	0.08	0.09	0.13

#### 5. Interaction energies between TCNE with GOs



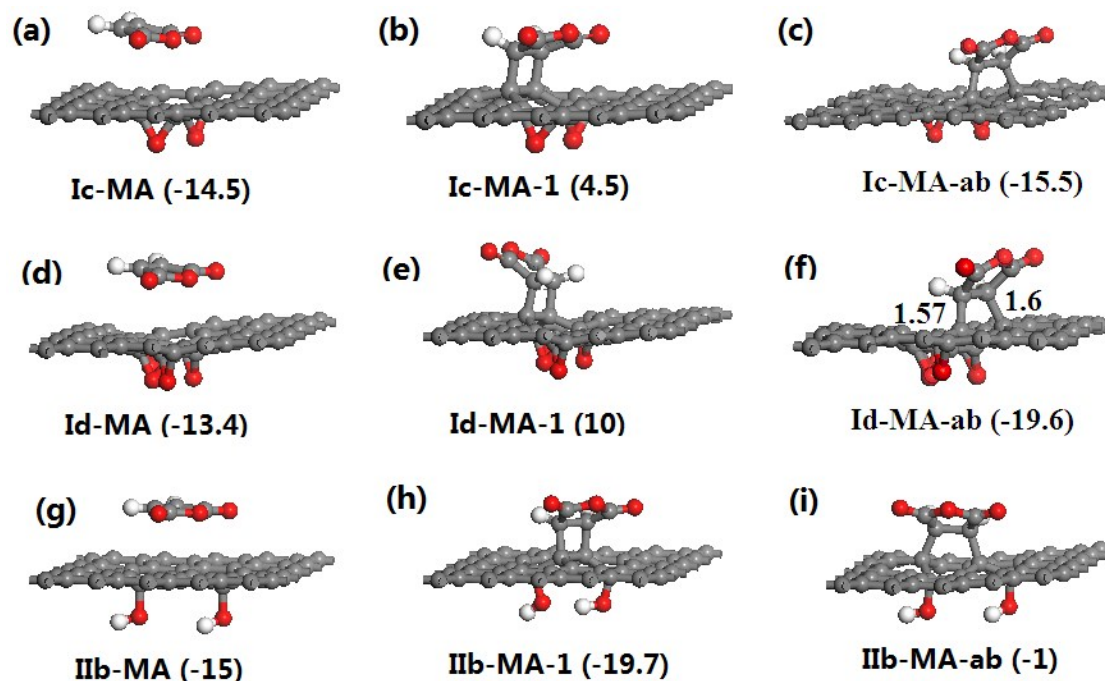
**Figure S4.** Reaction energies for the non-covalent complexation and cycloaddition of TCNE with graphene and different GO models. The reaction energies are relative to the separated addends and the graphene/GO substrate.

## 6. Effect of hydrogen bonds on the DA reactivity.



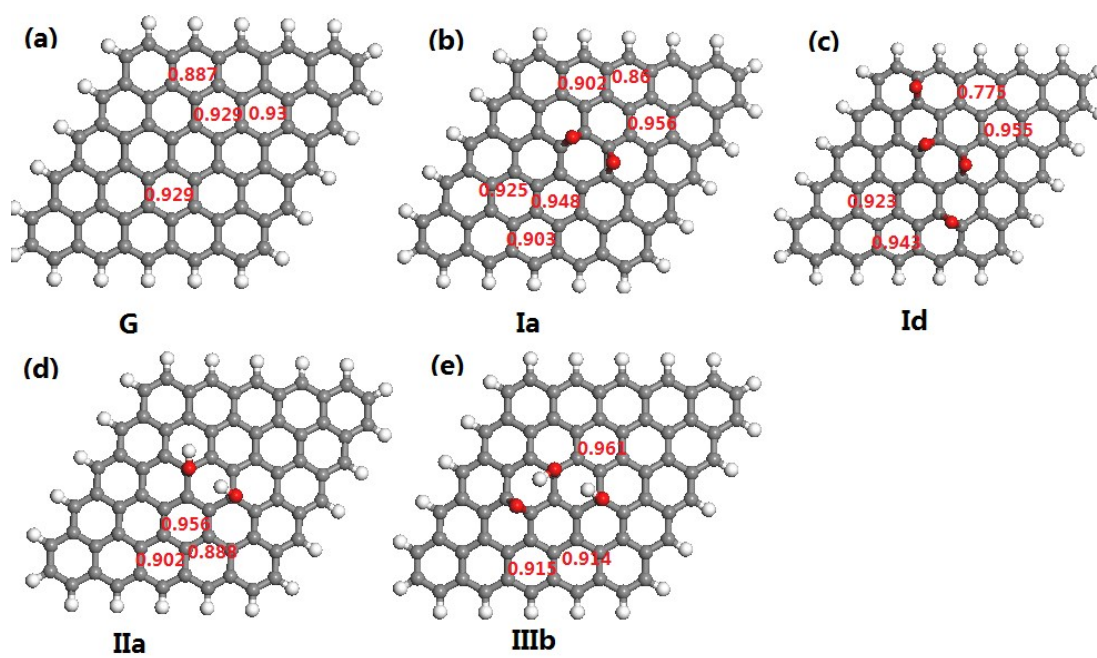
**Figure S5.** The geometric structures (distance in Å) and reaction energies (in kcal/mol) for the non-covalent interaction and cycloaddition reaction between MA/DMBD molecules and GO. In these models, the hydrogen bonds between the hydroxyl group and organic molecules are formed.

7. Comparison in reaction energy between (2+2) and (2+4) processes.



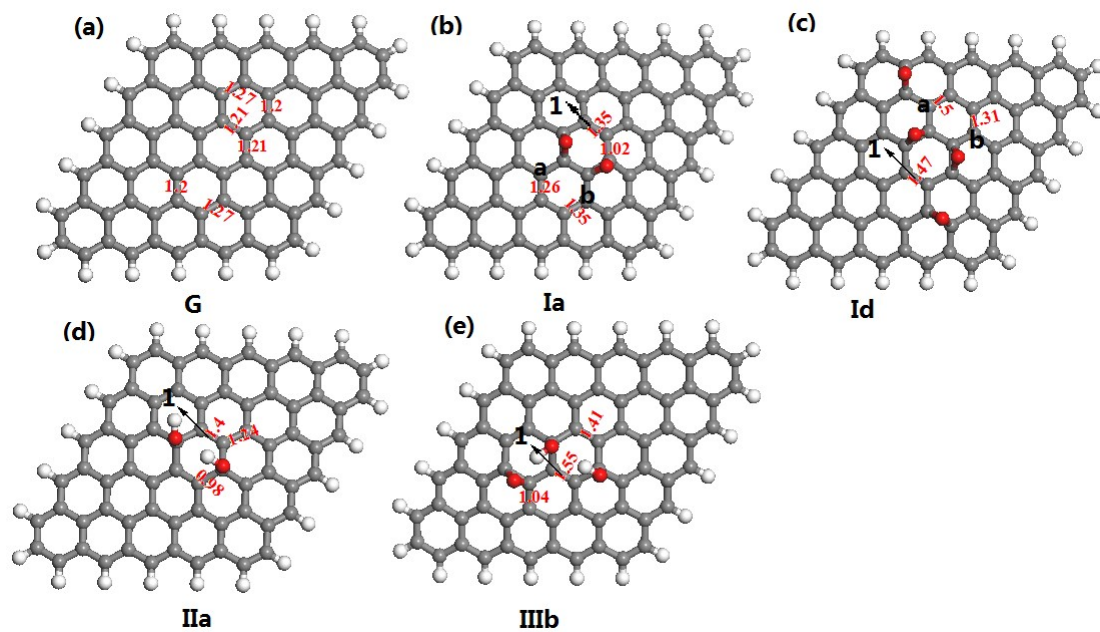
**Figure S6.** The key geometrical parameters (distance in Å) and reaction energies (in kcal/mol) for the non-covalent interaction and cycloaddition reactions of MA with different GOs substrate. The X-MA-1 and X-MA-ab represent the (2+2) and (2+4) adducts between MA and substrate X at sites **1** and **ab**, respectively.

## 8. HOMA and Mayer bond order



**Figure S7.** HOMA of the selected six-membered C rings of graphene and GOs.





**Figure S8.** The geometric structures of graphene and GO models based on the  $C_{66}H_{34}$  cluster and the Mayer bond orders of selected CC bonds.