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

Supporting Information

Cage Effect on Conformational Preference and Photophysics of Benzenediols in the Host-Guest Complex with 18-Crown-6

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Figure S1
Calculated IR spectra of 18C6•*cis*-HQ-I and 18C6•*trans*-HQ. The scaling factor of 0.9.346 is employed to reproduce the free OH stretching vibrational frequency of hydroquinone monomers.

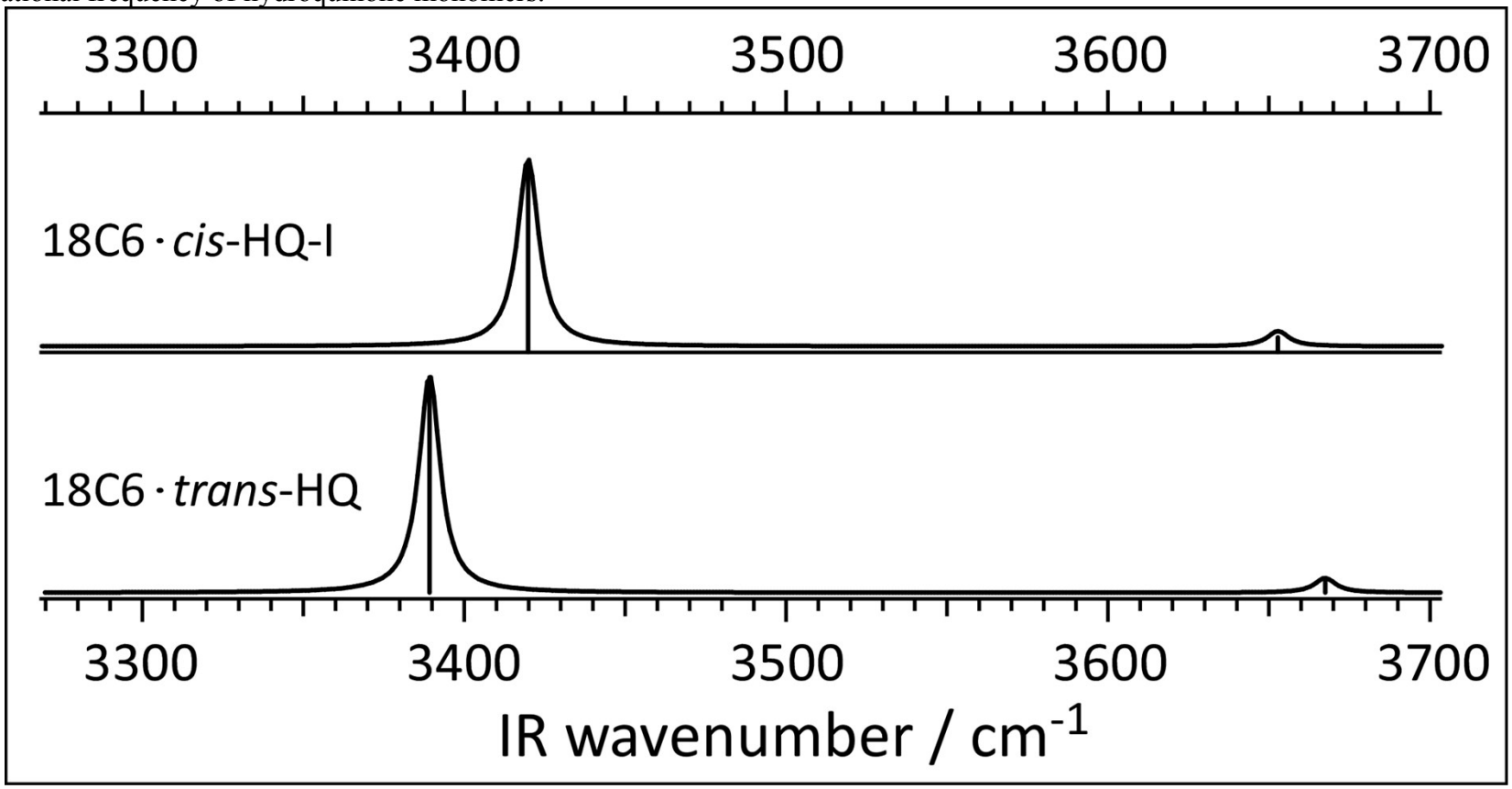


Figure S2
(a) The structure of 18C6-RE(I) complex. A dashed line represents the hydrogen bond.

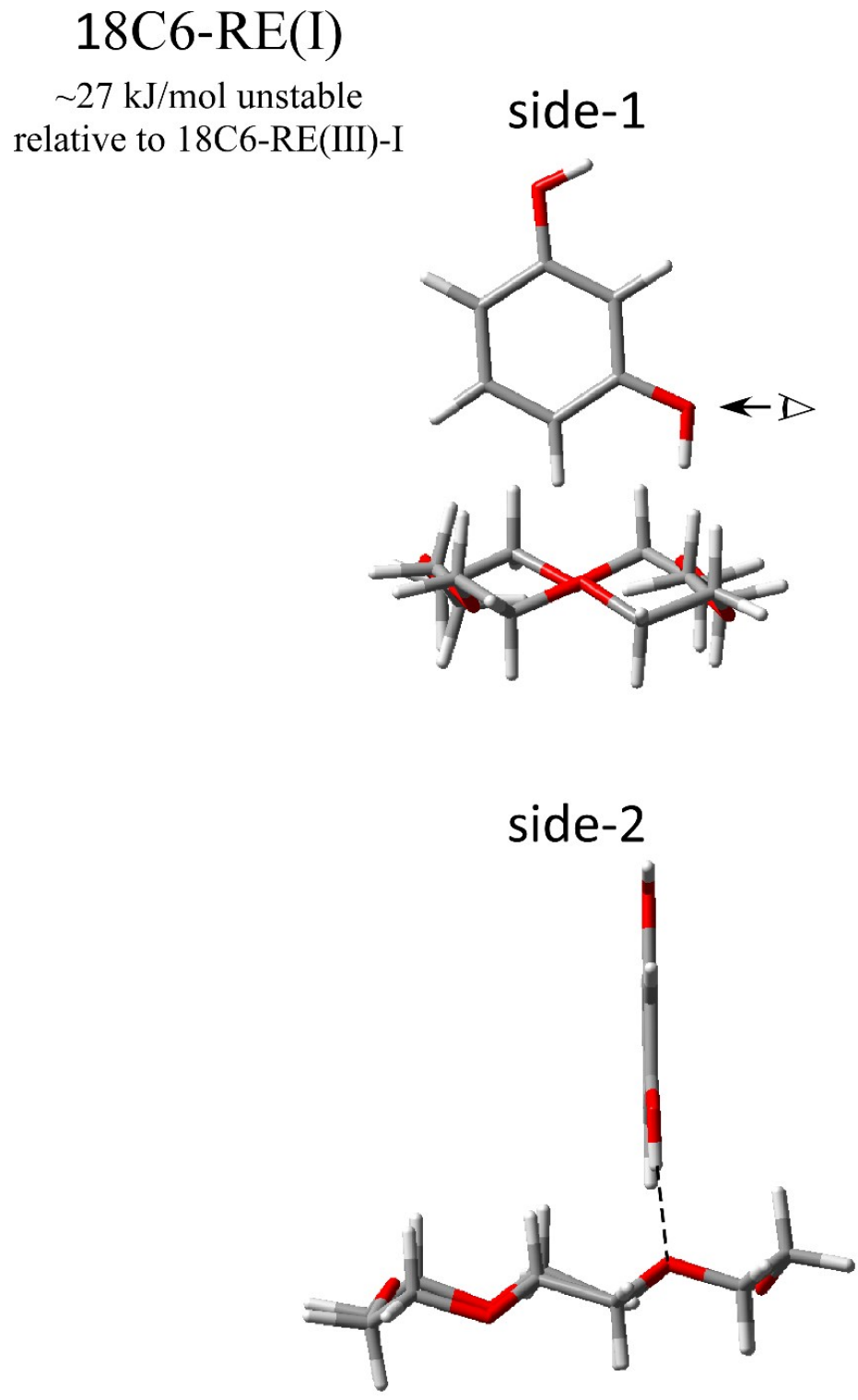


Figure S2
(b) The structure of unassigned 18C6-CA complex. The number listed in kJ/mol unit are the relative energy of the each isomer compare to the most stable A1 isomer (Figure 6). Dashed lines represent the hydrogen bond.

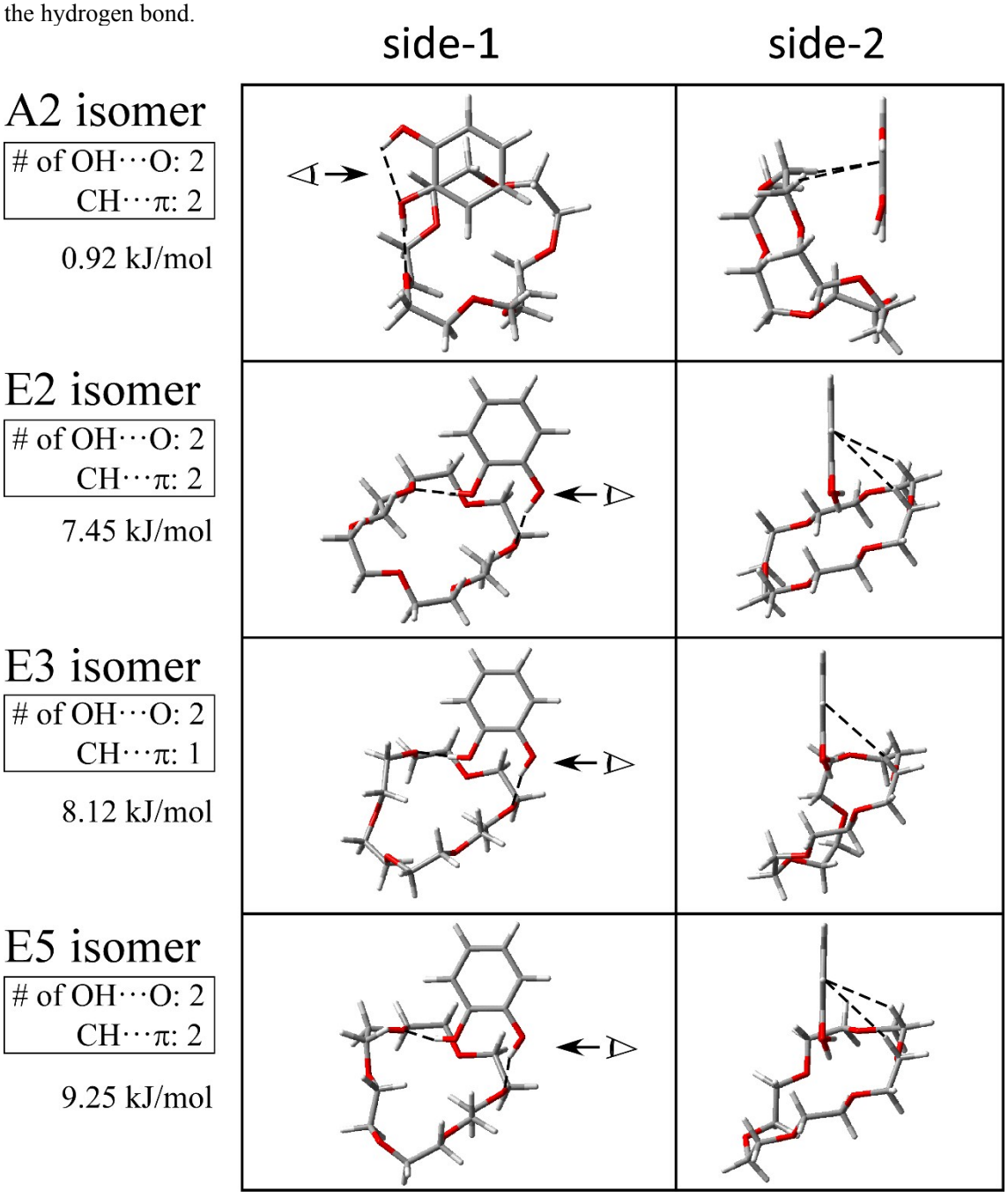
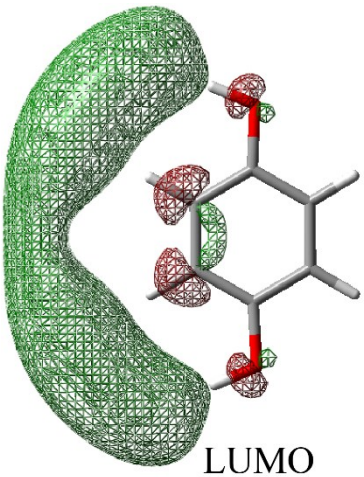
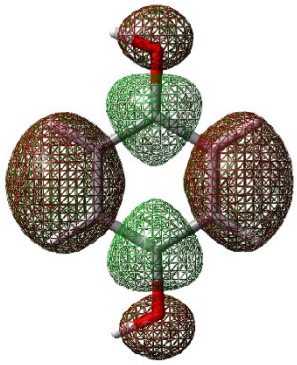


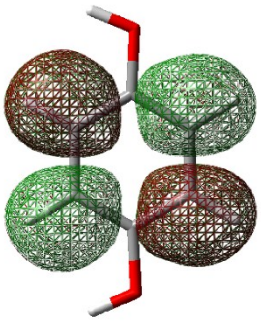
Figure S3
(a) The orbitals and transitions mainly involved in the S_1-S_0 and S_2-S_0 transitions with their coefficients for the *cis*-HQ monomer.



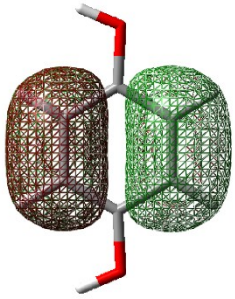
LUMO



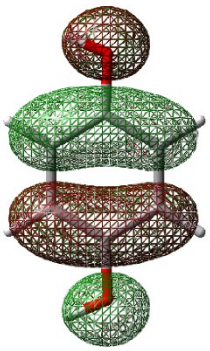
LUMO+2



LUMO+6



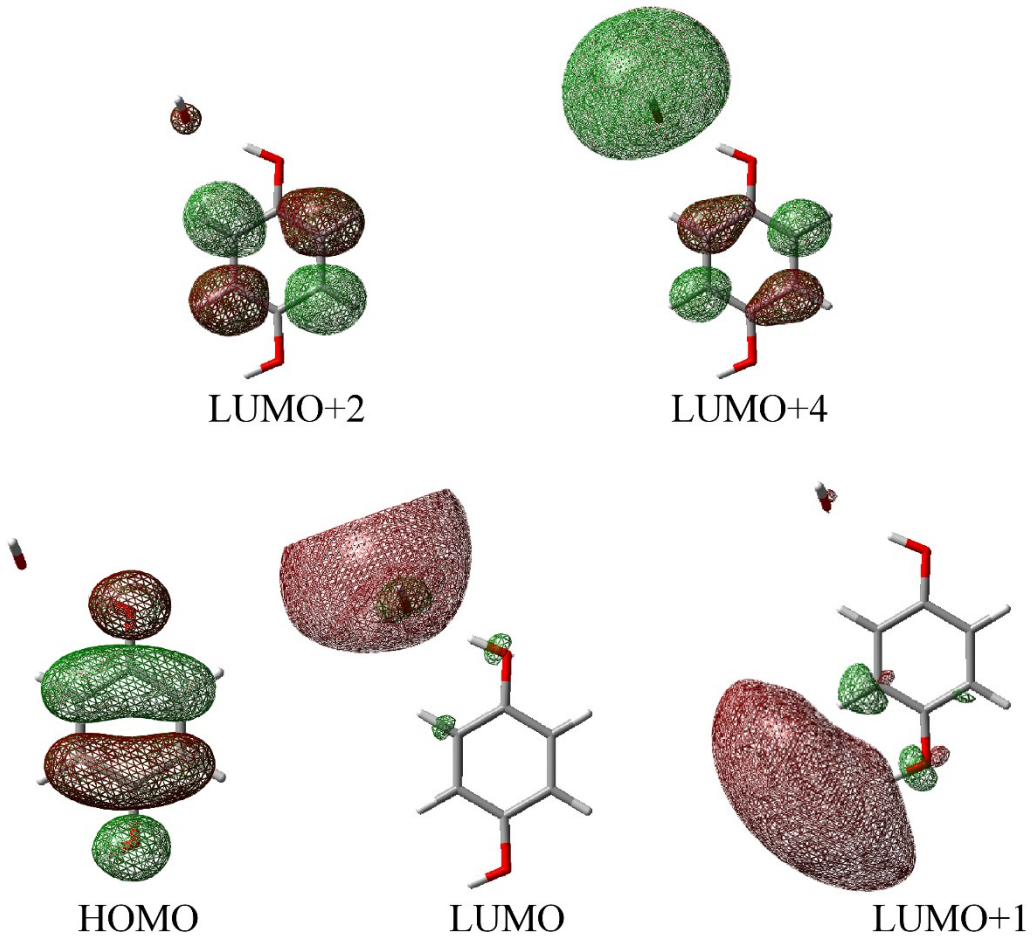
HOMO-1



HOMO

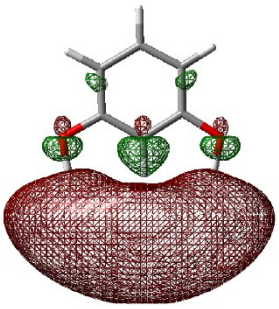
S_1-S_0 transition		S_2-S_0 transition	
Orb -> Orb*	Coefficient	Orb -> Orb*	Coefficient
HOMO-1 -> LUMO+6	0.20555	HOMO -> LUMO	0.66439
HOMO -> LUMO+2	0.67226		

(b) The orbitals and transitions mainly involved in the S_1-S_0 and S_2-S_0 transitions with their coefficients for the H_2O•*cis*-HQ 1:1 complex.

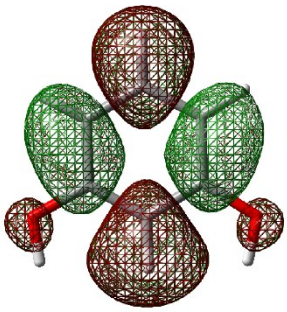


S_1-S_0 transition		S_2-S_0 transition	
Orb -> Orb*	Coefficient	Orb -> Orb*	Coefficient
HOMO -> LUMO+2	0.59820	HOMO -> LUMO	0.52745
HOMO -> LUMO+4	-0.31221	HOMO -> LUMO+1	0.40043

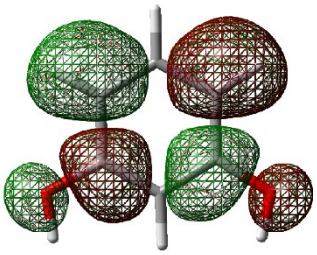
(c) The orbitals and transitions mainly involved in the S_1-S_0 and S_2-S_0 transitions with their coefficients for the RE (III) monomer.



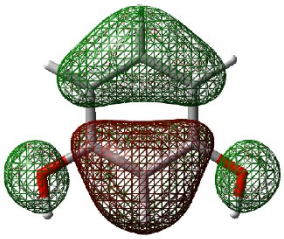
LUMO



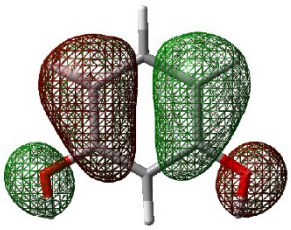
LUMO+3



LUMO+5



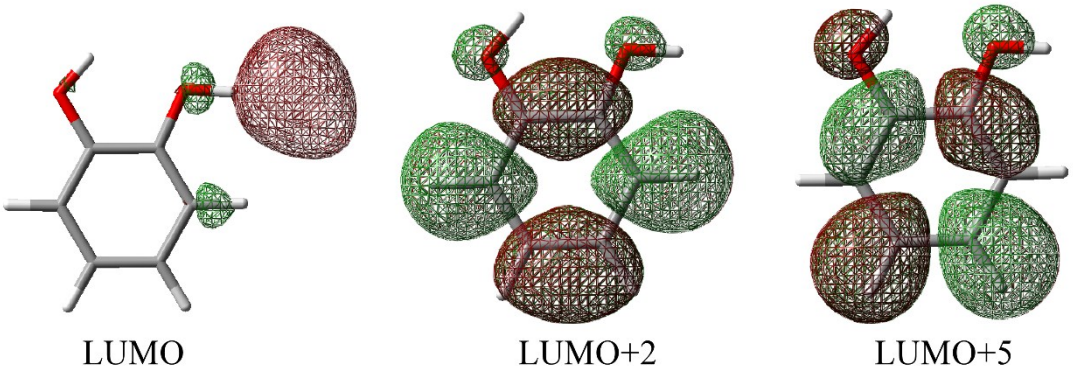
HOMO-1



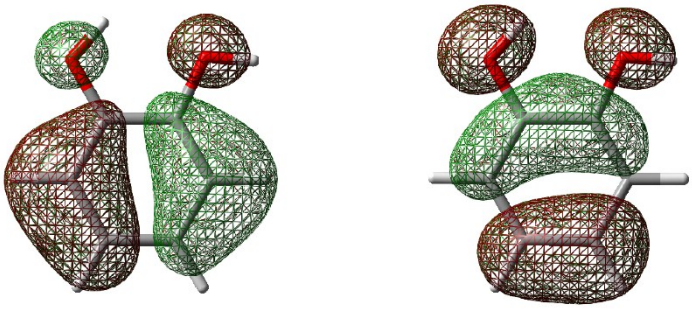
HOMO

S_1-S_0 transition		S_2-S_0 transition	
Orb -> Orb*	Coefficient	Orb -> Orb*	Coefficient
HOMO-1 -> LUMO+5	0.31059	HOMO -> LUMO	0.65193
HOMO -> LUMO+3	0.62861		

(d) The orbitals and transitions mainly involved in the S_1-S_0 and S_2-S_0 transitions with their coefficients for the CA monomer.



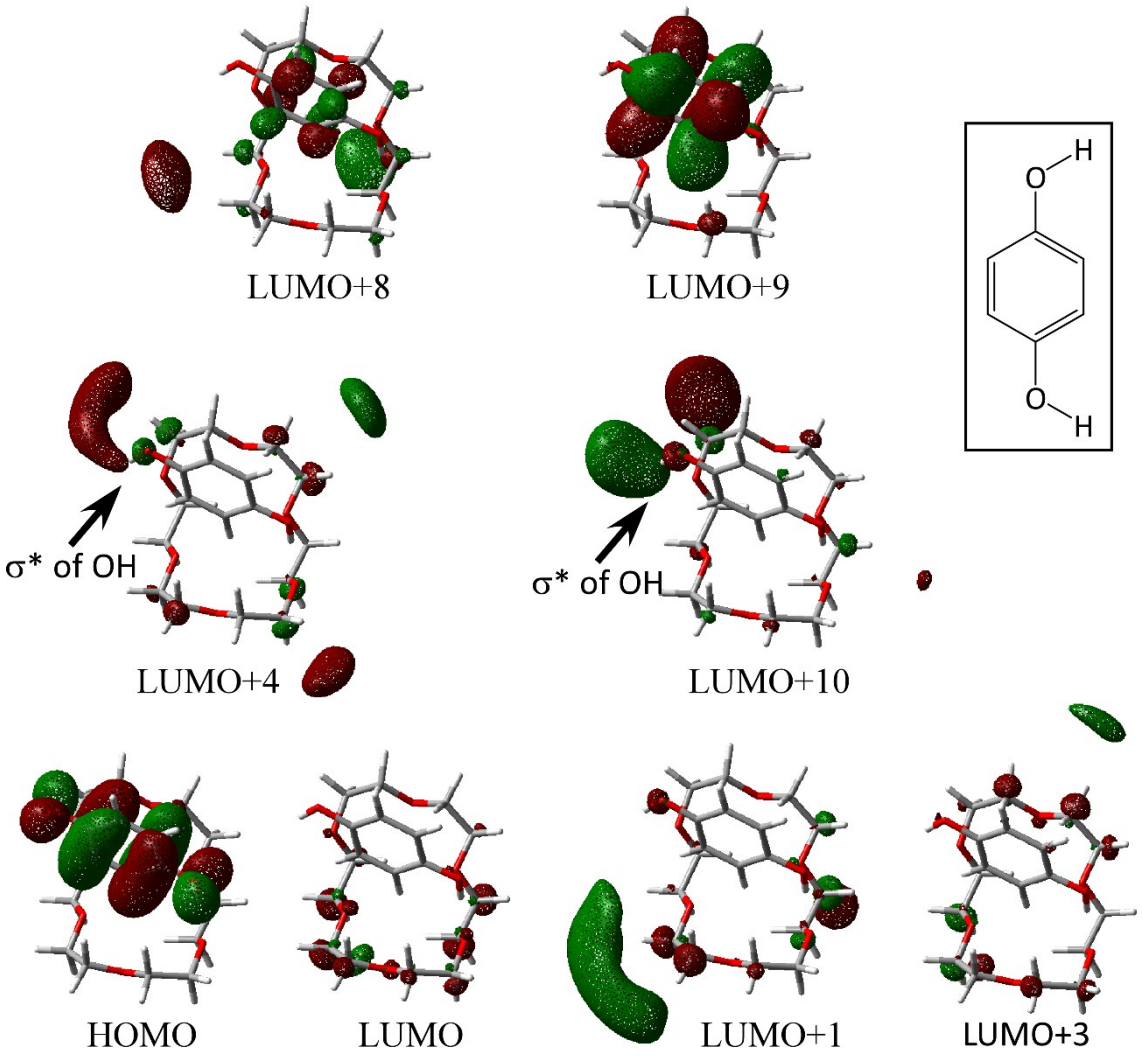
LUMO LUMO+2 LUMO+5



HOMO-1 HOMO

S_1-S_0 transition		S_2-S_0 transition	
Orb -> Orb*	Coefficient	Orb -> Orb*	Coefficient
HOMO-1 -> LUMO+5	-0.31677	HOMO -> LUMO	0.61810
HOMO -> LUMO+2	0.62206		

(e) The orbitals and transitions mainly involved in the S_1-S_0 and S_2-S_0 transitions with their coefficients for 18C6•HQ-I. The arrows indicate the σ* orbitals of free OH group.



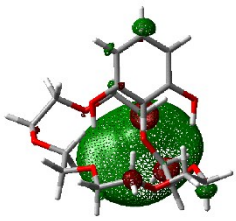
S_1-S_0 transition

Orb -> Orb*	Coefficient
HOMO -> LUMO+8	-0.21792
HOMO -> LUMO+9	0.59533

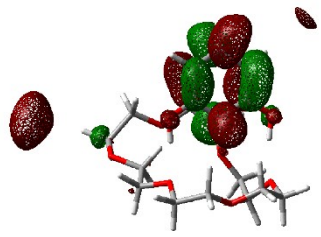
S_2-S_0 transition

Orb -> Orb*	Coefficient
HOMO -> LUMO	0.21089
HOMO -> LUMO+1	0.35140
HOMO -> LUMO+3	0.27927
HOMO -> LUMO+4	-0.13035
HOMO -> LUMO+10	0.12207

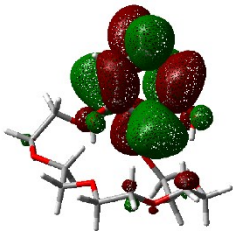
(f) The orbitals and transitions mainly involved in the S_1-S_0 and S_2-S_0 transitions with their coefficients for 18C6•RE(III)-I.



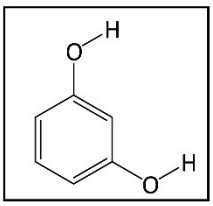
LUMO+5

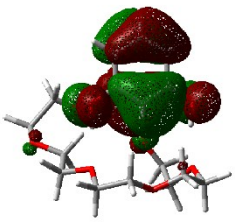


LUMO+9

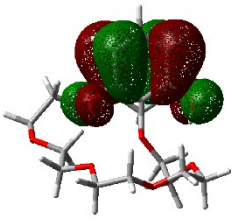


LUMO+10

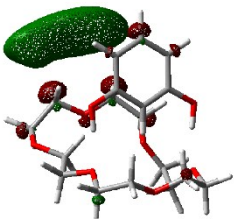




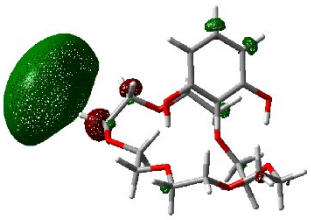
HOMO-1



HOMO



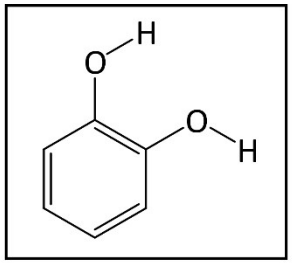
LUMO+3

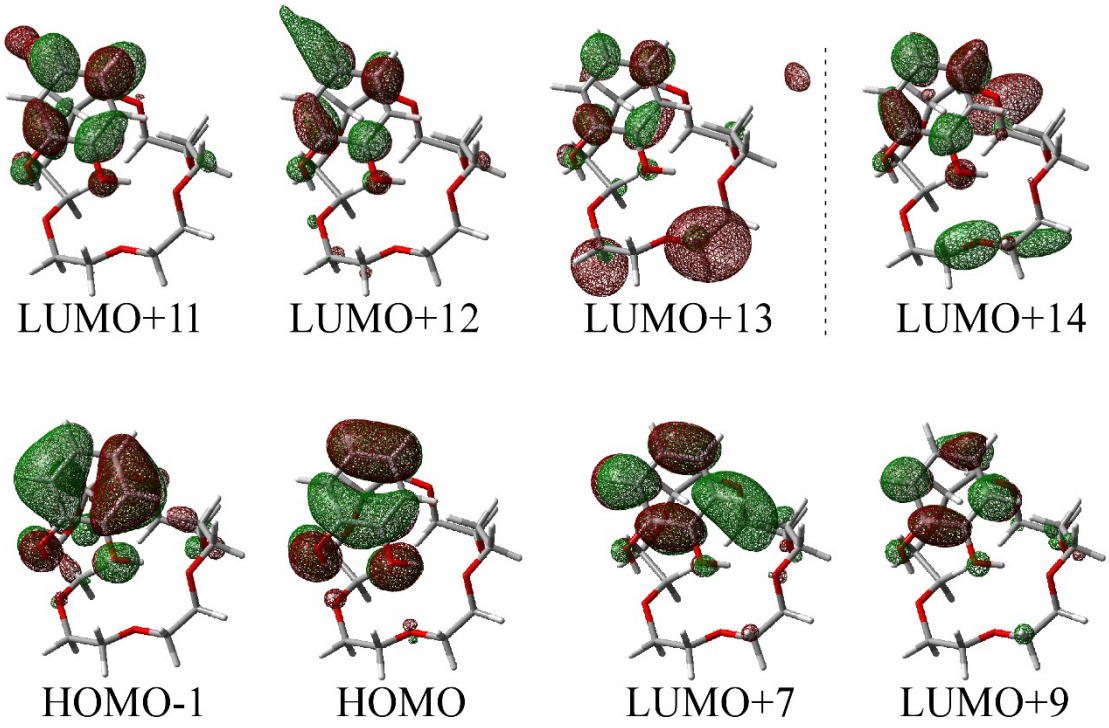


LUMO+4

S_1-S_0 transition		S_2-S_0 transition	
Orb -> Orb*	Coefficient	Orb -> Orb*	Coefficient
HOMO -> LUMO+9	0.30874	HOMO-1 -> LUMO+3	0.49718
HOMO -> LUMO+10	-0.50620	HOMO -> LUMO+4	-0.27960
		HOMO -> LUMO+5	-0.18789

(g) The orbitals and transitions mainly involved in the S_1-S_0 and S_2-S_0 transitions with their coefficients for 18C6•CA-E1





S_1-S_0 transition	
Orb -> Orb*	Coefficient
HOMO -> LUMO+7	0.50043
HOMO -> LUMO+9	0.26284

S_2-S_0 transition	
Orb -> Orb*	Coefficient
HOMO-1 -> LUMO+7	-0.29162
HOMO -> LUMO+11	-0.36542
HOMO -> LUMO+12	-0.25861
HOMO -> LUMO+13	-0.21039
HOMO -> LUMO+14	-0.22607