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Supporting Information: A DFT/TDDFT Study on the Optoelectronic Properties of the Amine-Capped Magic $(CdSe)_{13}$ Nanocluster

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1 Calibration

1.1 Geometry

Preliminary calculations on the isomers of $(CdSe)_{13}$ have shown that the PBE/DZ level of theory is able to reproduce the geometry delivered by the much expensive B3LYP/def2-TZVP (1144 Basis Functions for $(CdSe)_{13}$), see Table 1. Regarding the DZ basis set, enlarging the size of the frozen core from *3d*/*3p* (small core) to *4p*/*3d* (medium core) for Cd/Se atoms speeds up calculations remarkably but worst geometries are obtained. For the B3LYP functional, the performance of smaller sets has been tested, namely LANL2DZ (338 BFs), LANL2DZ* (442 BFs), SBKJC-VDZ (507 BFs) and SBKJC-VDZ* (637 BFs). LANL2DZ* and SBKJC-VDZ* include extra *d* orbitals for Se atoms as compared to the parent LANL2DZ and SBKJC-VDZ sets, given the importance of the polarization functions for the proper description of the highly-coordinated atoms in three-dimensional clusters [1, 2]. LANL2DZ is probably the most widely employed basis set to model CdSe nanostructures [3, 4, 5, 6, 7]. For the small $(CdSe)_{13}$ clusters studied here, it has shown to overestimate Cd-Se bond lengths, leading to an improper description of structure and energetics as compared to reference B3LYP/def2-TZVP calculations. This finding agrees with previous results by Nguyen and co. on [2]. For bigger $(CdSe)_n$ nanoclusters, the LANL2DZ set could benefit from basis sharing effects. The inclusion of *d* polarization functions for Se atoms slightly corrects the behavior of LANL2DZ. The SBKJC set previously employed for the characterization of CdSe nanoclusters provide better geometries [1, 2]. Again, extra polarization functions lead to the improvement of the geometry.

The inclusion of the Grimme's dispersion terms [8] produce little changes on the geometry of the bare $(CdSe)_{13}$ isomers, see Table 2. For the ligand-capped structures, on the contrary, the dispersion corrected PBE-D3 provides remarkably shorter nanocluster-ligand bonds than the parent PBE, see Table 3.

1.2 TDDFT

TDDFT spectra provided by the SBKJC-VDZ, SBKJC-VDZ*, LANL2DZ, and LANL2DZ* sets relative to the reference calculations carried out with def2-TZVP basis, in Figure 1.

2 Geometry

The geometry of the bare clusters remains unchanged upon solvation, see Table 4. However, the geometry of the surface-capped differs notably compared to the optimal arrangement *in vacuo*.

3 Energy Decomposition Analysis

4 Optoelectronics

Table 5 shows the gas phase valence excitation spectrum of the bare $(CdSe)_{13}$ isomers.

Figure 2 displays the Density of States of the $(CdSe)_{13}$ isomers, both bare and ligand-protected, in gas and solvent phases.

Figure 3 displays the simulated TDDFT spectra of the $(CdSe)_{13}$ isomers, both bare and ligand-protected, in gas and solvent phases.

Table 2: Average geometric parameters of the lowest-lying bare $(CdSe)_{13}$ isomer. Effect of the inclusion of the dispersion and the implicit solvent. Bond lengths in Å and bond angles in degrees.

		PBE (gas)	PBE-D3 (gas)	PBE (toluene)	PBE (water)
$(CdSe)_{13}$ - (a)	d(Cd(2)-Se)	2.526	2.526	2.530	2.535
	d(Cd(3)-Se)	2.658	2.655	2.658	2.657
	d(Cd(4)-Se)	2.752	2.748	2.753	2.747
	α(Se-Cd(2)-Se)	161.5	160.5	160.4	156.4
	α(Se-Cd(3)-Se)	119.8	119.8	119.7	119.5
	α(Se-Cd(4)-Se)	108.7	108.7	108.7	108.7
	α(Cd-Se(3)-Cd)	85.5	85.4	86.0	86.8
	α(Cd-Se(4)-Cd)	96.8	96.5	96.7	96.3

Table 1: Average geometric parameters of the bare $(CdSe)_{13}$ isomers. Effect of the functional, the basis set, and the size of the frozen core. Bond lengths in Å and bond angles in degrees.

Isomer		PBE				PBE-D3	B3LYP				
		Small Core		Medium Core		Small Core					
		DZ	DZ(Cd)/DZP(Se)	DZ	DZ(Cd)/DZP(Se)	DZ	LANL2DZ	LAL2DZ*	SBKJC	SBKJC*	def2-tzvp
$(CdSe)_{13}$ - (a)	d(Cd(2)-Se)	2.526	2.506	2.576	2.555	2.526	2.595	2.578	2.537	2.531	2.502
	d(Cd(3)-Se)	2.658	2.644	2.708	2.693	2.655	2.729	2.716	2.682	2.677	2.656
	d(Cd(4)-Se)	2.752	2.740	2.800	2.791	2.748	2.837	2.823	2.792	2.787	2.767
	α(Se-Cd(2)-Se)	161.5	163.5	160.2	162.5	160.5	155.1	156.6	158.3	158.6	159.0
	α(Se-Cd(3)-Se)	119.8	119.9	119.7	119.8	119.8	119.3	119.4	119.5	119.5	119.5
	α(Se-Cd(4)-Se)	108.7	108.8	108.7	108.7	108.7	108.4	108.5	108.5	108.5	108.5
	α(Cd-Se(3)-Cd)	85.5	84.6	85.9	84.9	85.4	88.5	87.7	87.4	87.3	87.1
	α(Cd-Se(4)-Cd)	96.8	96.0	97.2	96.3	96.5	98.5	97.8	98.0	97.9	97.7
$(CdSe)_{13}$ - (b)	d(Cd(3)-Se)	2.650									2.647
	α(Se-Cd(3)-Se)	118.6									118.4
	α(Cd-Se(3)-Cd)	91.7									92.8
$(CdSe)_{13}$ - (c)	d(Cd(3)-Se)	2.657									2.653
	d(Cd(4)-Se)	2.763									2.797
	α(Se-Cd(3)-Se)	117.5									117.2
	α(Se-Cd(4)-Se)	109.4									109.3
	α(Cd-Se(3)-Cd)	88.0									89.5
	α(Cd-Se(4)-Cd)	109.0									108.6

Table 3: Average geometric parameters of the lowest-lying amine-capped $(CdSe)_{13}$ isomer. Effect of the inclusion of the dispersion and the implicit solvent. Bond lengths in Å and bond angles in degrees.

		PBE(gas)	PBE-D3(gas)	PBE(toluene)	PBE(water)
$(CdSe)_{13}$ - (a)	d(Cd(2)-Se)	2.614	2.610	2.622	2.632
	d(Cd(3)-Se)	2.684	2.677	2.686	2.691
	d(Cd(4)-Se)	2.725	2.710	2.719	2.711
	d(Cd(2)-N)	2.438	2.416	2.416	2.388
	d(Cd(3)-N)	2.492	2.471	2.470	2.439
	d(Cd(4)-N)	-	-	-	-
	α(Se-Cd(2)-Se)	146.2	145.6	142.7	136.4
	α(Se-Cd(3)-Se)	118.8	119.0	118.3	117.4
	α(Se-Cd(4)-Se)	109.5	109.5	109.5	109.5
	α(Cd-Se(3)-Cd)	90.3	89.9	91.3	92.5
	α(Cd-Se(4)-Cd)	-	-	-	-

Table 4: Average geometric parameters of the bare and ligand-capped $(CdSe)_{13}$ isomers, optimized in implicit solvent. Resuls obtained at the PBE-D3/DZ(P) level of theory. Bond lengths in Å and bond angles in degrees.

Solvent	Toluene									
$(CdSe)_{13}$	(a)				(b)			(c)		
	Bare	$MeNH_2$	Pyr	An	Bare	$MeNH_2$	Pyr	Bare	$MeNH_2$	Pyr
d(Cd(2)-N)	-	2.398	2.416	2.466	-	-		-	-	-
d(Cd(3)-N)	-	2.450	2.525	2.560	-	2.443	2.499	-	2.408	2.479
d(Cd(4)-N)	-	-	-	-	-	-	-	-	2.501	-
d(Cd(2)-Se)	2.530	2.619	2.593	2.597	-	-	-	-	-	-
d(Cd(3)-Se)	2.654	2.678	2.675	2.667	2.644	2.664	2.656	2.652	2.685	2.665
d(Cd(4)-Se)	2.746	2.704	2.693	2.702	-	-	-	2.737	2.755	-
α(Se-Cd(2)-Se)	158.4	142.9	145.4	144.4	-	-	-	-	-	-
α(Se-Cd(3)-Se)	119.6	118.5	118.5	118.9	118.5	117.7	117.7	117.1	115.4	115.8
α(Se-Cd(4)-Se)	108.7	109.5	109.5	109.5	-	-	-	109.4	107.0	-
α(Cd-Se(3)-Cd)	86.1	90.7	90.5	89.4	91.9	95.3	95.0	88.6	89.6	92.2
α(Cd-Se(4)-Cd)	96.3	-	-	-	-	-	-	109.2	109.0	-
Solvent	Water									
$(CdSe)_{13}$	(a)				(b)			(c)		
	Bare	$MeNH_2$	Pyr	An	Bare	$MeNH_2$	Pyr	Bare	$MeNH_2$	Pyr
d(Cd(2)-N)	-	2.372	2.389	2.437	-	-	-	-	-	-
d(Cd(3)-N)	-	2.422	2.511	2.526	-	2.419	2.466	-	2.387	2.456
d(Cd(4)-N)	-	-	-	-	-	-	-	-	2.503	-
d(Cd(2)-Se)	2.535	2.630	2.604	2.605	-	-	-	-	-	-
d(Cd(3)-Se)	2.654	2.681	2.677	2.670	2.644	2.666	2.659	2.653	2.684	2.668
d(Cd(4)-Se)	2.747	2.697	2.687	2.698	-	-	-	2.726	2.754	-
α(Se-Cd(2)-Se)	154.7	138.6	141.3	144.3	-	-	-	-	-	-
α(Se-Cd(3)-Se)	119.5	117.7	117.9	118.5	118.3	117.1	117.2	116.7	114.4	115.0
α(Se-Cd(4)-Se)	108.5	109.5	109.5	109.5	-	-	-	109.4	106.9	-
α(Cd-Se(3)-Cd)	86.8	91.7	91.1	89.9	92.6	96.7	95.9	89.2	90.9	93.0
α(Cd-Se(4)-Cd)	94.6	-	-	-	-	-	-	109.3	108.8	-

Table 5: Gas phase valence excitation spectrum of the bare $(CdSe)_{13}$ isomers. Vertical excitation energy (in eV) and corresponding oscillator strength (f, in a.u.) are reported, along with the composition of the excited state. Results obtained at the B3LYP*/SBKJC-VDZ* level.

(a)

# Transition	E	f	Main monoexcitations	Weight (%)
1	3.17	0.0331	HOMO→LUMO	95
2	3.17	0.0331	HOMO-1→LUMO	95
3	3.21	0.0588	HOMO-3→LUMO	53
			HOMO-2→LUMO	43
4	3.27	0.0024	HOMO-2→LUMO	50
			HOMO-3→LUMO	43
5	3.35	0.0175	HOMO-4→LUMO	93
6	3.35	0.0176	HOMO-5→LUMO	93
7	3.59	0.0133	HOMO-6→LUMO	68
8	3.59	0.0133	HOMO-7→LUMO	68
9	3.63	0.0085	HOMO-8→LUMO	81
10	3.68	0.0068	HOMO-9→LUMO	20

(b)

# Transition	E	f	Main monoexcitations	Weight (%)
1	2.98	0.0097	HOMO→LUMO	91
2	3.09	0.0069	HOMO-1→LUMO	89
3	3.17	0.0288	HOMO-3→LUMO	87
4	3.30	0.0061	HOMO-2→LUMO	80
5	3.40	0.0210	HOMO-4→LUMO	71
6	3.41	0.0341	HOMO-5→LUMO	79
7	3.47	0.0262	HOMO-6→LUMO	63
8	3.51	0.0021	HOMO→LUMO+1	62
9	3.53	0.0578	HOMO-7→LUMO	64
10	3.57	0.0024	HOMO-8→LUMO	78

(c)

# Transition	E	f	Main monoexcitations	Weight (%)
1	2.90	0.0069	HOMO→LUMO	94
2	2.90	0.0065	HOMO-1→LUMO	94
3	3.11	0.0492	HOMO-3→LUMO	94
4	3.14	0.0000	HOMO-2→LUMO	93
5	3.27	0.0405	HOMO-4→LUMO	92
6	3.27	0.0384	HOMO-5→LUMO	92
7	3.42	0.0000	HOMO-6→LUMO	89
8	3.42	0.0000	HOMO-7→LUMO	89
9	3.61	0.0000	HOMO-11→LUMO	89
10	3.62	0.1063	HOMO-9→LUMO	83

Figure 1: Gas phase simulated absorption spectra of the lowest-lying bare $(CdSe)_{13}$ isomers, drawn by a Lorentzian convolution with FWHM = 0.2 eV, calculated taking into account the lowest 10 electronic transitions. Results obtained with the B3LYP functional, on top of the geometries optimized at the PBE/DZ level. Effect of the basis set.

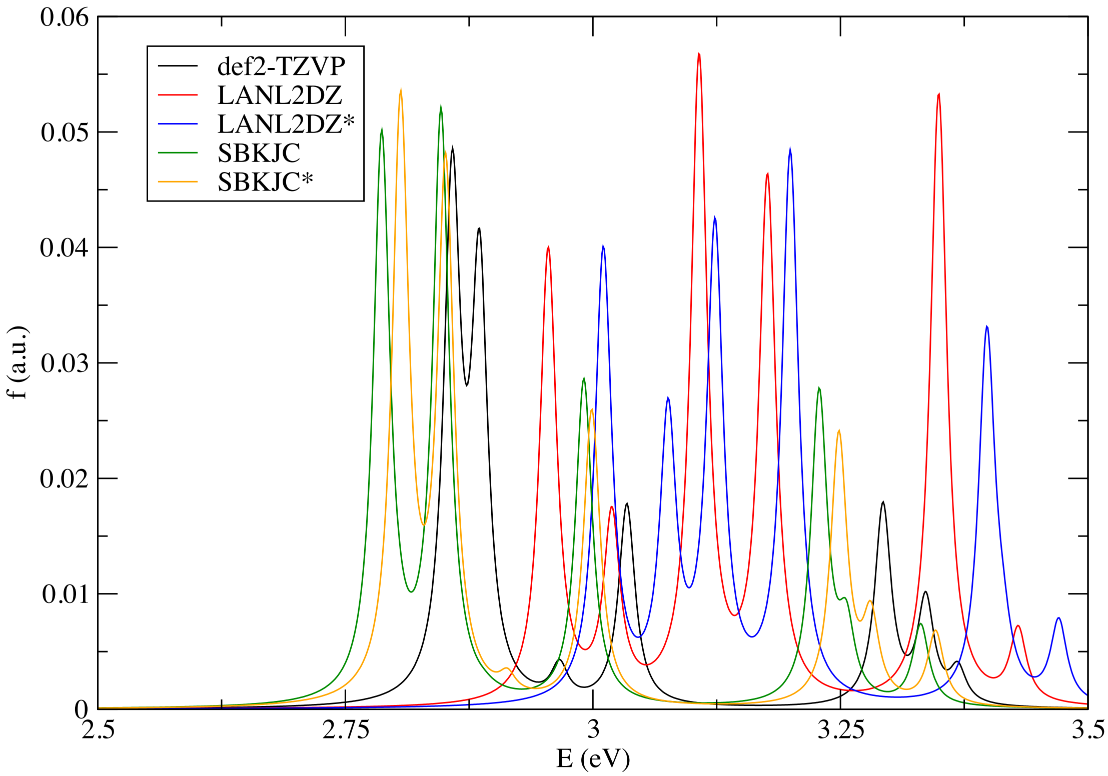


Figure 2: Density of states of the $(CdSe)_{13}$ isomers, both bare and ligand-protected, drawn by a Gaussian convolution of σ = 0.2 eV of the individual Kohn-Sham orbitals. Results obtained at the B3LYP*/SBKJC-VDZ* level.

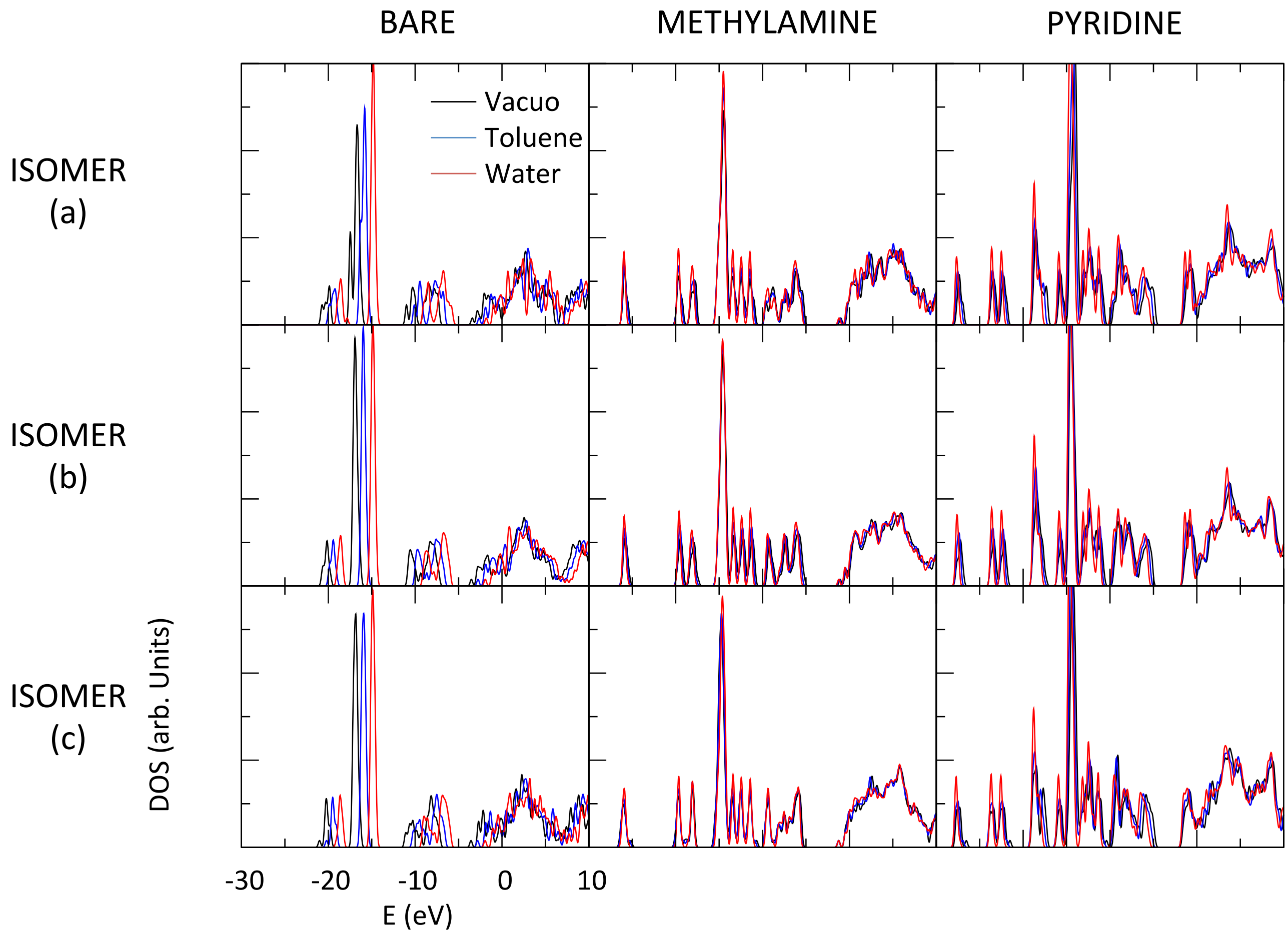
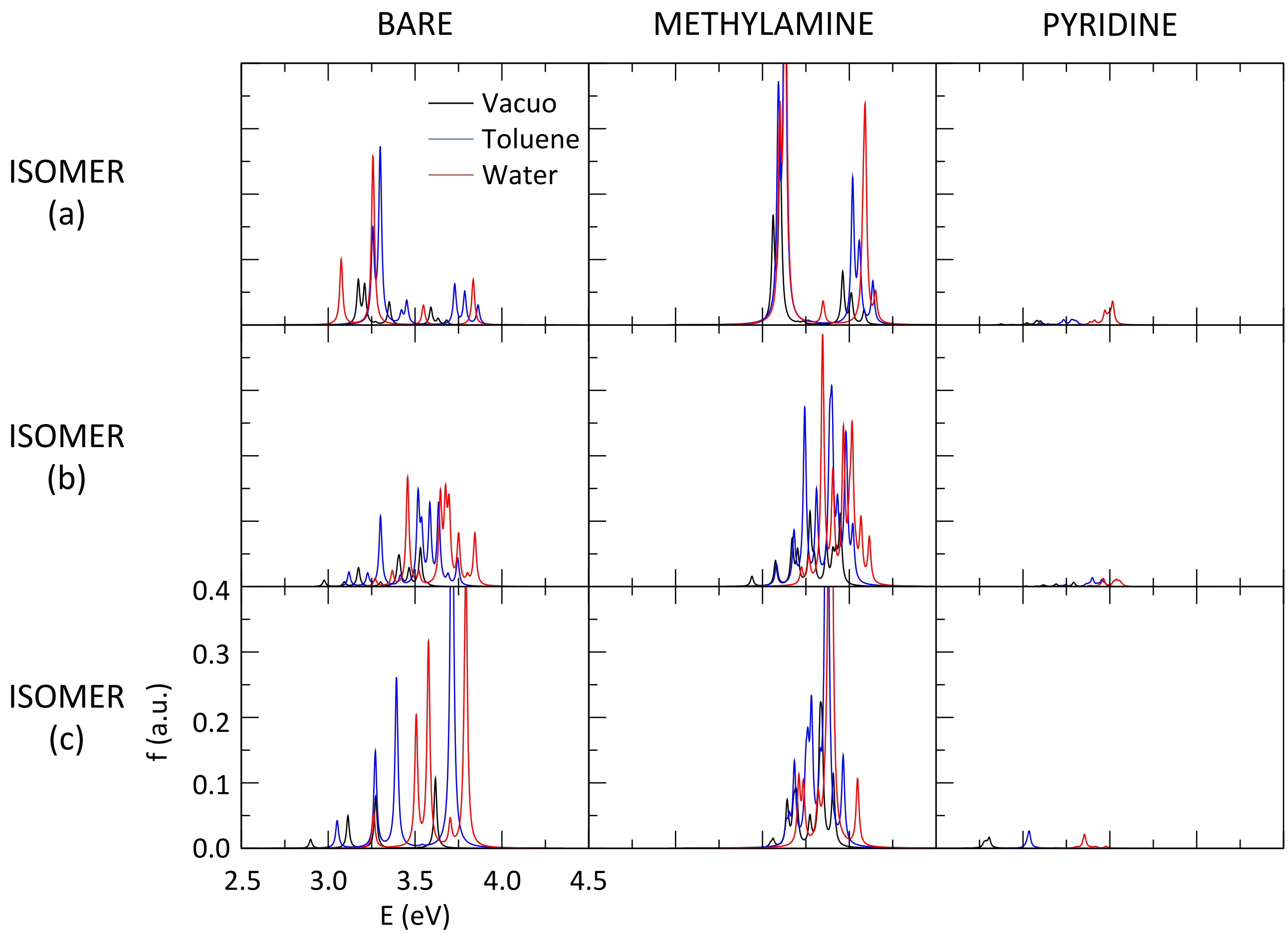


Figure 3: Simulated absorption spectra of the $(CdSe)_{13}$ isomers, both bare and ligand-protected, drawn by a Lorentzian convolution with FWHM = 0.2 eV, calculated taking into account the lowest 10 electronic transitions. Results obtained at the B3LYP*/SBKJC-VDZ* level.



References

[1] Matxain, J. M.; Mercero, J. M.; Fowler, J. E.; Ugalde, J. M. *J. Phys. Chem. A* **2004**, *108*, 10502–10508.

[2] Nguyen, K. A.; Day, P. N.; Pachter, R. *J. Phys. Chem. C* **2010**, *114*, 16197–16209.

[3] Yang, P.; Tretiak, S.; Masunov, A. E.; Ivanov, S. *J. Chem. Phys.* **2008**, *129*, 074729(1–12).

[4] Kilina, S.; Ivanov, S.; Tretiak, S. *J. Am. Chem. Soc.* **2009**, *131*, 7717–7726.

[5] Albert, V. V.; Ivanov, S. A.; Tretiak, S.; Kilina, S. V. *J. Phys. Chem. C* **2011**, *115*, 15793–15800.

[6] Fischer, S. A.; Crotty, A. M.; Kilina, S. V.; Ivanov, S. A.; Tretiak, S. *Nanoscale* **2012**, *4*, 904–914.

[7] Kuznetsov, A. E.; Balamurugan, D.; Skourtis, S. S.; Beratan, D. N. *J. Phys. Chem. C* **2012**, *116*, 6817–6830.

[8] Grimme, S.; Anthony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104(1–19).