Edge functionalization of graphyne nanoribbons for lithium-ion battery electrodes: A computational study

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Solvation parameters

The required PCM inputs for custom solvents are the solvent radius (r), static dielectric constant (ε_s) and dynamic dielectric constant (ε_d), also known as optic dielectric constant. Due to the lack of empirical data for ε_d and r of the exact mixture used, the ε_d has been approximated[1] to be the square of the mixture's refractive index (n_m) and determined through a series of equations (Eq. 1-4).[2]

$$v = \frac{M}{\rho} \tag{1}$$

$$\varphi = \frac{x_i \times v_i}{\sum x_t \times v_t} \tag{2}$$

$$\frac{n_m^2 - 1}{n_m^2 + 2} = \varphi_1 \times \frac{n_1^2 - 1}{n_1^2 + 2} + \varphi_2 \times \frac{n_2^2 - 1}{n_2^2 + 2} \tag{3}$$

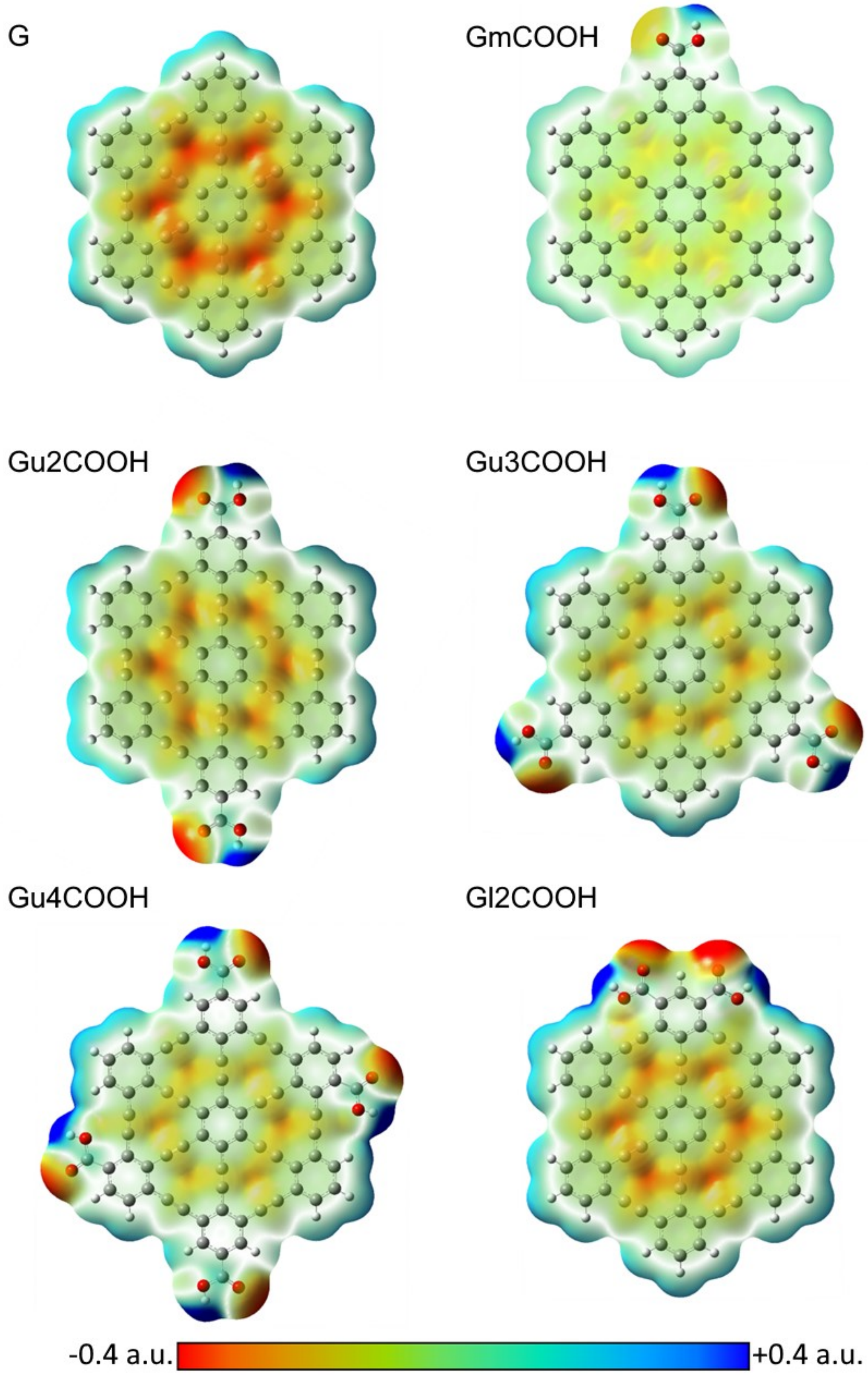
$$\varepsilon_d = n_m^2 \tag{4}$$

To start, the molar volumes (v) were calculated using the molar mass (M) and densities (ρ) of EC and DMC.[3] Then, the volume fractions (φ) were determined using the molar volumes and the 8:2 EC/DMC molar fractions of the mixture. The mixture's refractive index was calculated with the volume fractions and the refractive indices of each pure solvent (n_1, n_2)[4,5] and finally the dynamic dielectric constant used in the PCM was determined.

Lastly, the solvent radius parameter was determined from the mixture molecular mass (m), the packing density (Δ_{pd}), and density (ρ).[3] The packing density was set as 0.5 because the experimental value for the crystal structure of this exact mixture is not known.

$$r^3 = \frac{3 \times m \times \Delta_{pd}}{4 \times \pi \times \rho} \times (10^{24}) \tag{5}$$

Electrostatic potential maps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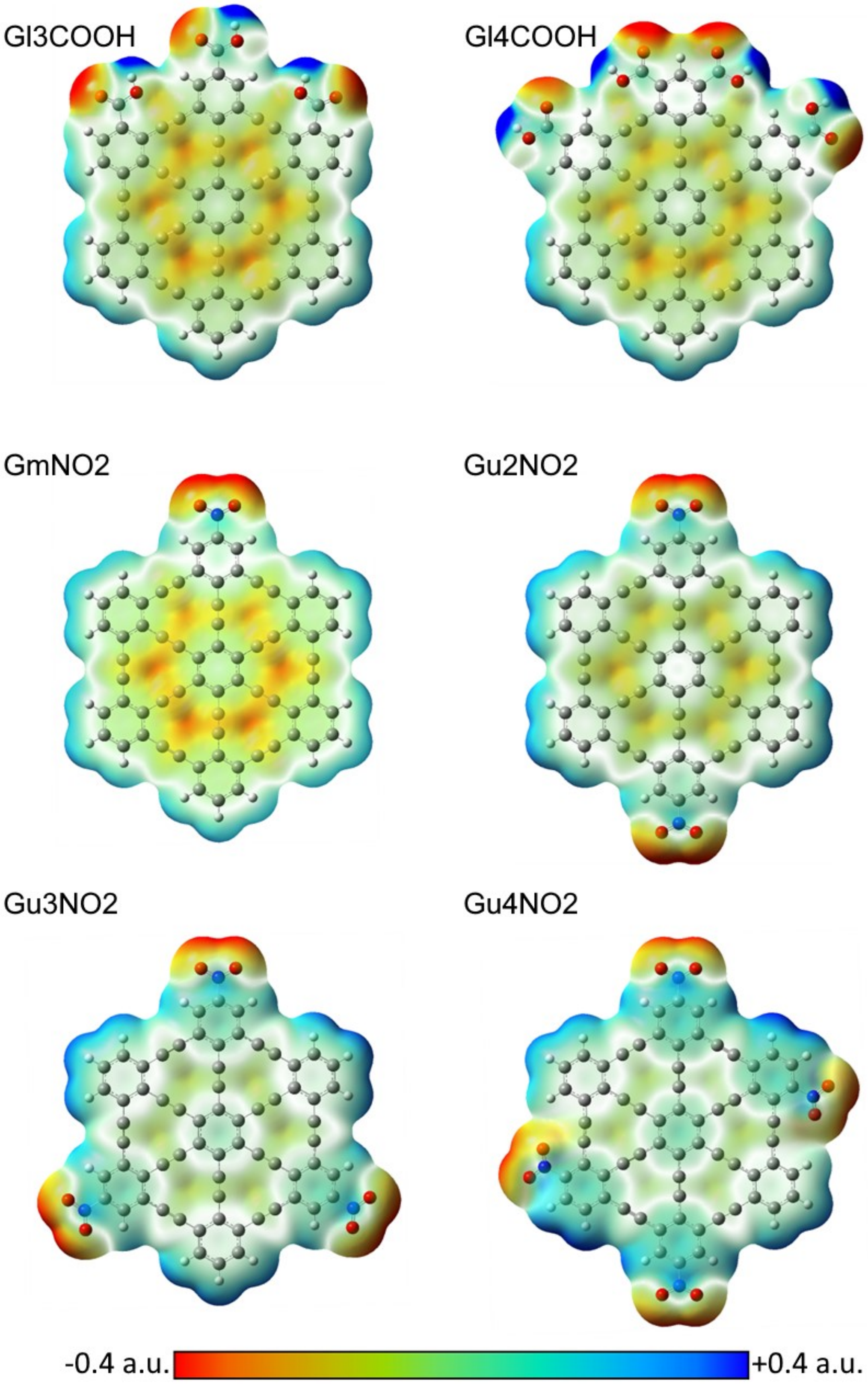
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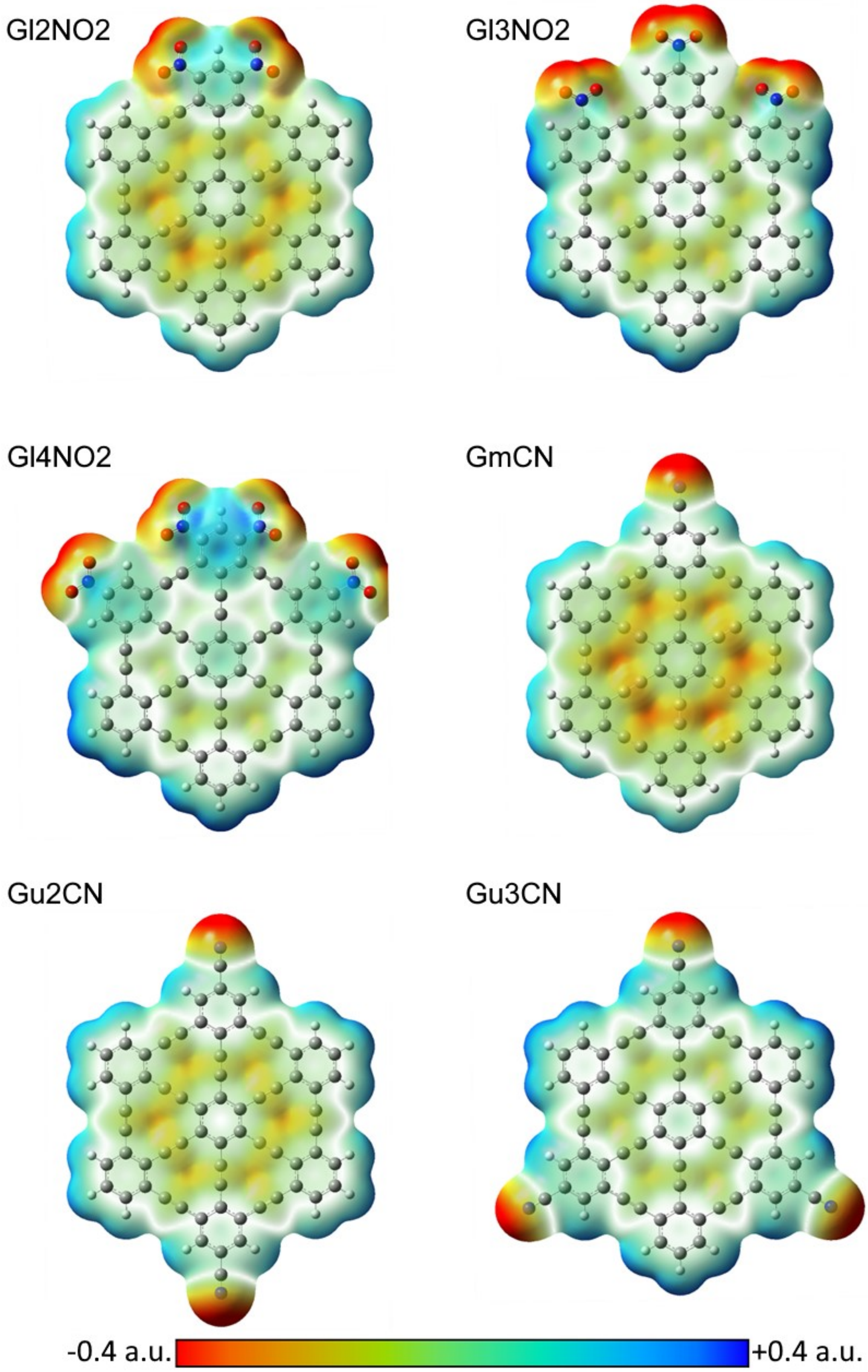
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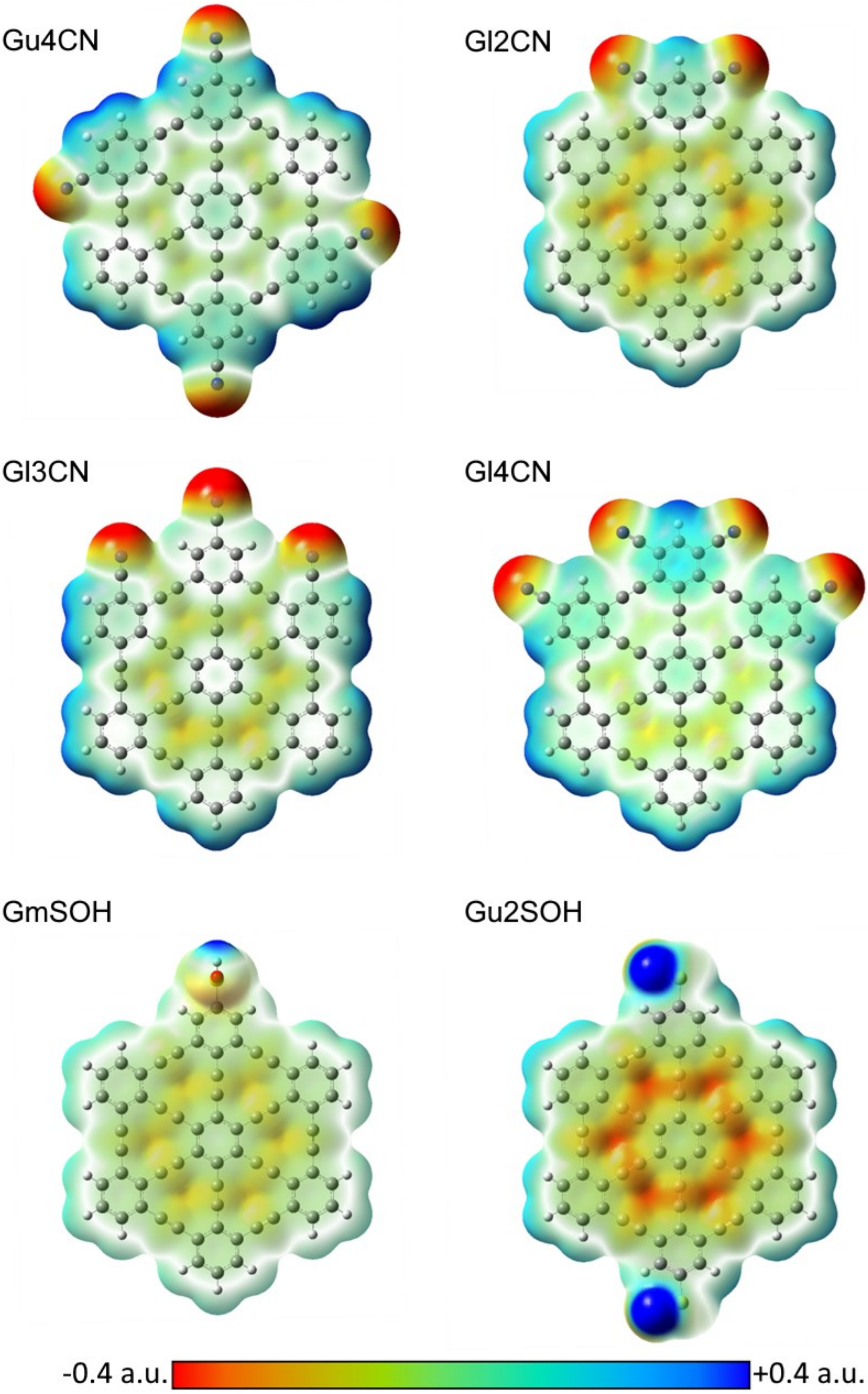
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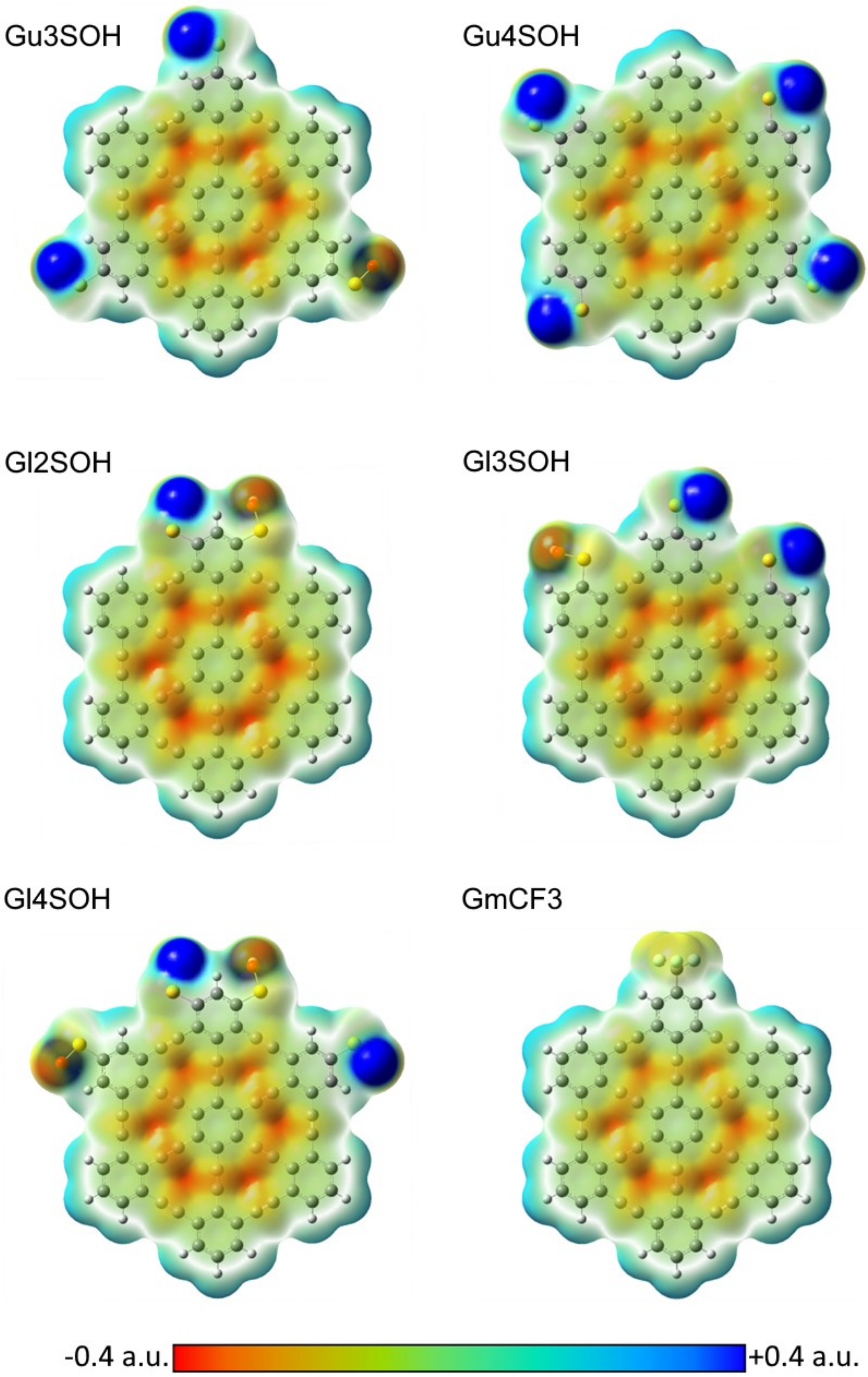
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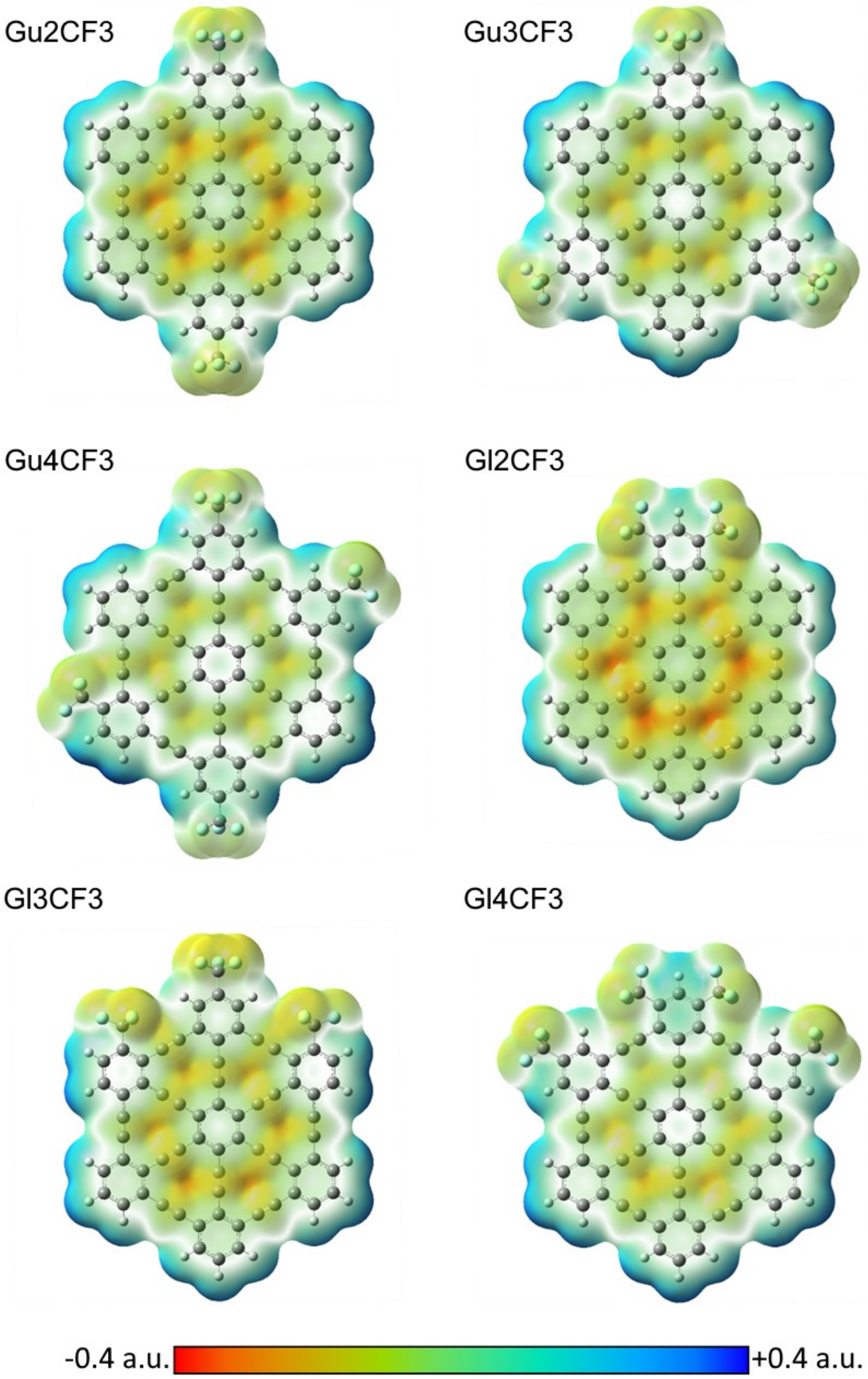
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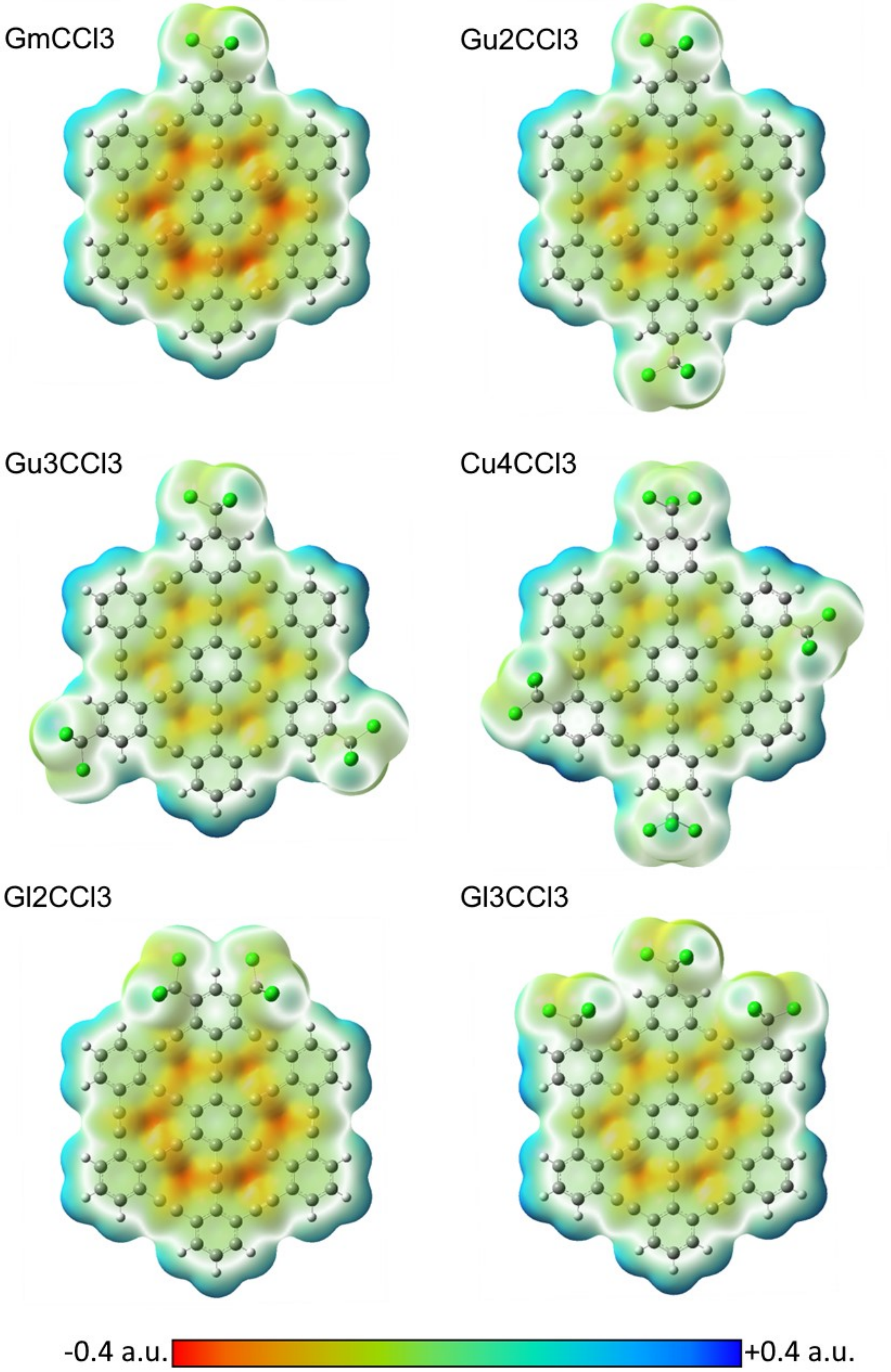
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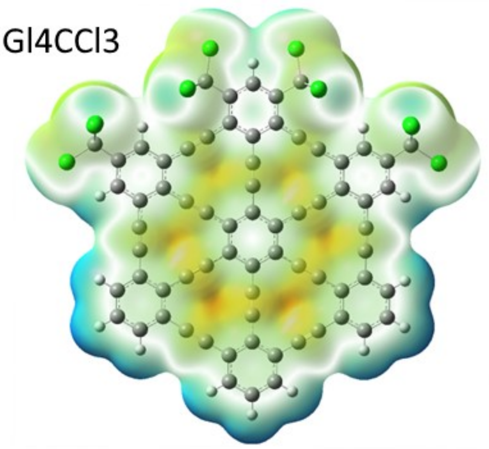

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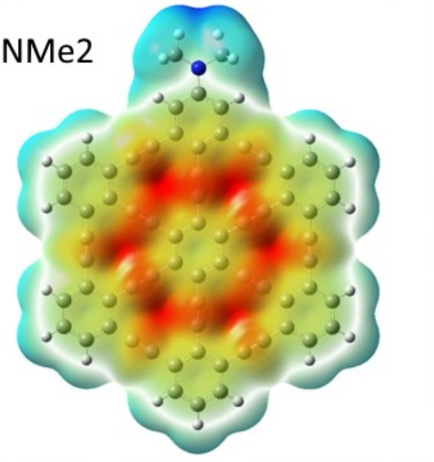

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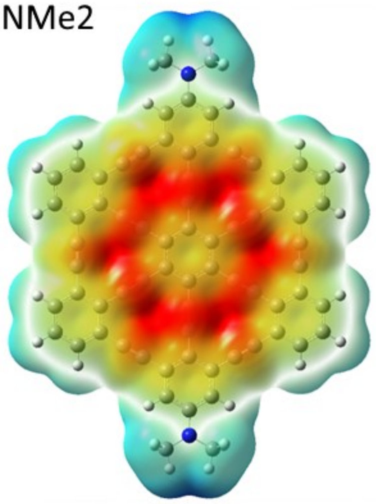

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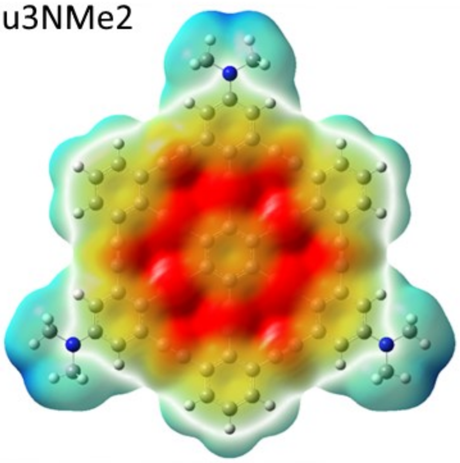

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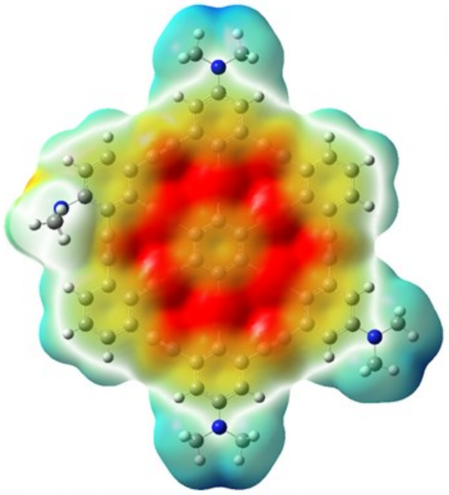

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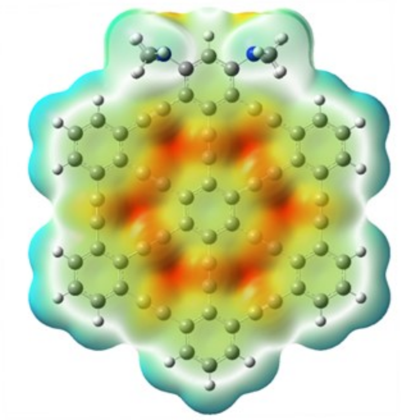

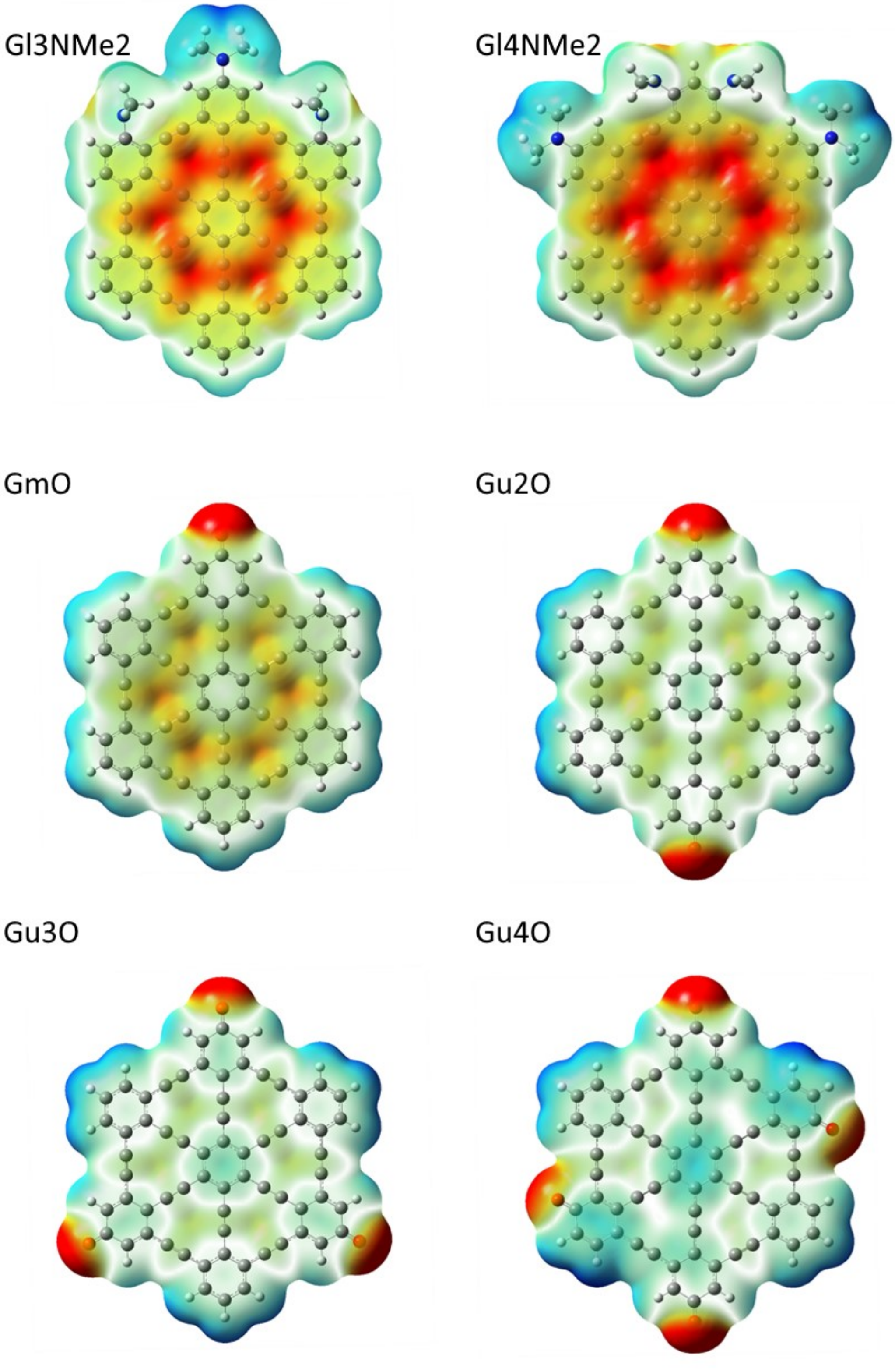
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Gl4NMe2
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Gu2O
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-0.4 a.u.
+0.4 a.u.

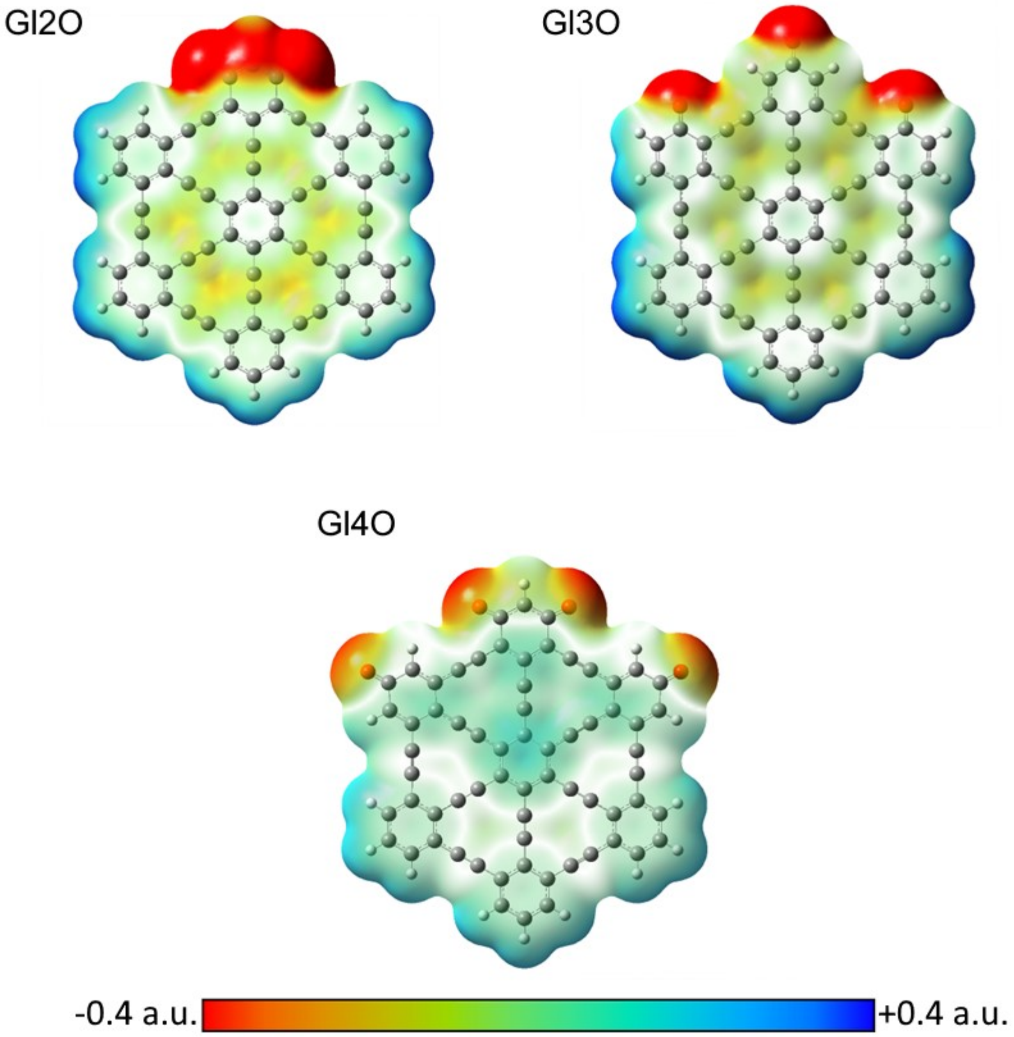

Fig. 1: Colored electrostatic potential maps on an isodensity surface of 0.001 a.u. for all graphyne compounds.

Li^+ binding energies

Total geometry optimizations of lithium ions adsorbed on functionalized graphynes were carried out using the MN15/6-31+G(d,p) level of DFT. The corresponding ion binding energies were evaluated according to the following equation:

$$\Delta E_{bind} = E_{graph/Li} - E_{graph} - E_{Li} \qquad (6)$$

where $E_{graph/Li}$ denotes the energy of the graphyne with the lithium adsorbed on its surface, E_{graph} represents the energy of functionalized graphyne, and E_{Li} corresponds to the energy of the isolated lithium ion. No correction factors were applied to the basis set superposition error (BSSE), as this effect was anticipated to be negligeable across all the interacting systems. The calculated ΔE_{bind} values for all studied cases are presented in Figure 2 and compared to the pristine reference line.

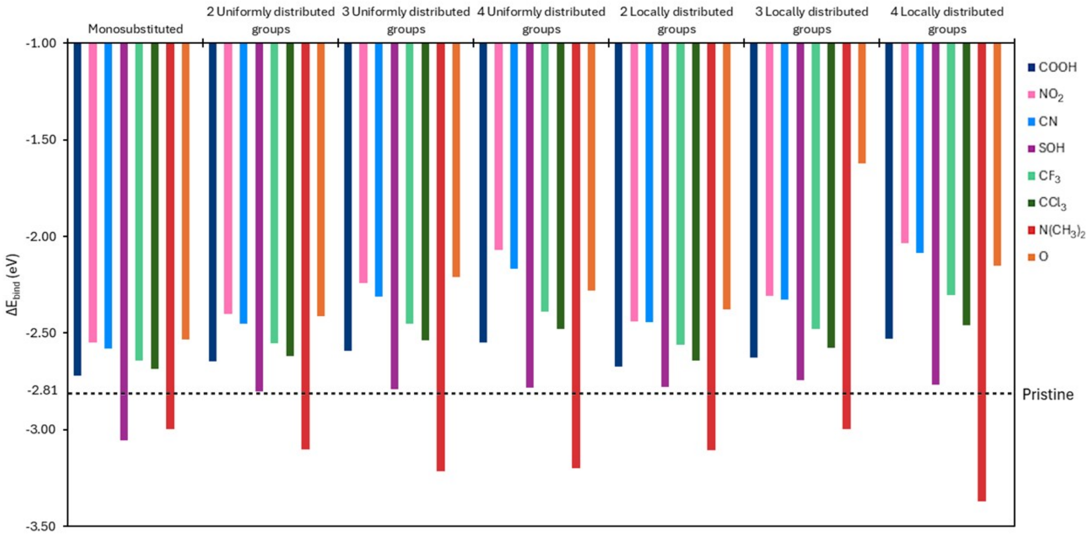

Fig. 2: Binding energies in eV for the graphyne compounds grouped by substituent configuration. The baseline for comparison is the pristine line crossing the bars with the value of -2.81 V.

References

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2. R. Mehra, *J. Chem. Sci.*, 2003, **115,** 147-154.
3. R. Naejus, D. Lemordant, R. Coudert and P. Willmann, *J. Chem. Thermodyn.*, 1997, **29,** 1503-1515.
4. W. J. Peppel, *Ind. Eng. Chem.*, 1958, **50,** 767-770.
5. M. Moosavi, A. Motahari, A. Vahid, V. Akbar, A. A. Rostami and A. Omrani, *J. Chem. Eng. Data*, 2016, **61,** 1981-1991.