Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Can Inorganic Salts Tune Electronic Properties of Graphene Quantum Dots?

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Table S1. Energies and localization (in parentheses) of HOMO and LUMO in the LiCl@GQD complexes. See Table 1 in the main text for the definition of configurations. Energy of molecular orbitals is provided in electronvolts for simpler comparison. Global MO shows a global consecutive number of the corresponding molecular orbital in the considered complex. Designations in parentheses indicate where the corresponding MO is preferentially localized (on GQD or on the ions)

Global MO	Pristine graphene	Energy, eV			
		(a)	(b)	(c)	(d)
LUMO+15	—	-0.1831 [ions]	—	—	—
LUMO+5	—	—	-1.9045 [ions]	—	—
LUMO+4	—	—	—	-1.8784 [ions]	—
LUMO+2	—	—	—	—	-2.0031 [ions]
LUMO	-2.5629 [gr.]	-2.8980 [gr.]	-2.8161 [gr.]	-2.7546 [gr.]	-2.7092 [gr.]
HOMO	-4.4559 [gr.]	-4.7876 [gr.]	-4.7092 [gr.]	-4.6480 [gr.]	-4.6023 [gr.]

Table S2. Energies and localization (in parentheses) of HOMO and LUMO in the NaCl@graphene complexes. See Table 1 in the main text for the definition of configurations. Energy of molecular orbitals is provided in electronvolts for simpler comparison. Global MO shows a global consecutive number of the corresponding molecular orbital in the considered complex. Designations in parentheses indicate where the corresponding MO is preferentially localized (on the graphene sheet or on the ions)

Global MO	Pristine graphene	Energy, eV			
		(a)	(b)	(c)	(d)
LUMO+15	—	-0.0923 [ions]	—	—	—
LUMO+9	—	—	-1.2635 [ions]	—	—
LUMO+5	—	—	—	-1.5709 [ions]	-1.7236 [ions]
LUMO	-2.5629 [gr.]	-2.9840 [gr.]	-2.8853 [gr.]	-2.8066 [gr.]	-2.7486 [gr.]
HOMO	-4.4559 [gr.]	—	—	—	—
HOMO-2	—	—	-4.7781 [gr.]	-4.6999 [gr.]	-4.6421 [gr.]
HOMO-3	—	-4.8709 [gr.]	—	—	—

Table S3. Energies and localization (in parentheses) of HOMO and LUMO in the $MgCl_2$@graphene complexes. See Table 1 in the main text for the definition of configurations. Energy of molecular orbitals is provided in electronvolts for simpler comparison. Global MO shows a global consecutive number of the corresponding molecular orbital in the considered complex. Designations in parentheses indicate where the corresponding MO is preferentially localized (on the graphene sheet or on the ions)

Global MO	Pristine graphene	Energy, eV			
		(a)	(b)	(c)	(d)
LUMO+4	—	-1.8436 [ions]	—	—	—
LUMO+2	—	—	-2.5174 [ions]	—	—
LUMO+1	—	—	—	-2.5889 [gr.]	-2.5821 [gr.]
LUMO	-2.5629 [gr.]	-2.6763 [gr.]	-2.5960 [gr.]	-2.6689 [ions]	-2.7462 [ions]
HOMO	-4.4559 [gr.]	-4.5182 [gr.]	-4.4809 [gr.]	-4.4785 [gr.]	-4.4736 [gr.]

Table S4. Energies (in eV) of HOMO and LUMO in the isolated ionic clusters. Note that we do not study HOMO of inorganic ions in the manuscript, since they lie very low at the energy scale. In turn, LUMO energy levels are reasonable close to the conduction band of GQD

#	Cl^- and Li^+	Cl^- and Na^+	$2Cl^-$ and Mg^{+2}
HOMO	-5.7027	-4.6611	-7.4807
LUMO	-2.1767	-1.9143	-2.5108

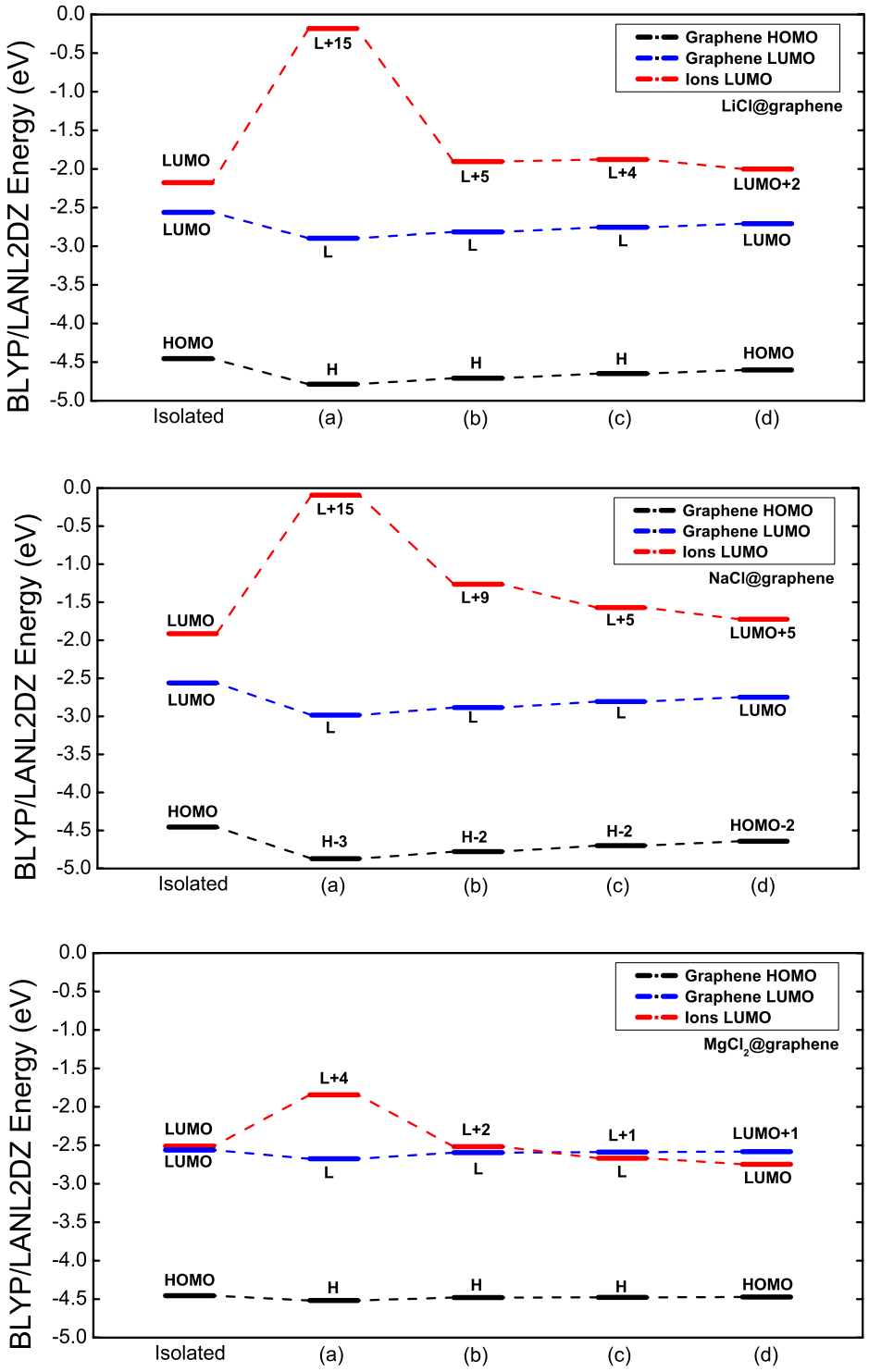

Figure S1. Energy levels of molecular orbitals localized on graphene and ion clusters in the simulated systems. Note that orbitals are designated by their number in the complex. That is, "L+15" means LUMO of the ions, whereas being LUMO+15 in the LiCl@graphene system. In turn, LUMO of graphene coincides with LUMO in the LiCl@graphene system.

Table S5. Binding energies keeping ionic clusters (LiCl, NaCl, $MgCl_2$) and graphene together

	LiCl@graphene		NaCl@graphene		$MgCl_2$@graphene	
	E [kcal mol^{-1}]	BSSE [kcal mol^{-1}]	E [kcal mol^{-1}]	BSSE [kcal mol^{-1}]	E [kcal mol^{-1}]	BSSE [kcal mol^{-1}]
(a)	-159.1	21.8	-133.2	19.6	-461.2	45.4
(b)	-154.2	18.2	-131.2	16.6	-525.7	31.8
(c)	-153.4	17.6	-130.3	15.7	-527.3	29.7
(d)	-152.8	17.6	-129.7	15.6	-527.3	29.7

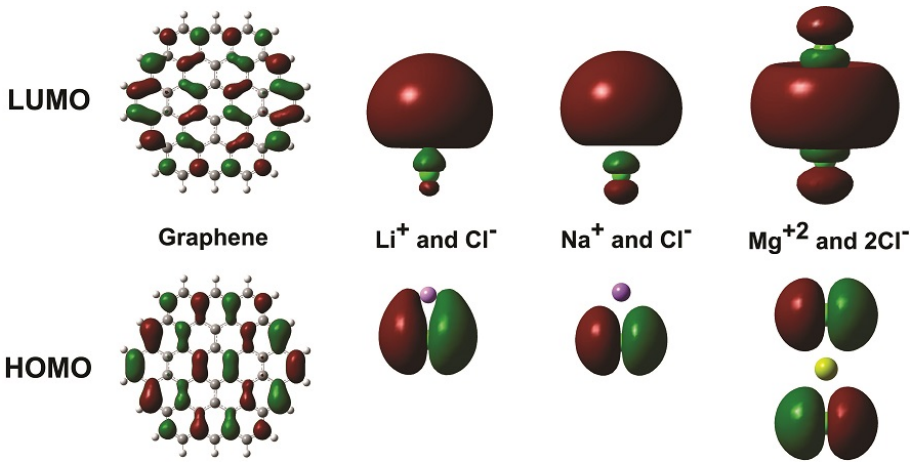

Figure S2. Localization of HOMO and LUMO of GQD in the investigated setups (see Table 1).

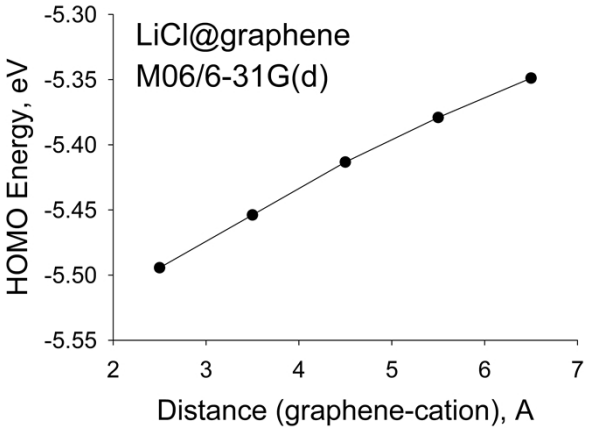

Figure S3. HOMO energy as a function of distance between LiCl and graphene (see Table 1). The simulation has been conducted using the M06 hybrid density functional (*Y. Zhao and D. G. Truhlar, "Comparative DFT study of van der Waals complexes: Rare-gas dimers, alkaline-earth dimers, zinc dimer, and zinc-rare-gas dimers", J. Phys. Chem., 110 (2006) 5121-5129*) and 6-31G(d) basis set.

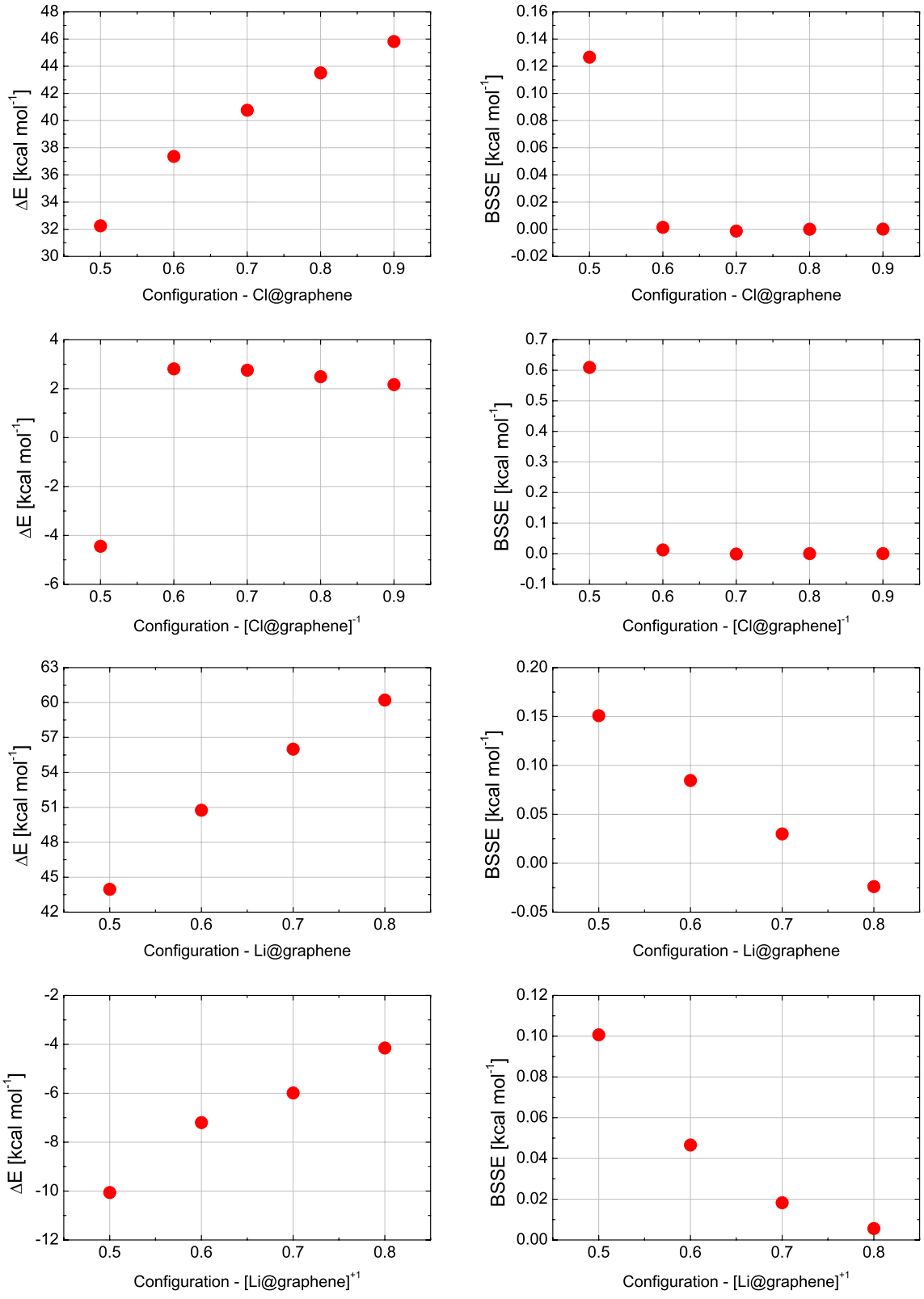

Figure S4. Binding energy (left) and base set superposition error (BSSE, right) to: a) GQD – Cl neutral atom; b) GQD – Cl^{-1} ion; c) GQD – Li neutral atom and d) GQD – Li^{+} ion.