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Supporting information

Tuneable optical property and zero-field splitting of transition metal adatom-graphene quantum dot systems

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Table S1 Calculated frontier orbital(LUMO+2 ~ HOMO-2) of three different sized TM-GQDs with time depedent density functional theory ZORA and SOC perturbation level methods. All the energy are indicates as absolute values. At the top of table, there are an atom species and basis-set used for it. All units are "eV".

GQD-27	Cr [ZORA-DEF2-TZVP]			Mo [Old-ZORA-TZVP]			W [SARC-ZORA-TZVP]			Pd [Old-ZORA-TZVP]			Pt [SARC-ZORA-TZVP]			Plain		
	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE
LUMO+2	0.965	0.964	0.001	1.158	1.176	0.018	1.236	1.172	0.066	0.795	0.832	0.037	0.903	0.891	0.012	0.422	0.425	0.003
LUMO+1	1.75	1.751	0.001	1.877	1.921	0.044	1.989	1.962	-0.027	1.624	1.659	0.035	1.728	1.718	0.01	0.91	0.913	0.003
LUMO	1.871	1.805	0.066	1.966	1.981	0.015	2.491	2.459	-0.032	1.747	1.793	0.046	2.652	2.621	0.031	1.712	1.714	0.002
HOMO	3.957	3.969	0.012	3.945	3.966	0.021	3.954	3.939	0.015	5.027	5.122	0.095	5.305	5.312	0.007	5.546	5.549	0.003
HOMO-1	4.379	4.384	0.005	4.263	4.261	-0.002	4.089	4.090	0.001	5.114	5.182	0.068	5.344	5.349	0.005	6.419	6.422	0.003
HOMO-2	4.685	4.71	0.025	4.557	4.583	0.026	4.646	4.634	0.012	5.231	5.356	0.125	5.44	5.467	0.027	7.095	7.098	0.003
GQD-55	Cr [ZORA-DEF2-TZVP]			Mo [Old-ZORA-TZVP]			W [SARC-ZORA-TZVP]			Pd [Old-ZORA-TZVP]			Pt [SARC-ZORA-TZVP]			Plain		
	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE
LUMO+2	1.707	1.709	0.002	1.836	1.842	0.006	1.852	1.832	0.02	1.349	1.369	0.02	1.390	1.387	0.003	1.207	1.21	0.003
LUMO+1	2.099	2.025	0.074	2.048	2.096	0.048	2.376	2.367	0.007	1.865	1.89	0.025	2.496	2.493	0.003	1.419	1.421	0.002
LUMO	2.330	2.332	0.002	2.384	2.39	0.006	2.764	2.726	0.038	2.491	2.513	0.022	2.569	2.55	0.019	2.621	2.623	0.002
HOMO	4.262	4.271	0.009	4.233	4.243	0.01	4.212	4.210	0.002	4.545	4.579	0.034	4.789	4.774	0.015	4.735	4.738	0.003
HOMO-1	4.346	4.352	0.006	4.443	4.454	0.011	4.387	4.394	0.007	5.372	5.441	0.069	5.440	5.461	0.021	5.972	5.974	0.002
HOMO-2	4.886	4.887	0.001	4.566	4.557	0.009	4.466	4.469	0.003	5.514	5.562	0.048	5.563	5.592	0.029	6.156	6.159	0.003
GQD-67	Cr [ZORA-DEF2-TZVP]			Mo [Old-ZORA-TZVP]			W [SARC-ZORA-TZVP]			Pd [Old-ZORA-TZVP]			Pt [SARC-ZORA-TZVP]			Plain		
	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE	ZORA	SOC	ΔE
LUMO+2	1.861	1.864	0.003	1.97	1.976	0.004	1.986	1.969	0.013	1.785	1.801	0.016	1.807	1.804	0.003	1.385	1.387	0.002
LUMO+1	2.18	2.103	0.077	2.107	2.154	0.047	2.832	2.793	0.039	1.891	1.919	0.028	2.659	2.641	0.018	1.837	1.838	0.001
LUMO	2.983	2.983	0	3.043	3.05	0.007	3.052	3.048	0.004	2.974	2.99	0.016	3.11	3.099	0.012	3.04	3.042	0.002
HOMO	4.017	4.024	0.007	3.957	3.964	0.007	3.933	3.93	0.003	4.278	4.295	0.017	4.285	4.283	0.002	4.377	4.379	0.002
HOMO-1	4.321	4.326	0.005	4.433	4.445	0.012	4.427	4.428	0.001	5.11	5.156	0.046	5.276	5.28	0.004	5.543	5.545	0.002
HOMO-2	4.719	4.723	0.004	4.64	4.627	0.013	4.492	4.502	0.01	5.393	5.438	0.045	5.467	5.488	0.021	6.044	6.046	0.002

Table S2 Comparison between the formal TD-DFT and TDA. ZFS, intersystem-crossing gap and the energy gap between singlet ground state and first triplet excited state of Pt-GQDs, Mo-GQDs and W-GQDs are shown. Open shell structure such as Mo-GQDs and W-GQDs are significantly different compare with TDA results. The energy values of Mo-GQD-67 and all the W-GQDs are unavailable as they turn out to be pure imaginary (indicated as "-"). All units are "eV".

Open / Close shell	Closed shell molecule						Open shell molecule											
	Pt-GQD						Mo-GQD						W-GQD					
	Formal TD-DFT			TDA			Formal TD-DFT			TDA			Formal TD-DFT			TDA		
	ZFS	ISC	T_1-S_0 gap	ZFS	ISC	T_1-S_0 gap	ZFS	ISC	T_1-S_0 gap	ZFS	ISC	T_1-S_0 gap	ZFS	ISC	T_1-S_0 gap	ZFS	ISC	T_1-S_0 gap
GQD -27	0.092	2.14	0.51	0.092	2.08	0.57	0.061	1.73	0.25	0.015	1.54	0.44	-	-	-	0.026	1.44	0.016
GQD -55	0.060	1.47	0.75	0.063	1.41	0.81	0.027	1.43	0.42	0.013	1.3	0.55	-	-	-	0.014	1.45	0.0001
GQD -67	0.005	0.92	0.25	0.003	0.77	0.40	-	-	-	0.014	0.88	0.029	-	-	-	0.012	0.86	0.023