SUPPLEMENTARY INFORMATION

On the interaction of toxic Heavy Metals (Cd, Hg, Pb) with graphene quantum dots and infinite graphene

Ivan Shtepliuk[1], Nuala M. Caffrey[1,2], Tihomir Iakimov[1], Volodymyr Khranovskyy[1], Igor A. Abrikosov[1,3] and Rositsa Yakimova[1]

[1]*Department of Physics, Chemistry and Biology, Linköping University, SE-58183, Linköping, Sweden*

[2]*School of Physics and CRANN, Trinity College, Dublin 2, Ireland*

[3]*Materials Modeling and Development Laboratory, National University of Science and Technology "MISIS", Moscow, Russia*

Corresponding author: Ivan Shtepliuk, e-mail: ivan.shtepliuk@liu.se

Table S1. Structures of zigzag edged and armchair-edged GQDs. "ZZ" and "AC" denotes a kind of edge, while the following integer corresponds to the number of hexagonal rings in GQD.

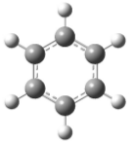
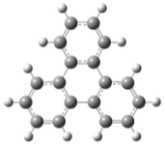
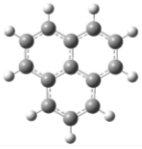
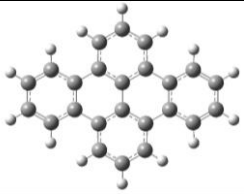
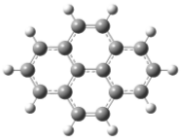
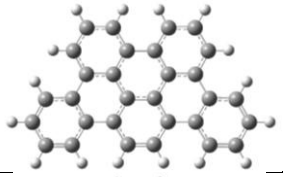
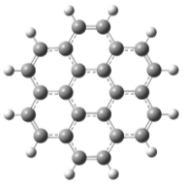
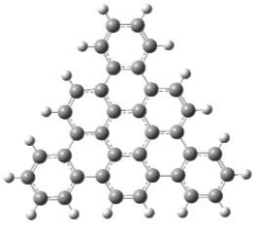
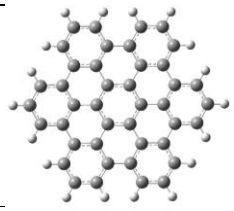
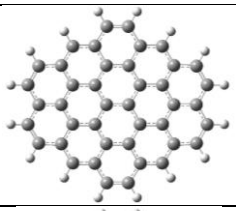
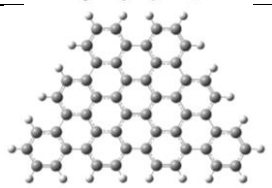
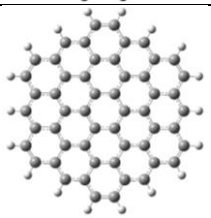
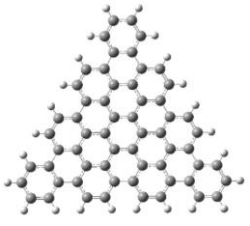
Zigzag Graphene Quantum Dots	**Structure**	**Armchair Graphene Quantum Dots**	**Structure**
Benzene C_6H_6 ZZ-1		Triphenylene $C_{18}H_{12}$ AC-4	
$C_{13}H_9$ ZZ-3		$C_{23}H_{14}$ AC-6	
Pyrene $C_{16}H_{10}$ ZZ-4		Tribenzo (b,n,pqr)perylene $C_{30}H_{16}$ AC-8	
Coronene $C_{24}H_{12}$ ZZ-7		Tribenzo(A,D,G)Coronene $C_{36}H_{18}$ AC-10	
Ovalene $C_{32}H_{14}$ ZZ-10		HexabenzoCoronene $C_{48}H_{24}$ AC-13	
Circumpyrene $C_{42}H_{16}$ ZZ-14		$C_{54}H_{22}$ AC-17	
Circumcoronene $C_{54}H_{18}$ ZZ-22		$C_{60}H_{26}$ AC-19	

Table S2. Structures of zigzag edged and armchair-edged GQDs interacting with neutral heavy metal species. "ZZ" and "AC" denotes a kind of edge, while the following integer corresponds to the number of hexagonal rings in GQD.

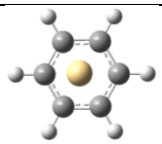
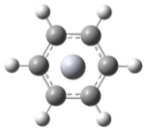
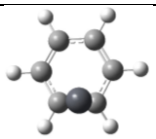
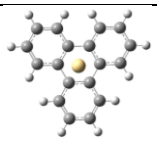
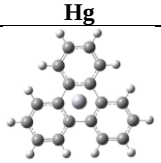
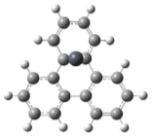
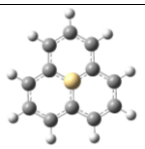
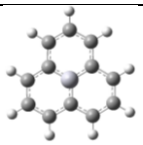
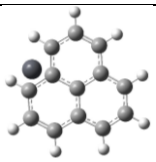
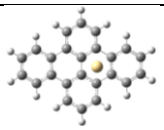
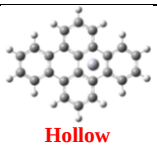
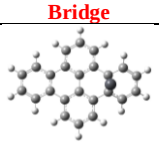
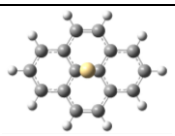
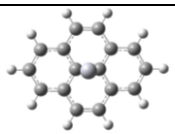
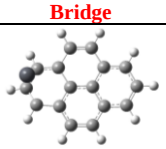
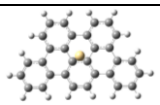
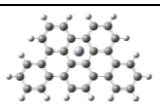
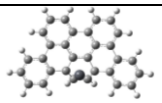
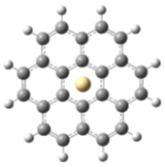
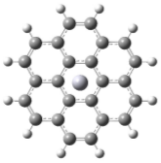
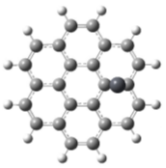
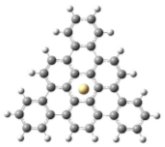
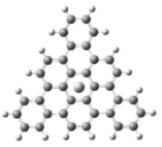
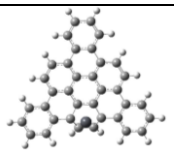
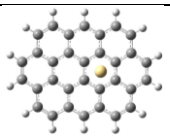
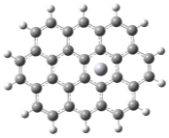
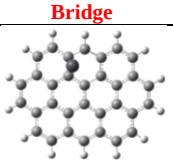
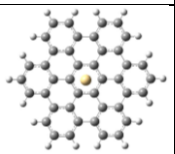
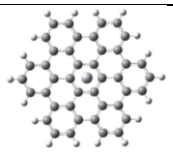
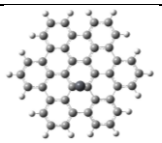
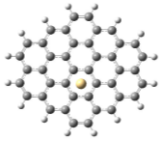
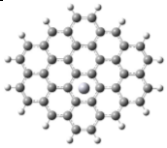
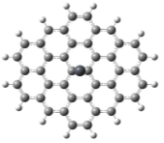
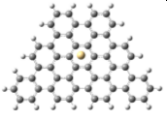
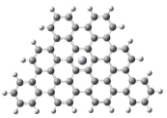
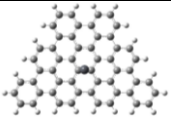
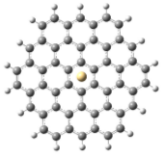
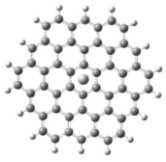
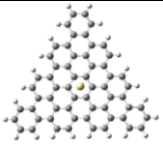
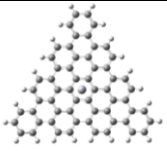
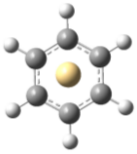
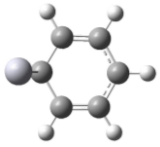
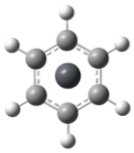
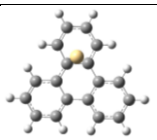
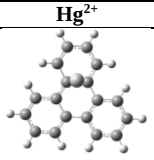
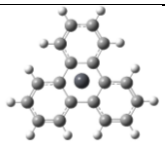
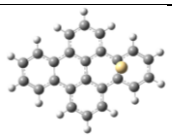
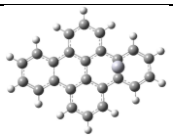
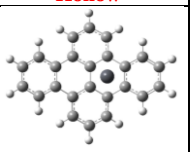
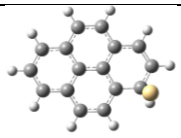
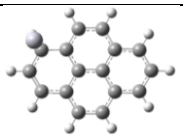
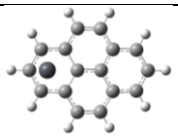
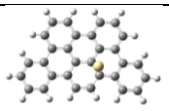
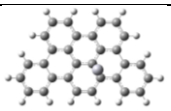
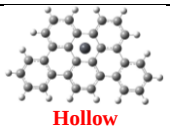
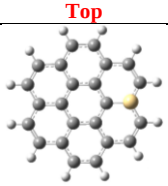
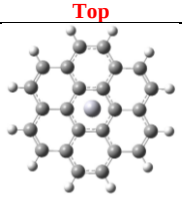
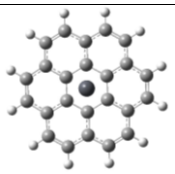
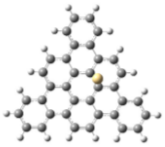
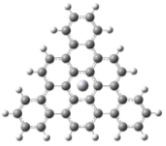
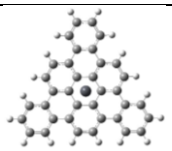
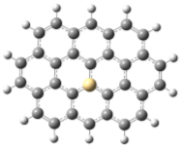
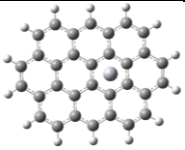
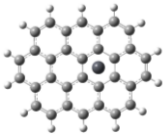
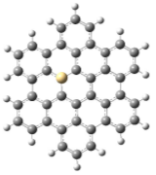
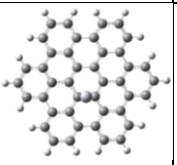
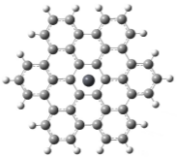
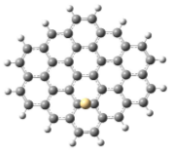
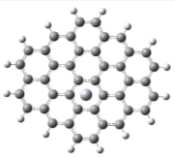
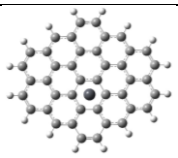
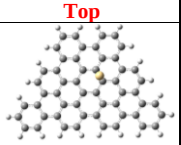
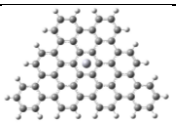
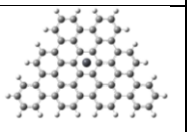
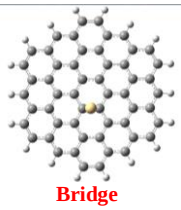
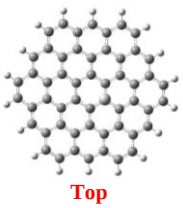
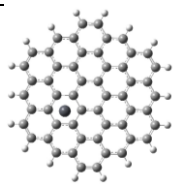
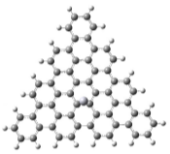
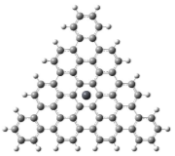
ZZ-GQD	Structure			AC-GQD	Structure		
	Cd	Hg	Pb		Cd	Hg	Pb
ZZ-1	 Hollow	 Hollow	 Bridge	AC-4	 Hollow	 Hollow	 Bridge
ZZ-3	 Top	 Top	 Bridge	AC-6	 Hollow	 Hollow	 Bridge
ZZ-4	 Bridge	 Bridge	 Bridge	AC-8	 Bridge	 Hollow	 Bridge
ZZ-7	 Hollow	 Hollow	 Bridge	AC-10	 Hollow	 Hollow	 Bridge
ZZ-10	 Hollow	 Hollow	 Bridge	AC-13	 Hollow	 Hollow	 Bridge
ZZ-14	 Hollow	 Hollow	 Bridge	AC-17	 Hollow	 Hollow	 Bridge
ZZ-22	 Hollow	 Hollow	 Bridge	AC-19	 Hollow	 Hollow	 Bridge

Table 3. Structures of zigzag edged and armchair-edged GQDs interacting with divalent heavy metal ions. "ZZ" and "AC" denotes a kind of edge, while the following integer corresponds to the number of hexagonal rings in GQD.

ZZ-GQD	Structure			AC-GQD	Structure		
	Cd^{2+}	Hg^{2+}	Pb^{2+}		Cd^{2+}	Hg^{2+}	Pb^{2+}
ZZ-1	 Hollow	 Top	 Hollow	AC-4	 Bridge	 Bridge	 Hollow
				AC-6	 Bridge	 Bridge	 Hollow
ZZ-4	 Top	 Top	 Hollow	AC-8	 Bridge	 Bridge	 Hollow
ZZ-7	 Top	 Hollow	 Hollow	AC-10	 Bridge	 Hollow	 Hollow
ZZ-10	 Top	 Hollow	 Hollow	AC-13	 Top	 Bridge	 Hollow
ZZ-14	 Bridge	 Hollow	 Hollow	AC-17	 Bridge	 Hollow	 Hollow
ZZ-22	 Bridge	 Top	 Hollow	AC-19	 Bridge	 Bridge	 Hollow

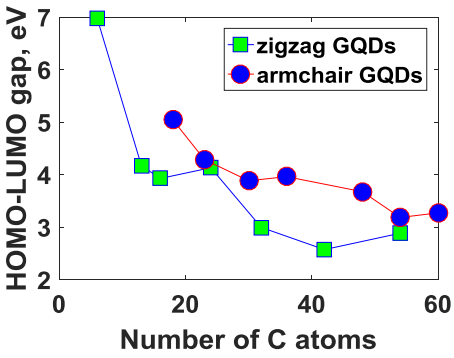


Figure S1 Dependence of the HOMO-LUMO gap of the zigzag-edged and armchair-edged graphene quantum dots on the size of the quantum dot

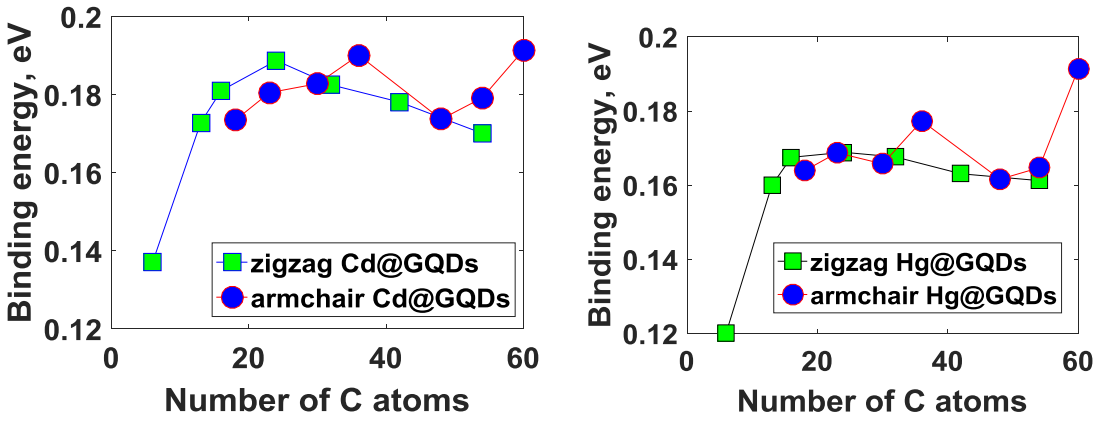


Figure S2 Dependence of the binding energy of (left panel) Cd and (right panel) Hg adsorbed on the surface of zigzag-edged and armchair-edged graphene quantum dots on the size of the quantum dot.

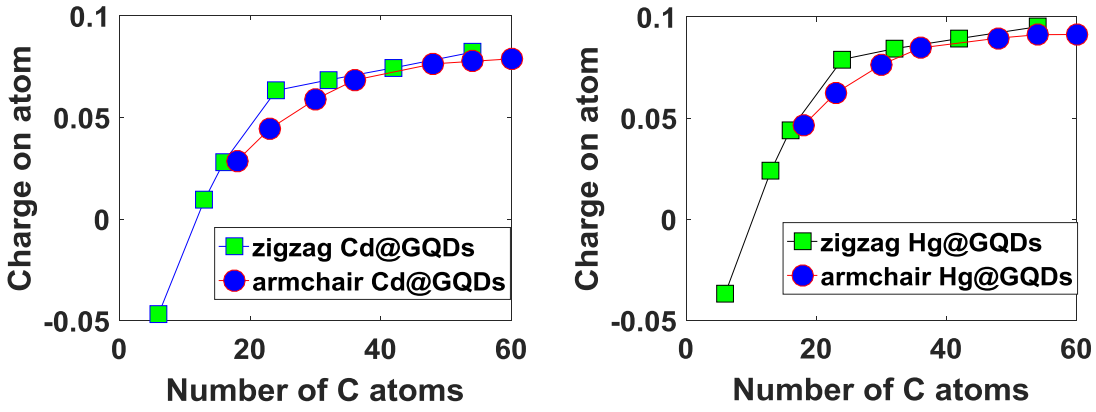


Figure S3 Dependence of the magnitude of Mulliken charge on (left panel) Cd and (right panel) Hg adsorbed on the surface of zigzag-edged and armchair-edged graphene quantum dots on the size of the quantum dot. The positive charges on atoms imply these adatoms are electron-donating species and charge transfer occurs from metal atom to GQD.

Table S4 Parameters of the Zigzag-edged Graphene Quantum dots after interaction with neutral lead atoms.

Zigzag Graphene Quantum Dots	Binding energy, eV	Charge on HM	HOMO-LUMO gap, eV
Pb-Benzene C_6H_6	0.4670	0.11	0.99
Pb-$C_{13}H_9$	1.9117	0.30	2.64
Pb-pyrene $C_{16}H_{10}$	0.7065	0.36	1.68
Pb-coronene $C_{24}H_{12}$	0.2103	0.11	0.75
Pb-ovalene $C_{32}H_{14}$	0.6572	0.50	1.43
Pb-Circumpyrene $C_{42}H_{16}$	0.2993	0.34	0.81
Pb-Circumcoronene $C_{54}H_{18}$	0.1991	0.19	0.73

Table S5 Parameters of the Armchair-edged Graphene Quantum dots after interaction with neutral lead atoms.

Armchair Graphene Quantum Dots	Binding energy, eV	Charge on HM	HOMO-LUMO gap, eV
Pb-triphenylene $C_{18}H_{12}$	0.3808	0.27	1.24
Pb-$C_{23}H_{14}$	0.3557	0.27	1.17
Pb-Tribenzo (b,n,pqr)perylene $C_{30}H_{16}$	0.4994	0.57	2.40
Pb-Tribenzo(A,D,G)Coronene $C_{36}H_{18}$	0.4602	0.56	2.35
Pb-HexabenzoCoronene $C_{48}H_{24}$	0.2878	0.27	0.90
Pb-$C_{54}H_{22}$	0.2461	0.23	0.85
Pb-$C_{60}H_{26}$	0.2894	0.29	0.88

Table S6 Electronic transitions responsible for the adsorption peaks of the zigzag and armchair graphene quantum dots after complexation with divalent metal ions.

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs	Minor contribs
Cd^{2+} on Armchair Graphene Quantum Dots ($C_{54}H_{22}$)						
1	3245.57	3081.11	0.0005	Singlet-A	H-1->LUMO (95%)	HOMO->LUMO (5%)
2	4990.15	2003.94	0.0275	Singlet-A	HOMO->LUMO (114%)	H-1->LUMO (5%)
3	6629.07	1508.50	0.0498	Singlet-A	H-2->LUMO (93%)	H-4->LUMO (7%)
4	11624.8	860.22	0.0109	Singlet-A	H-5->LUMO (85%), H-3->LUMO (13%)	
5	11970.8	835.36	0.1191	Singlet-A	H-4->LUMO (86%)	H-6->LUMO (3%), H-2->LUMO (7%), H-1->L+1 (3%)
6	13253.3	754.52	0.5419	Singlet-A	H-5->LUMO (12%), H-3->LUMO (85%)	
7	13793.6	724.96	0.0024	Singlet-A	H-6->LUMO (94%)	H-7->LUMO (2%), H-4->LUMO (3%)
8	16185.9	617.82	0.0072	Singlet-A	H-7->LUMO (97%)	
9	17499.8	571.43	0.0026	Singlet-A	H-8->LUMO (98%)	
10	19058.8	524.68	0.0003	Singlet-A	H-9->LUMO (97%)	
11	19310.5	517.85	0.0006	Singlet-A	H-10->LUMO (96%)	
12	20321.9	492.07	0.0312	Singlet-A	HOMO->L+1 (88%)	H-11->LUMO (9%)
Cd^{2+} on Zigzag Graphene Quantum Dots ($C_{54}H_{18}$)						
1	3882.75	2575.49	0.0162	Singlet-A	H-1->LUMO (121%)	
2	9030.18	1107.39	0.0001	Singlet-A	H-3->LUMO (99%)	
3	9899.64	1010.13	0.0484	Singlet-A	H-4->LUMO (94%)	H-5->LUMO (5%)
4	12016.0	832.22	0.2318	Singlet-A	H-2->LUMO (90%), HOMO->L+1 (11%)	
5	15812.4	632.41	0.1198	Singlet-A	H-5->LUMO (90%)	H-4->LUMO (4%), HOMO->L+2 (4%)
6	17857.1	560.00	0.0002	Singlet-A	H-6->LUMO (97%)	
7	18573.3	538.40	0.0198	Singlet-A	H-1->L+1 (96%)	HOMO->L+2 (2%)

8	20410.6	489.93	0.1804	Singlet-A	H-1->L+2 (59%), HOMO->L+1 (37%)	H-2->LUMO (3%)
Hg^{2+} on Armchair Graphene Quantum Dots ($C_{54}H_{22}$)						
1	3222.99	3102.70	0.0004	Singlet-A	HOMO->LUMO (100%)	
2	6521.79	1533.31	0.0004	*Singlet-A*	H-2->LUMO (100%)	
3	6783.92	1474.07	0.0532	Singlet-A	H-4->LUMO (10%), H-1->LUMO (92%)	
4	11713.5	853.70	0.0059	Singlet-A	H-5->LUMO (91%)	H-3->LUMO (8%)
5	11989.4	834.06	0.1348	Singlet-A	H-4->LUMO (84%), H-1->LUMO (10%)	H-6->LUMO (3%), HOMO->L+1 (3%)
6	13612.2	734.63	0.63	Singlet-A	H-3->LUMO (90%)	H-5->LUMO (7%), HOMO->L+2 (2%)
7	13873.5	720.79	0.0039	Singlet-A	H-6->LUMO (93%)	H-7->LUMO (3%), H-4->LUMO (3%)
8	16125.4	620.13	0.0095	Singlet-A	H-7->LUMO (96%)	
9	17398.9	574.74	0.0042	Singlet-A	H-8->LUMO (98%)	
10	18982.2	526.80	0.0001	Singlet-A	H-9->LUMO (97%)	
11	19339.5	517.07	0.0019	Singlet-A	H-10->LUMO (96%)	
12	20892.1	478.64	0.021	Singlet-A	H-11->LUMO (90%)	H-1->L+1 (5%)
Hg^{2+} on Zigzag Graphene Quantum Dots ($C_{54}H_{18}$)						
1	6950.07	1438.83	0.0019	Singlet-A	H-1->LUMO (100%)	
2	8948.72	1117.47	0.0001	Singlet-A	H-3->LUMO (99%)	
3	9900.45	1010.05	0.0536	Singlet-A	H-4->LUMO (93%)	H-5->LUMO (6%)
4	12193.4	820.10	0.2465	Singlet-A	H-2->LUMO (88%), HOMO->L+1 (12%)	
5	15980.2	625.77	0.1457	Singlet-A	H-5->LUMO (89%)	H-4->LUMO (5%), HOMO->L+2 (5%)
6	21457.5	466.03	0.824	Singlet-A	H-2->LUMO (12%), HOMO->L+1 (85%)	
Pb^{2+} on Armchair Graphene Quantum Dots ($C_{54}H_{22}$)						
1	10046.4	995.37	0.0021	Singlet-A	HOMO->LUMO (96%)	H-2->LUMO (3%)
2	10791.6	926.63	0.0017	Singlet-A	H-1->LUMO (25%), HOMO->L+1 (74%)	
3	11774.0	849.32	0.0002	Singlet-A	H-1->L+1 (98%)	
4	12553.2	796.60	0.0203	Singlet-A	H-2->LUMO (96%)	HOMO->LUMO (3%)
5	12592.7	794.10	0.0137	Singlet-A	H-2->L+1 (88%)	H-1->LUMO (6%), HOMO->L+1 (5%)
6	13551.7	737.91	0.024	Singlet-A	H-2->L+1 (11%), H-1->LUMO (68%), HOMO->L+1 (20%)	
7	16750.5	596.99	0.001	Singlet-A	H-3->LUMO (99%)	
8	16844.0	593.68	0.0191	Singlet-A	H-3->L+1 (97%)	
9	17451.4	573.01	0.0015	Singlet-A	HOMO->L+2 (95%)	
10	18876.5	529.75	0.066	Singlet-A	H-4->LUMO (10%), H-1->L+4 (12%), HOMO->L+3 (73%)	
11	19058.8	524.68	0.0004	Singlet-A	H-1->L+2 (97%)	
12	19219.3	520.30	0.0184	Singlet-A	H-4->LUMO (83%), HOMO->L+3 (12%)	
Pb^{2+} on Zigzag Graphene Quantum Dots ($C_{54}H_{18}$)						
1	6817.80	1466.74	0.0006	Singlet-A	H-1->LUMO (88%), HOMO->L+1 (11%)	
2	6908.13	1447.56	0.0047	Singlet-A	HOMO->LUMO (98%)	
3	7225.92	1383.90	0.0085	Singlet-A	H-1->LUMO (11%), HOMO->L+1 (88%)	
4	8415.58	1188.27	0.0314	Singlet-A	H-1->L+1 (96%)	
5	14742.2	678.32	0.0027	Singlet-A	H-2->LUMO (91%)	HOMO->L+2 (7%)
6	14940.6	669.31	0.0003	Singlet-A	HOMO->L+2 (93%)	H-2->LUMO (7%)
7	15244.6	655.96	0.0028	Singlet-A	H-2->L+1 (92%)	H-3->LUMO (7%)
8	16089.1	621.53	0.0006	Singlet-A	H-4->LUMO (91%)	H-3->L+1 (6%)
9	16237.5	615.85	0.0022	Singlet-A	H-3->L+1 (91%)	H-4->LUMO (6%)
10	16239.1	615.79	0.0015	Singlet-A	H-4->L+1 (85%), H-3->LUMO (12%)	
11	16786.8	595.70	0.0088	Singlet-A	H-3->LUMO (69%), HOMO->L+3 (12%)	H-4->L+1 (8%), H-2->L+1 (6%), H-1->L+4 (4%)

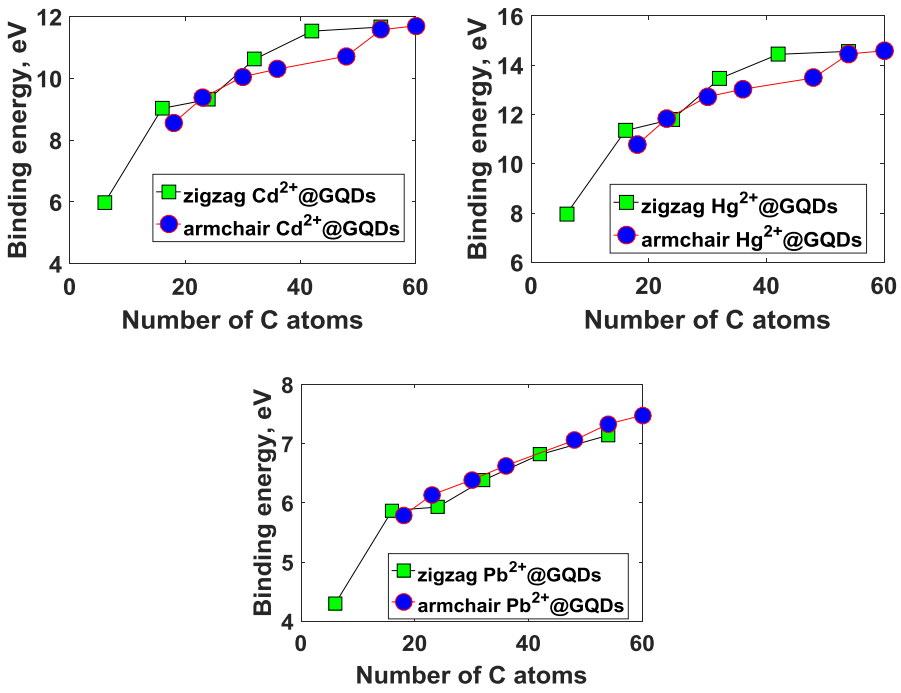


Figure S4 Dependence of the binding energy of (top left panel) Cd^{2+}, (top right panel) Hg^{2+} and (bottom panel) Pb^{2+} adsorbed on the surface of zigzag-edged and armchair-edged graphene quantum dots on the size of the quantum dot.

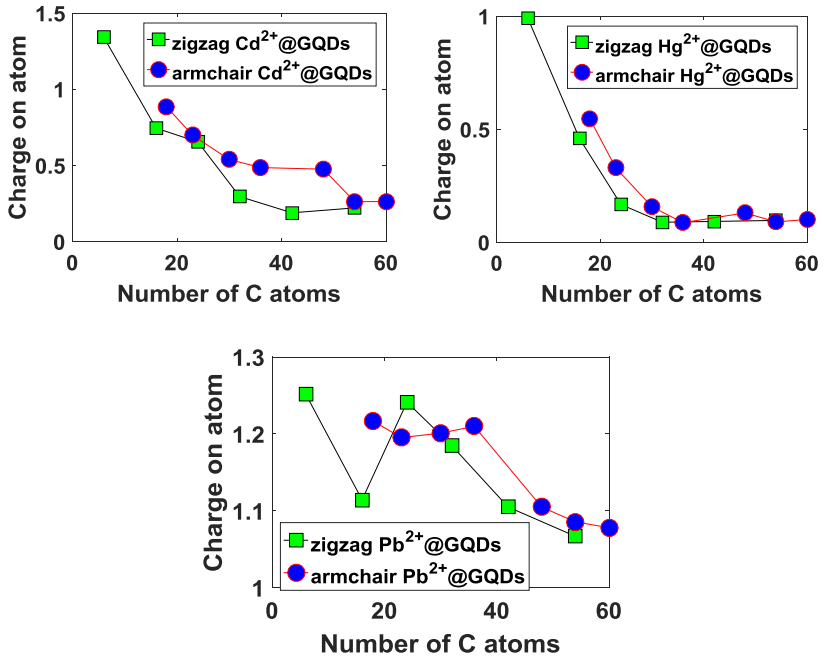


Figure S5 Dependence of the magnitude of Mulliken charge on (top left panel) Cd^{2+}, (top right panel) Hg^{2+} and (bottom panel) Pb^{2+} adsorbed on the surface of zigzag-edged and armchair-edged graphene quantum dots on the size of the quantum dot. The deviation of the magnitude of the charge from +2 towards lower values of positive charge imply the HM ions are hole-donating species and charge transfer occurs from GQD atom to metal.

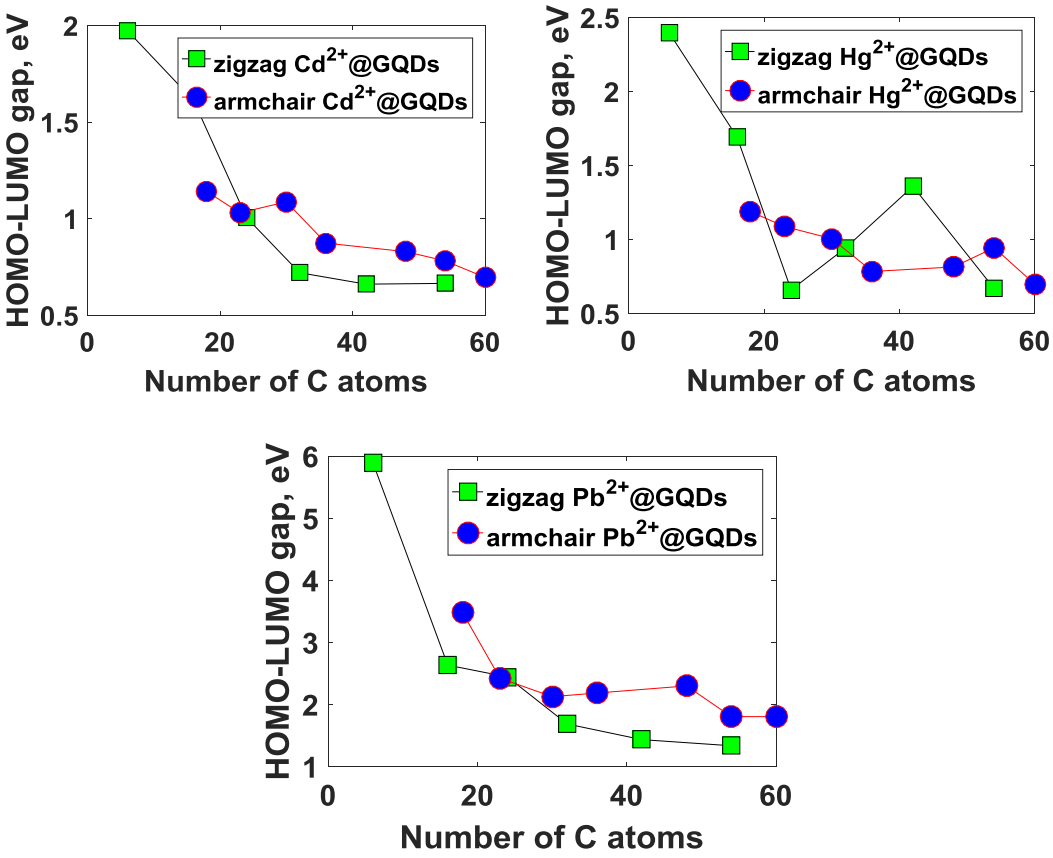


Figure S6 Dependence of the binding energy of (top left panel) Cd^{2+}, (top right panel) Hg^{2+} and (bottom panel) Pb^{2+} adsorbed on the surface of zigzag-edged and armchair-edged graphene quantum dots on the size of the quantum dot.