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

Supplementary Information

Assessing the Structure and First Hyperpolarizability of $Li@B_{10}H_{14}$ in Solution: a Sequential QM/MM Study Using the ASEC-FEG Method

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Table S1 MP2/(Li-aug)-cc-pVDZ and [MP2/cc-pVDZ] bond lengths (Å) for $Li@B_{10}H_{14}$ and $[B_{10}H_{14}]$ obtained in gas phase and in chloroform (converged value) and water (last step value) solvents using the ASEC-FEG method. Lithium, boron and hydrogen atom labels are defined in Fig. 1.

	Gas-phase		$CHCl_3$		H_2O	
Length	$Li@B_{10}H_{14}$	$B_{10}H_{14}$	$Li@B_{10}H_{14}$	$B_{10}H_{14}$	$Li@B_{10}H_{14}$	$B_{10}H_{14}$
B4 – B7	1.814	1.811	1.812	1.810	1.820	1.809
B7 – B17	1.882	1.806	1.874	1.804	1.851	1.802
B7 – B3	1.778	1.771	1.779	1.770	1.792	1.770
B4 – B3	1.804	1.802	1.802	1.800	1.796	1.798
B17 – B4	1.772	1.746	1.773	1.746	1.755	1.746
B17 – B8	1.882	1.806	1.874	1.804	1.851	1.802
B8 – B1	1.778	1.771	1.778	1.770	1.792	1.770
B1 – B3	1.759	1.796	1.760	1.794	1.758	1.794
B18 – B17	3.504	3.603	3.466	3.603	3.503	3.600
B7 – B8	2.933	2.868	2.929	2.866	2.900	2.862
B8 – B5	1.863	1.993	1.860	1.992	1.841	1.992
B18 – H22	1.317	1.350	1.315	1.350	1.309	1.351
B5 – H22	1.413	1.332	1.406	1.330	1.396	1.328
B18 – H24	1.201	1.197	1.200	1.196	1.200	1.195
B18 - Li	2.620		2.749		3.439	
H20 - Li	2.043		2.170		2.840	
H21 - Li	2.043		2.172		2.844	
H22 - Li	2.043		2.171		2.829	
H22 - Li	2.043		2.169		2.819	

Table S2 MP2/aug-cc-pVDZ differences (Δq) between the values of q for corresponding sites of $B_{10}H_{14}$ and $Li@B_{10}H_{14}$ in gas phase, chloroform (converged value) and water (last step value). Lithium, Boron and hydrogen atoms labels are shown in Fig 1.

	$\Delta q(e)$		
Atom	Gas-phase	$CHCl_3$	H_2O
B1	-0.15	-0.17	-0.10
B2	0.19	0.19	0.02
B5	0.07	0.06	0.04
B17	-0.06	-0.10	-0.04
H9	0.01	0.01	-0.06
H10	-0.06	-0.07	-0.08
H13	-0.03	-0.04	-0.07
H19	-0.02	-0.02	-0.04
H20	-0.17	-0.16	-0.07
Li	0.74	0.81	0.97

[a]Equivalent atoms are defined as follows: B1=B3, B2=B4, B5=B6=B7=B8, B17=B18, H9=H11, H10=H12, H13=H14=H15=H16, H19=H24 and H20=H21=H22=H23.

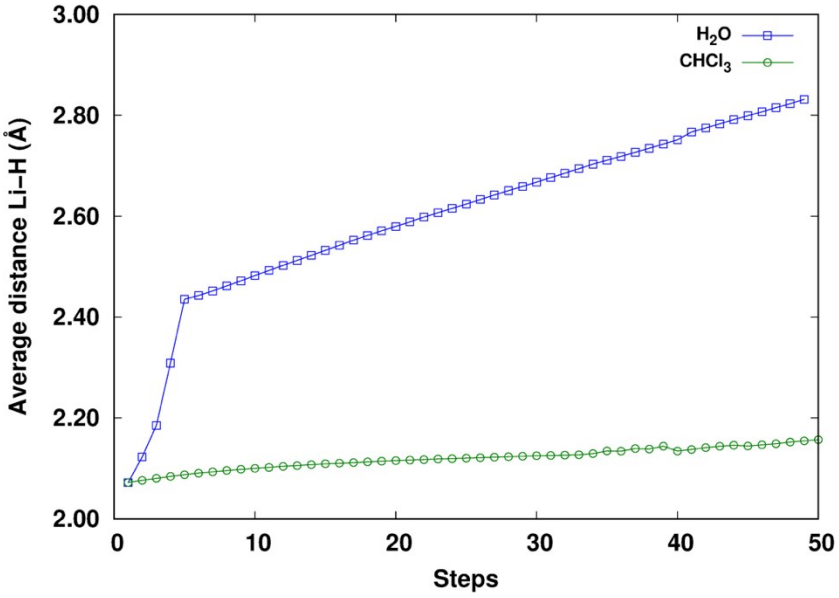

Fig. S1 MP2/aug-cc-pVDZ results for average distance between the Li atom and H atoms (H20, H21, H22, H23) of the $B_{10}H_{14}$ basket-shaped molecule (see Fig. 1).

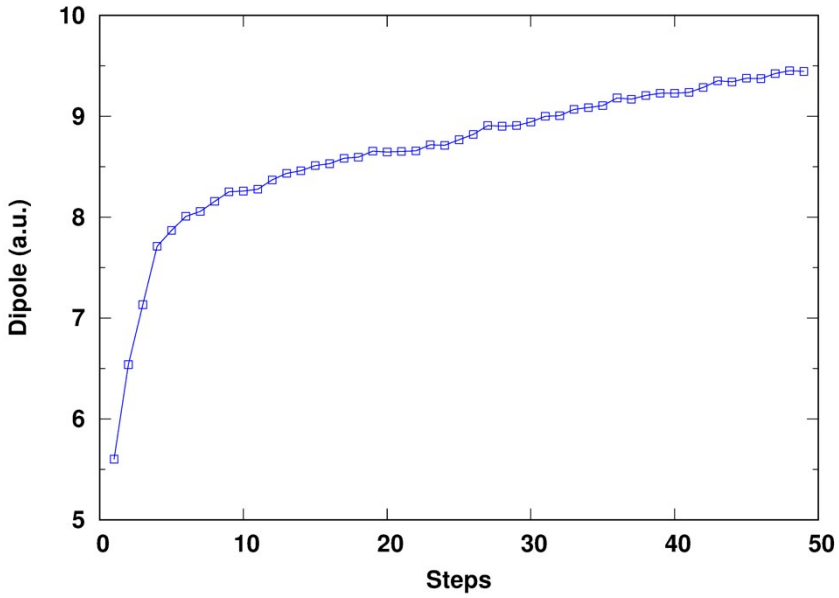

Fig. S2 Evolution of the ground state permanent dipole moment of $Li@B_{10}H_{14}$ in water solvent as a function of step number of the iterative process. The in-water values of μ increase almost linearly with the number of iteractions

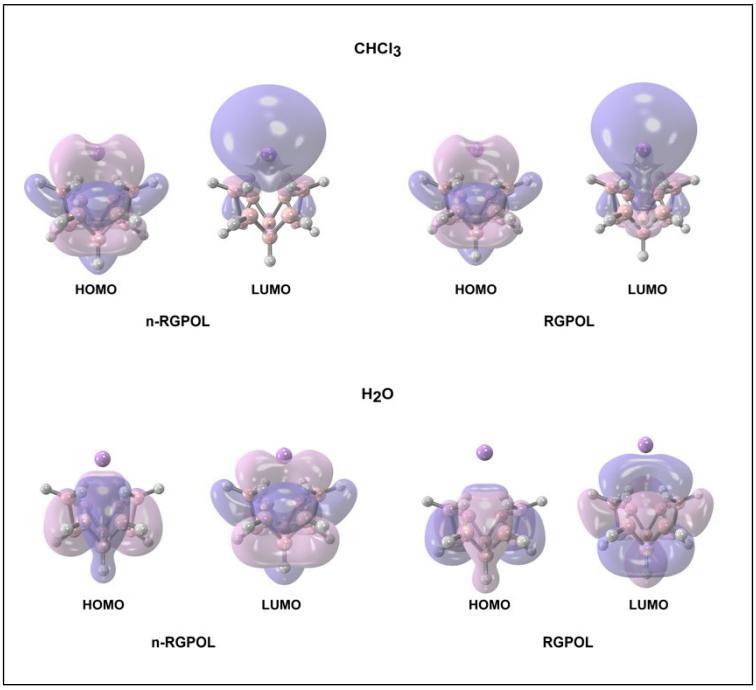

Fig. S3 Molecular orbitals obtained in solution with both non-relaxed geometry polarized (n-RGPOL) and relaxed geometry polarized (RGPOL) models.

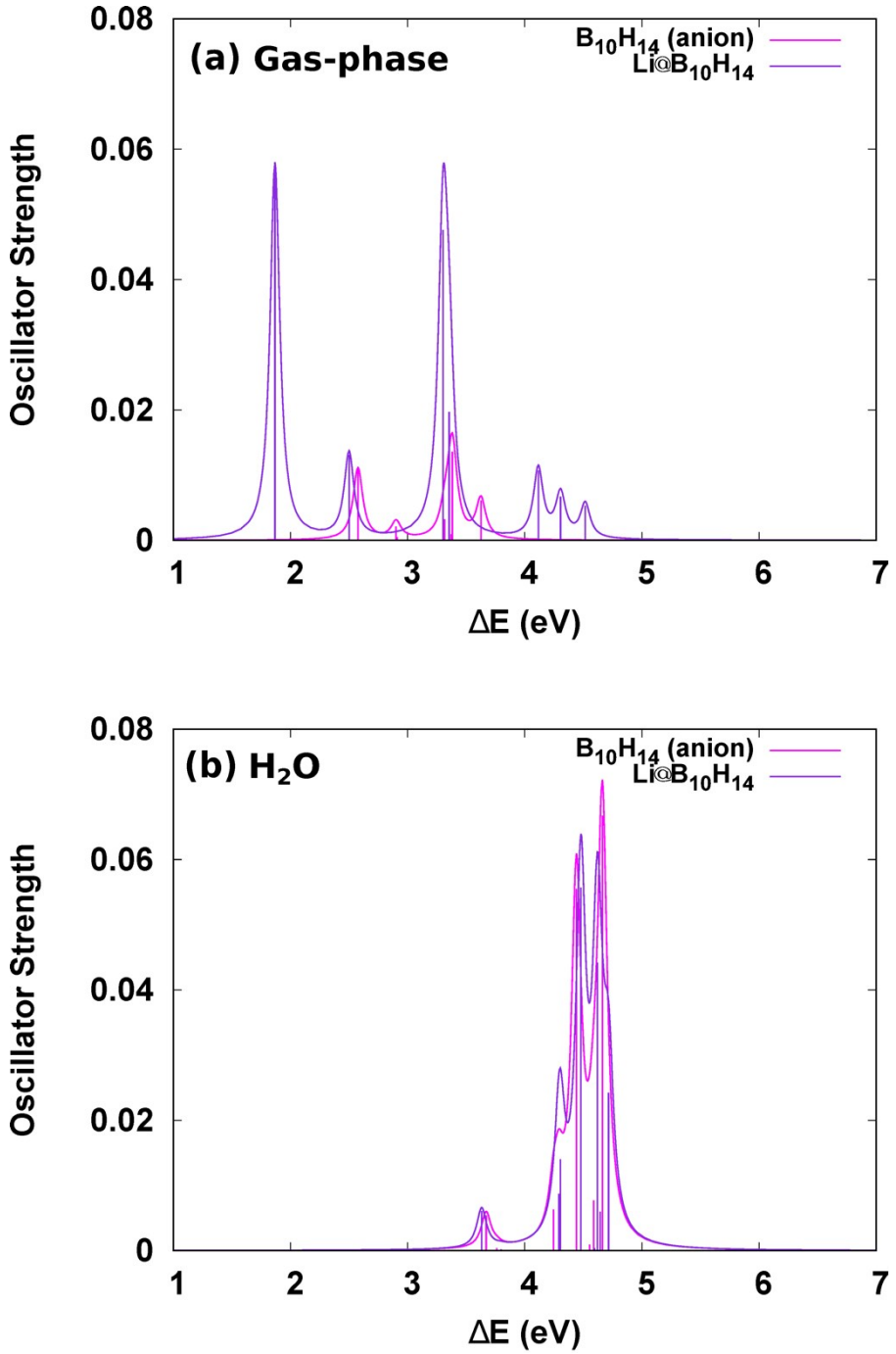

Fig. S4 CAM-B3LYP/aug-cc-pVDZ results for the absorption spectra of $B_{10}H_{14}$ anion and Li@$B_{10}H_{14}$ in gas phase and in water. Results for $B_{10}H_{14}$ anion in water were obtained with the non-relaxed geometry polarized (n-RGPOL) model.

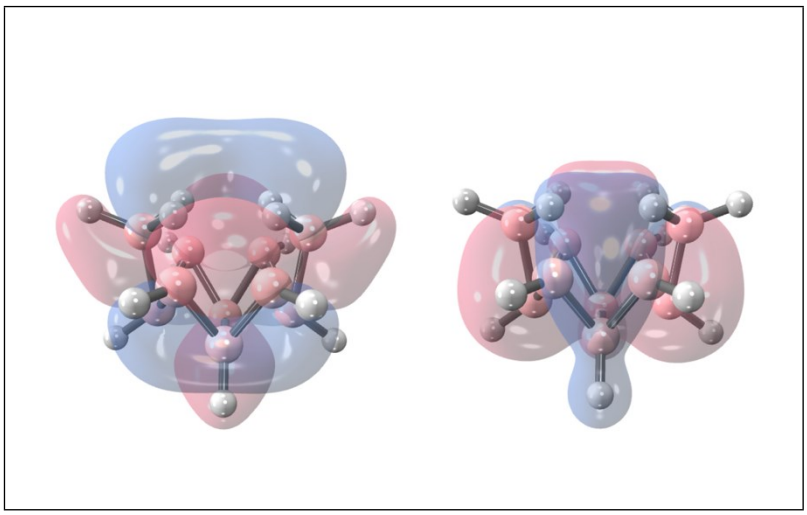

Fig. S5 HOMO orbitals of $B_{10}H_{14}$ anion in gas phase (left) and in water (right). The shape of the orbital in water was obtained with the non-relaxed geometry polarized (n-RGPOL) model.

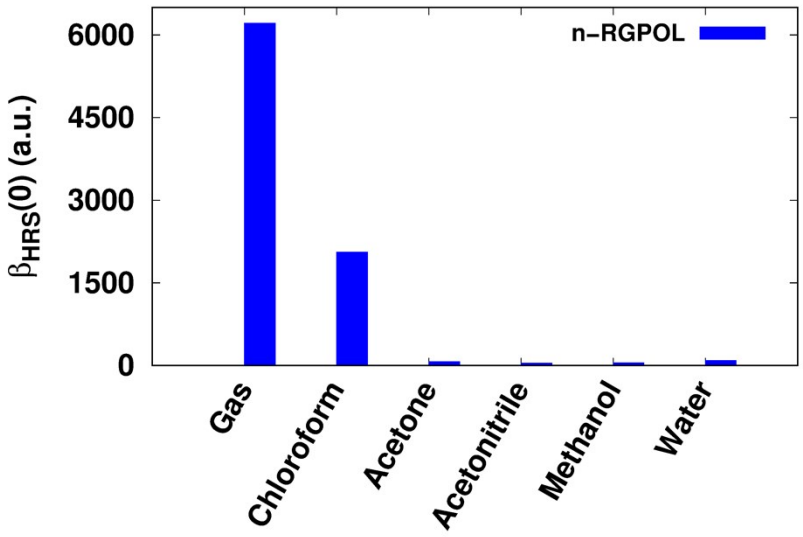

Fig. S6 MP2/aug-cc-pVDZ results for β_{HRS} of $Li@B_{10}H_{14}$ in gas phase and in solvents of increasing polarity. Results in solution were obtained with the non-relaxed geometry polarized (n-RGPOL) model.

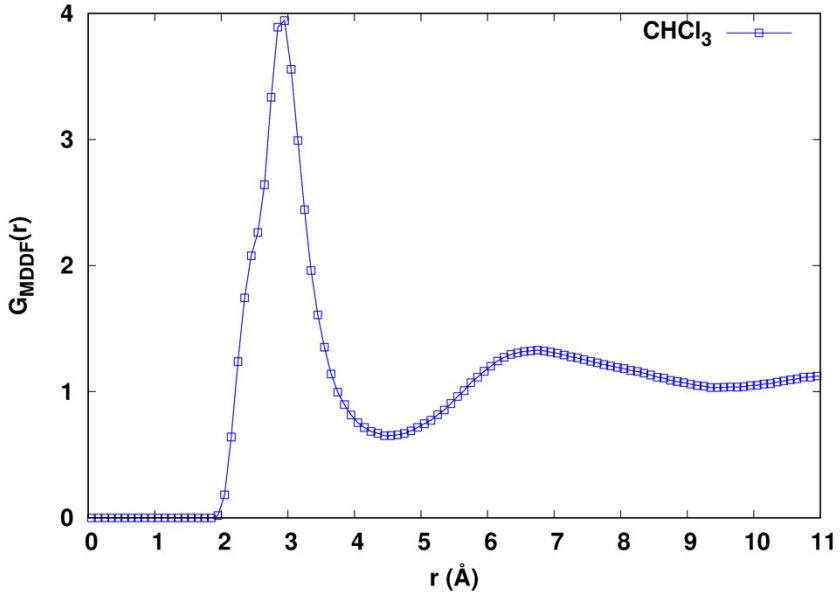

Fig. S7 Minimum-distance distribution function for $Li@B_{10}H_{14}$ in chloroform.