Formal reactions of "capping" of open oligomers with different thermal groups could be written in the following way.

$X_3[HGaNH]_nY_3 + GaH_3 + NH_3 = XGa[HGaNH]_nNY + 2HX + 2HY + H_2$

Table S1 Standard enthalpies ΔH^0_{298} (in kcal/mol) of the formal reactions of "capping" oligomers with XGa and NY groups.

X	Y	*n*=9	*n*=30
H	H	-26.24	-51.56
H	CH3	-74.36	-99.60
H	F	-150.12	-179.96
H	CF3	-62.81	-93.75
CH3	H	-49.54	-75.76
CH3	CH3	-97.70	-123.80
CH3	F	-173.09	-204.32
CH3	CF3	-85.63	-118.05
F	H	34.10	13.30
F	CH3	-14.00	-34.75
F	F	-91.22	-115.13
F	CF3	-4.27	-28.62
CF3	H	-37.68	-57.34
CF3	CH3	-85.79	-105.64
CF3	F	-163.04	-186.03
CF3	CF3	-76.20	-99.80

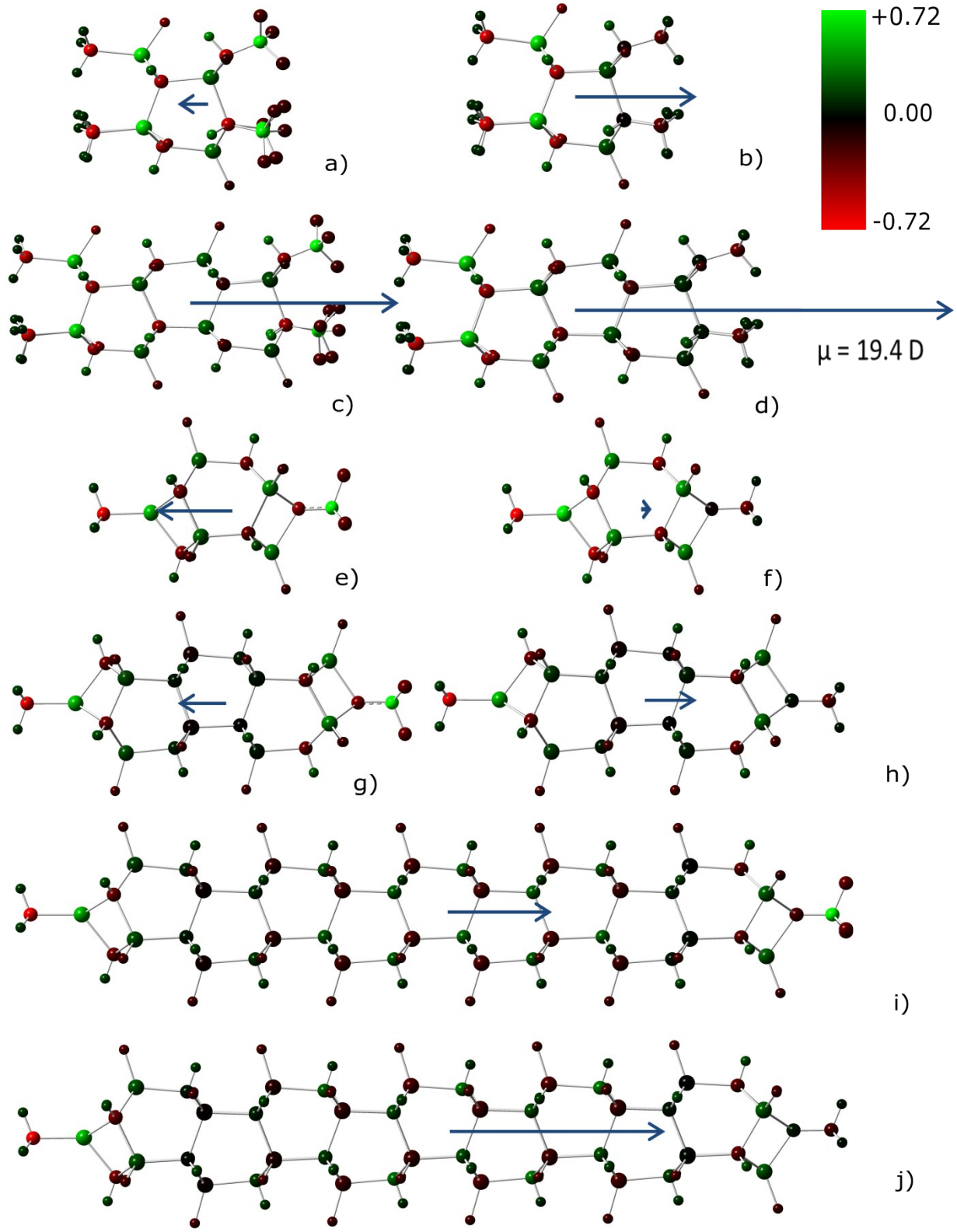


Figure S1 Dipole moment vectors and ECP charge distribution over atoms of oligomers: $(CH_3)_3[HGaNH]_6(CF3)_3$ (a), $(CH_3)_3[HGaNH]_6(CH_3)_3$ (b), $(CH_3)_3[HGaNH]_{12}(CF3)_3$ (c), $(CH_3)_3[HGaNH]_{12}(CH_3)_3$ (d), $CH_3Ga[HGaNH]_6NCF_3$ (e), $CH_3Ga[HGaNH]_6NCH_3$ (f), $CH_3Ga[HGaNH]_{12}NCF_3$ (g), $CH_3Ga[HGaNH]_{12}NCH_3$ (h), $CH_3Ga[HGaNH]_{12}NCF_3$ (i), $CH_3Ga[HGaNH]_{12}NCH_3$ (j)

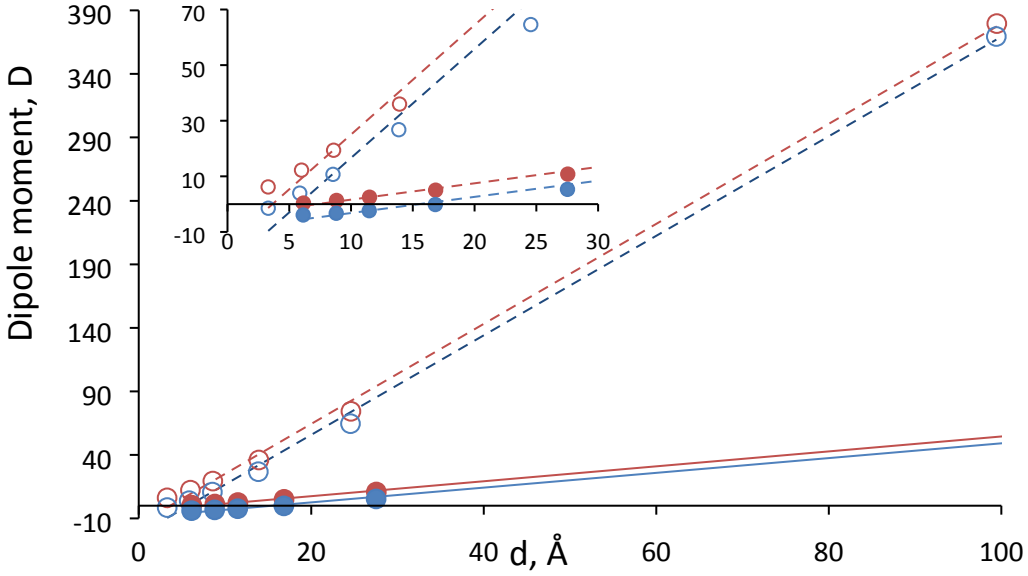


Figure S2 Dipole moments as functions of the lengths of oligomers $(CH_3)_3[HGaNH]_n(CH_3)_3$ (red open circles), $(CH_3)_3[HGaNH]_n(CF_3)_3$ (blue open circles), $CH_3Ga[HGaNH]_nNCH_3$ (red filled circles), $CH_3Ga[HGaNH]_nNCF_3$ (blue filled circles) with n=6, 9, 12, 18, 30, 114. Lines are linear approximation. Lengths are defined as distances between Ga and N atoms/planes at opposite ends of the oligomer.

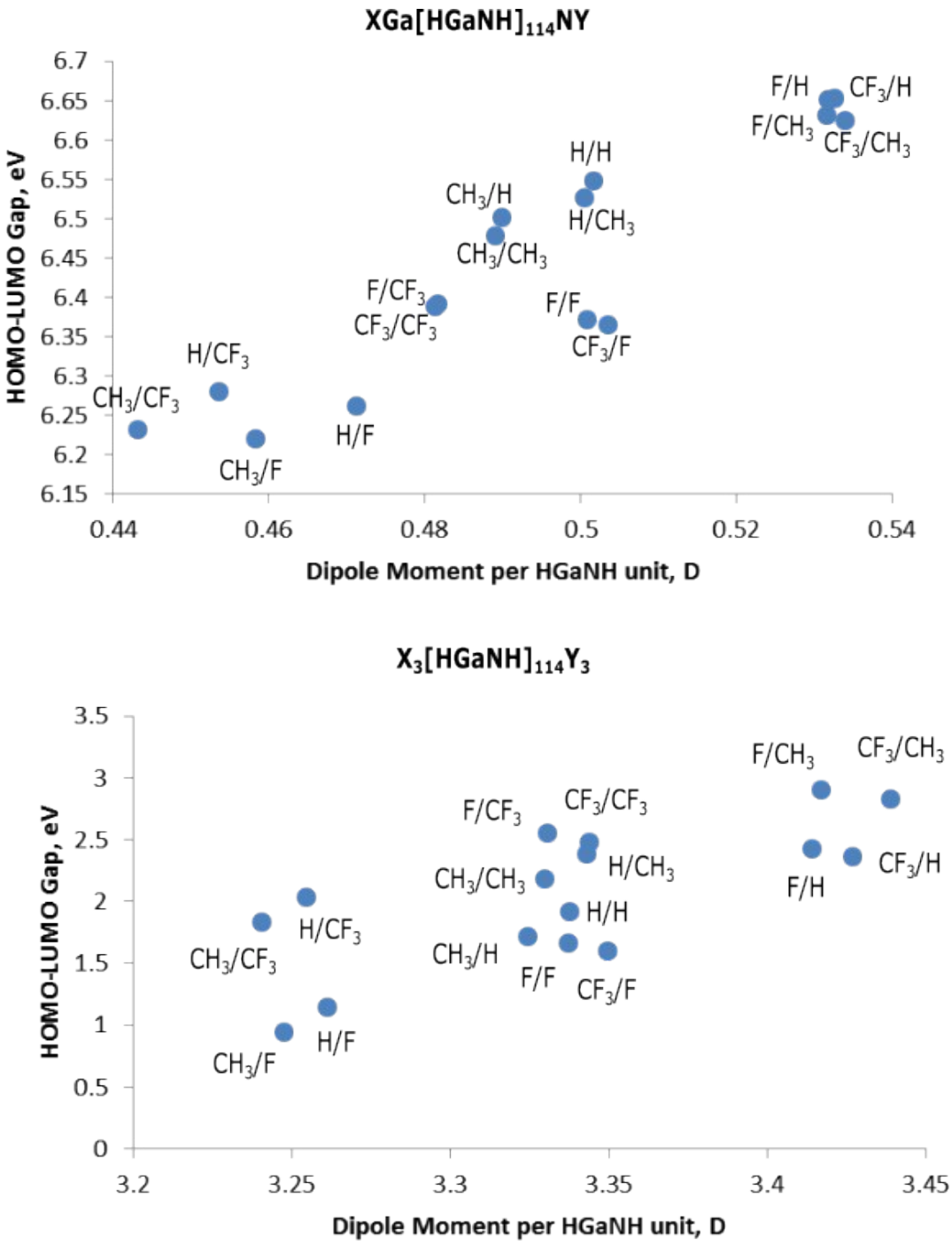
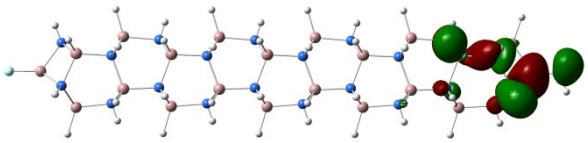
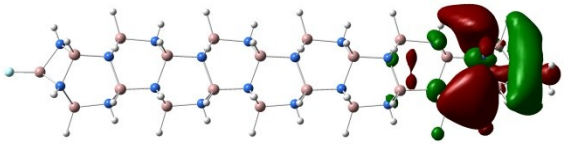


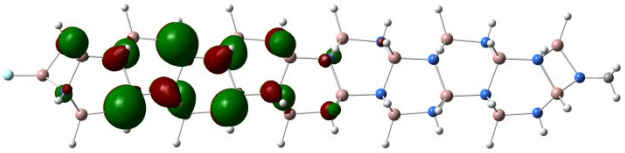
Figure S3 HOMO-LUMO gaps of the $XGa[HGaNH]_{114}NY$ and $X_3[HGaNH]_{114}Y_3$ oligomers with respect of their dipole moment values calculated per HGaNH unit. Tooltips for the particular oligomers are written in X/Y format.



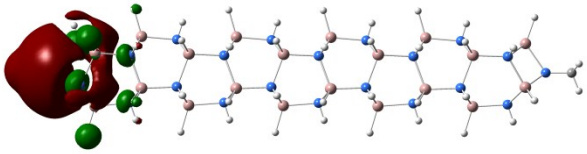
a)



b)



c)



d)

Figure S4 HOMO (a), LUMO(b) , HOMO-2(c) and LUMO+3 of $FGa(HGaNH_{30})NCH_3$ oligomer. Relatively to the HOMO energy, LUMO has energy 6.6 eV , LUMO has 6.8 eV and HOMO-2 has energy -0.1 eV. Blue color refers to N, pink to Ga, white to H, gray to C and light blue to F atoms.