Determining structure and Zn-specific Lewis acid-base descriptors for diorganozincs in non-coordinating solvents using X-ray spectroscopy

Article

Supplemental Material

Supplementary Material

Supplementary information material for:

Determining structure and Zn-specific Lewis acid-base descriptors for diorganozincs in non-coordinating solvents using X-ray spectroscopy

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This pdf includes:

Supplementary tables

Supplementary Table 1. Calculated $ZnEt_2$ (PCM toluene) bend angle and self-consistent field (SCF) energy.

C-Zn-C bend angle / °	SCF energy / E_h	SCF energy / kJ mol^{-1}	SCF energy difference relative to 180° / kJ mol^{-1}
180	-1937.931040	-5088037.947	0.00
174	-1937.930684	-5088037.011	0.94
168	-1937.929975	-5088035.150	2.80
162	-1937.928594	-5088031.523	6.42
157	-1937.926747	-5088026.673	11.27
151	-1937.924378	-5088020.454	17.49
145	-1937.921562	-5088013.061	24.89
140	-1937.918185	-5088004.195	33.75

Supplementary Table 2. Calculated $ZnEt_2$ (PCM hexane) dihedral angle (C-C-Zn-C-C) and self-consistent field (SCF) energy.

C-C-Zn-C-C dihedral angle / °	SCF energy / E_h	SCF energy / kJ mol^{-1}	SCF energy difference relative to 180° / kJ mol^{-1}
180	-1964.018061	-5156529.419	0.00
165	-1964.018056	-5156529.406	0.01
150	-1964.018056	-5156529.406	0.01
135	-1964.018069	-5156529.439	-0.02
120	-1964.018077	-5156529.461	-0.04
105	-1964.018100	-5156529.520	-0.10
90	-1964.018084	-5156529.479	-0.06

Supplementary Table 3. Calculated $ZnPh_2$ (PCM hexane) dihedral angle (C-C-Zn-C-C) and self-consistent field (SCF) energy.

C-C-Zn-C-C dihedral angle / °	SCF energy / E_h	SCF energy / kJ mol^{-1}	SCF energy difference relative to 178° / kJ mol^{-1}
178	-2269.290069	-5958021.076	0.00
150	-2269.290141	-5958021.266	-0.19
138	-2269.290186	-5958021.385	-0.31
118	-2269.290311	-5958021.711	-0.64
101	-2269.290333	-5958021.771	-0.69

Supplementary Table 4. Calculated staggered and eclipsed conformers of $Zn(C_6F_5)_2$ and $ZnPh_2$ (PCM toluene) and resultant (SCF) energy.

Sample	Orientation	PCM	C-C-Zn-C-C angle / °	SCF energy / E_h	SCF energy / kJ mol^{-1}	SCF energy difference/ kJ mol^{-1}
$ZnPh_2$	Staggered	Toluene	90	-2269.292704	-5958027.995	0.63
	Eclipsed	Toluene	180	-2269.292466	-5958027.371	
$Zn(C_6F_5)_2$	Staggered	Toluene	110	-3263.583982	-8568539.744	0.59
	Eclipsed	Toluene	172	-3263.584204	-8568540.329	

Supplementary Table 5. Calculated valence molecular orbitals for ZnR_2 complexes. Valence molecular orbitals with strong Zn 4p (green) and Zn 4s (red) contributions have been highlighted.

	HOMO-5	HOMO-4	HOMO-3	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4
$ZnMe_2$				Zn s 27%	Zn p 18%	Zn s 59%	Zn p 86%	Zn p 86%		
$ZnEt_2$				Zn s 23%	Zn p 16%	Zn s 49%	Zn p 70%	Zn p 80%		
$Zn(n\text{-}Pr)_2$				Zn s 21%	Zn p 16%	Zn s 53%	Zn p 76%	Zn p 81%		
$Zn(n\text{-}Bu)_2$				Zn s 19%	Zn p 15%	Zn s 54%	Zn p 75%	Zn p 80%		
$Zn(i\text{-}Pr)_2$				Zn s 22%	Zn p 15%	Zn p 75%	Zn s 44%	Zn p 68%		
$Zn(t\text{-}Bu)_2$				Zn s 22%	Zn p 14%	Zn s 32%	Zn p 66%	Zn p 66%		
stag $ZnPh_2$	Zn s 18.4%	Zn p 15%				Zn p 42%	Zn p 46%	Zn s 54%		
ecl $ZnPh_2$	Zn s 18.3%	Zn p 15%				Zn p 41%	Zn s 52%	Zn p 70%		
ecl $Zn(C_6F_5)_2$	Zn s 23%	Zn p 17%				Zn p 38%	Zn p 38%	Zn s 49%		
stag $Zn(C_6F_5)_2$	Zn s 23%	Zn p 17%				Zn p 35%	Zn p 35%	Zn s 45%		
stag $Zn(2,6\text{-}C_6F_2H_3)_2$	Zn s 20%	Zn p 16%				Zn p 37%	Zn p 29%	Zn s 67%		
ecl $Zn(3,5\text{-}C_6F_2H_3)_2$	Zn s 20%	Zn p 16%				Zn p 36%	Zn p 52%	Zn s 55%		
stag $Zn(3,4,5\text{-}C_6F_3H_2)_2$	Zn s 21%	Zn p 16%				Zn p 41%	Zn p 42%	Zn s 53%		
ecl $Zn(2,3,5,6\text{-}C_6F_4H_1)_2$	Zn s 22%	Zn p 17%				Zn p 35%	Zn p 16%	Zn p 47%	Zn s 62%	
stag $Zn(2,4,6\text{-}C_6F_3H_2)_2$	Zn s 23%	Zn p 17%				Zn p 41%	Zn p 42%			Zn s 67%
stag $Zn(4\text{-}C_6F_1H_4)_2$	Zn s 21%	Zn p 16%				Zn p 48%	Zn p 50%	Zn s 54%		

Supplementary Table 6. Calculated valence molecular orbitals for organozinc complexes. Valence molecular orbitals with strong Zn 4p (green) and Zn 4s (red) contributions have been highlighted.

	HOMO-32	HOMO-16	HOMO-15	HOMO-14	HOMO-10	HOMO-9	HOMO-8	HOMO-7	HOMO-6	HOMO-5	HOMO-1	HOMO
$ZnEt_2$											Zn s 23%	**Zn p 16%**
$ZnCl_2(THF)_2$								Zn s 3% Zn p 6%	**Zn p 9%**	Zn p 2%		
$[Zn(NCMe)_6]^{2+}$	Zn s 3%	**Zn p 7%**	**Zn p 7%**	**Zn p 7%**								
$[Zn(OH_2)_6]^{2+}$				Zn 4s 10%	**Zn 4p 7%**	**Zn 4p 6%**	**Zn 4p 6%**					

LUMO	LUMO+1	LUMO+2	LUMO+3
Zn s 49%	**Zn p 70%**	**Zn p 80%**	
Zn s 25% Zn p 22%	Zn p 27%	**Zn p 46%**	**Zn p 48%**
Zn s 29%	**Zn p 35%**	**Zn p 36%**	**Zn p 36%**
Zn s 19%	**Zn p 61%**	**Zn p 61%**	**Zn 4p 65%**

Supplementary Table 7. Electronic structure descriptors for ZnR_2 and common zinc-containing species: calculated *E*(Zn 1s) energy, *E*(OMO,Zn p), *E*(UMO,Zn p), Zn-specific hardness (μ_{Zn}), Zn-specific absolute electronegativity (χ_{Zn}), Global electrophilicity index (ω_{Zn}), Taft inductive substituent constant (I_R), and experimental R-VtC-XES energy gap, *E*(gap, exp).

Sample	PCM	*E*(Zn 1s) / eV	*E*(OMO,Zn p) / eV	*E*(UMO,Zn p) / eV	Zinc-specific hardness, η_{Zn} / eV	Zinc-specific absolute electronegativity, χ_{Zn} / eV	Global electrophilicity index, ω_{zn} / eV	Taft constant, I_R / kcal mol^{-1}	R-VtC-XES energy gap[c], *E*(gap,exp) / eV
$ZnMe_2$	Toluene	9674.62	9.37	-1.75	11.12	3.81	0.65	0.0 [a]	6.02
$ZnEt_2$	Toluene	9674.52	8.71	-1.63	10.33	3.54	0.61	-0.10 [a]	5.30
Zn(*i*-Pr)$_2$	Toluene	9674.50	8.29	-1.61	9.90	3.34	0.56	-0.19 [a]	4.92
Zn(*n*-Pr)$_2$	Toluene	9674.53	8.71	-1.61	10.32	3.55	0.61	0.10 [a]	
Zn(*n*-Bu$_{2)}$	Toluene	9674.53	8.67	-1.62	10.29	3.52	0.60		
Zn(*t*-Bu)$_2$	Toluene	9674.53	8.05	-1.75	9.80	3.15	0.51	-0.30 [a]	
Staggered $ZnPh_2$	Toluene	9675.02	9.58	-1.17	10.76	4.20	0.82	0.60 [a]	5.54
Eclipsed $ZnPh_2$	Toluene	9675.02	9.58	-1.01	10.59	4.29	0.87		
Staggered $Zn(C_6F_5)_2$	Toluene	9676.15	11.66	-0.58	12.24	5.54	1.25		7.01
Eclipsed $Zn(C_6F_5)_2$	Toluene	9676.15	11.65	-0.26	11.91	5.69	1.36		
Zn(4-$C_6F_1H_4)_2$	Toluene	9675.16	9.90	-1.20	11.10	4.45	0.85		
Zn(2,6-$C_6F_2H_3)_2$	Toluene	9675.57	10.85	-0.75	11.60	5.05	1.10		
Zn(3,5-$C_6F_2H_3)_2$	Toluene	9675.48	10.24	-0.61	10.85	4.82	1.07		
Zn(3,4,5-$C_6F_3H_2)_2$	Toluene	9675.59	10.46	-0.86	11.32	4.80	1.02		
Zn(2,4,6-$C_6F_3H_2)_2$	Toluene	9675.71	11.14	-0.74	11.88	5.20	1.14		
Zn(2,3,5,6-$C_6F_4H_1)_2$	Toluene	9676.02	11.45	-0.26	11.71	5.60	1.34		
$ZnEt_2$	Hexane	9674.61	8.75	1.58	7.17	5.17	1.86		
$[Zn(NCMe)_6]^{2+}$	MeCN	9675.29	15.53	1.75	13.78	8.64	2.71		13.23
$[Zn(OH_2)_6]^{2+}$	Water	9675.09	15.67	1.75	13.92	8.71	2.73		16.06
$ZnCl_2(THF)_2$	THF	9674.94	11.30	-2.30	13.60	4.50	0.74		10.04
$[ZnCl_4]^{2-}$	Ionic Liquid[b]	9673.96	10.69	-3.32	14.01	3.69	0.48		10.18

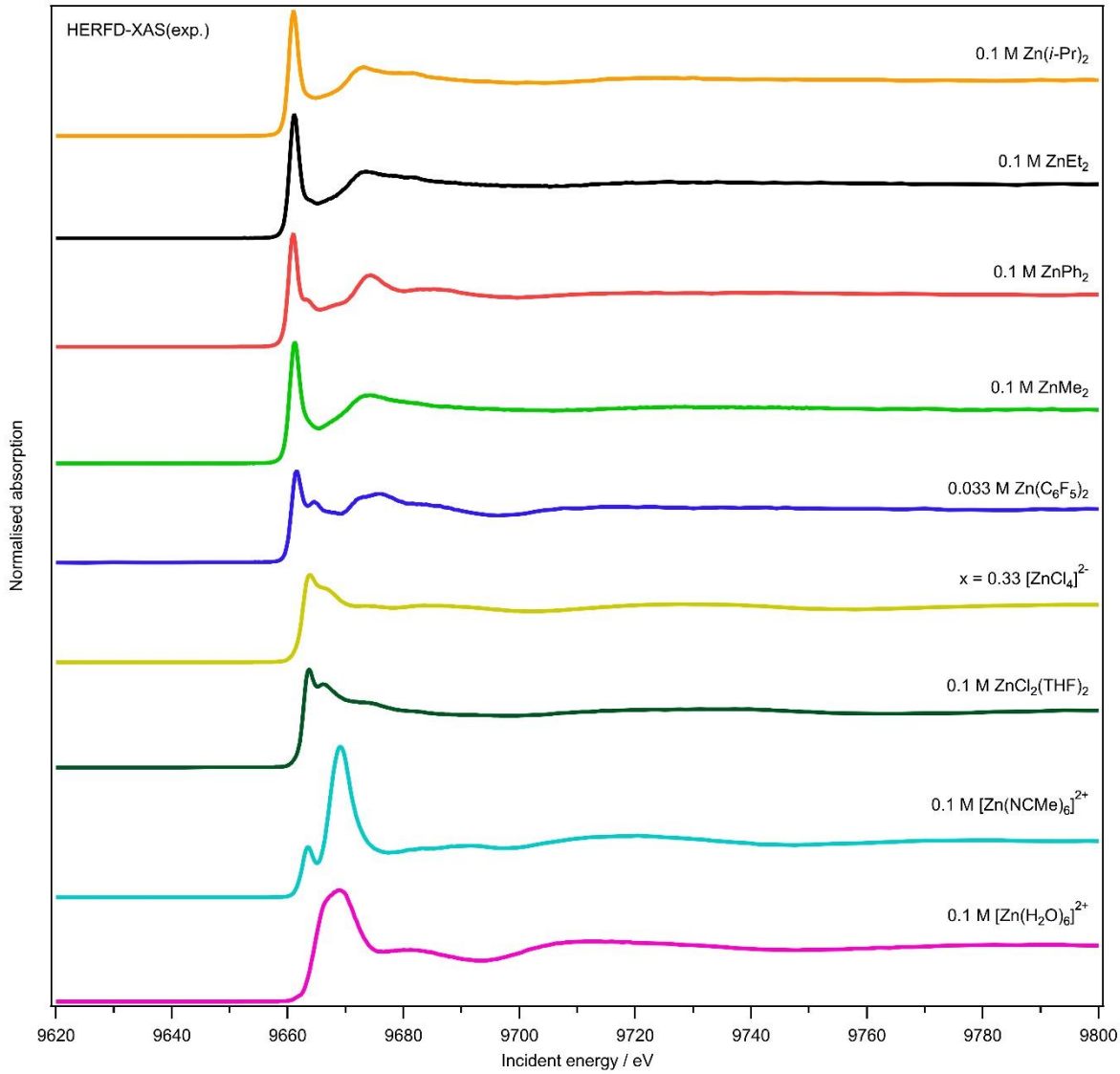
[a] Taken from reference [1]. [b] Dielectric constant of 11.40. [c] Obtained by fitting a gaussian peak to R-VtC-XE spectra and shifting by the elastic shift in Supplementary Table 8.

Supplementary Table 8. Experimental fitting of the R-VtC-XE spectra for ZnR_2 and zinc-containing species.

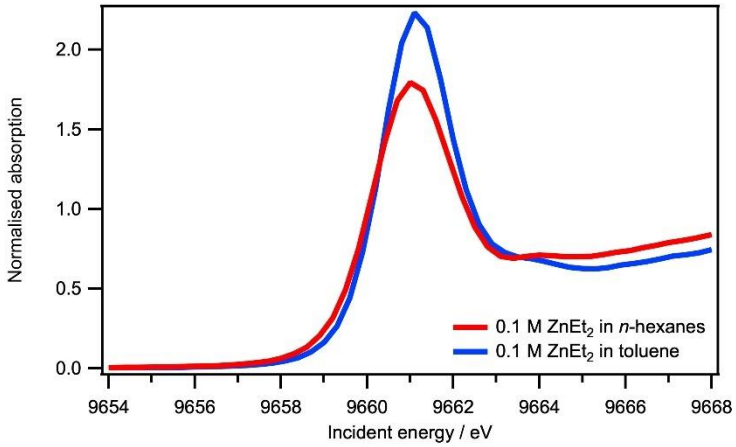
Compound	Scan type	Scan	Incident energy / eV	Fitting type	Elastic peak / eV	Difference / eV	Applied shift	
							NR-VtC-XES / eV	R-VtC-XES / eV[a]
0.1 M $ZnMe_2$ in toluene	RXES	207495	9661.40	Gauss	9661.46	-0.06	-0.06	0.06
0.1 M $ZnEt_2$ in toluene	RIXS map	164772	9661.10	Gauss	9660.73	0.37	0.37	-0.37
0.1 M Zn(*i*-Pr)$_2$ in toluene	RXES	183901	9661.00	Gauss	9660.56	0.44	0.44	-0.44
0.1 M $ZnPh_2$ in toluene	RXES	183933	9661.00	Gauss	9660.63	0.37	0.37	-0.37
0.033 M $Zn(C_6F_5)_2$ in toluene	RXES	184090	9661.50	Gauss	9661.15	0.35	0.35	-0.35
0.1 M $ZnCl_2$ in THF ($ZnCl_2(THF)_2$)	RXES	234217	9663.60	Gauss	9665.26	-1.66	-1.66	1.66
0.1 M $Zn(OTf)_2$ in MeCN ($[Zn(NCMe)_6]^{2+}$)	RXES	184237	9663.40	Gauss	9662.93	0.47	0.47	-0.47
0.1 M $ZnCl_2$ in water ($[Zn(OH_2)_6]^{2+}$)	RIXS map	164936	9665.80	Gauss	9665.43	0.37	0.37	-0.37
x = 0.33 $ZnCl_2$ in omimCl ($[ZnCl_4]^{2-}$)	RIXS map	142503	9663.80	Gauss	9663.90	-0.01	-0.01	0.01

[a] R-VtC-XES shifts are inverted to align with energy transfer plotting conventions.

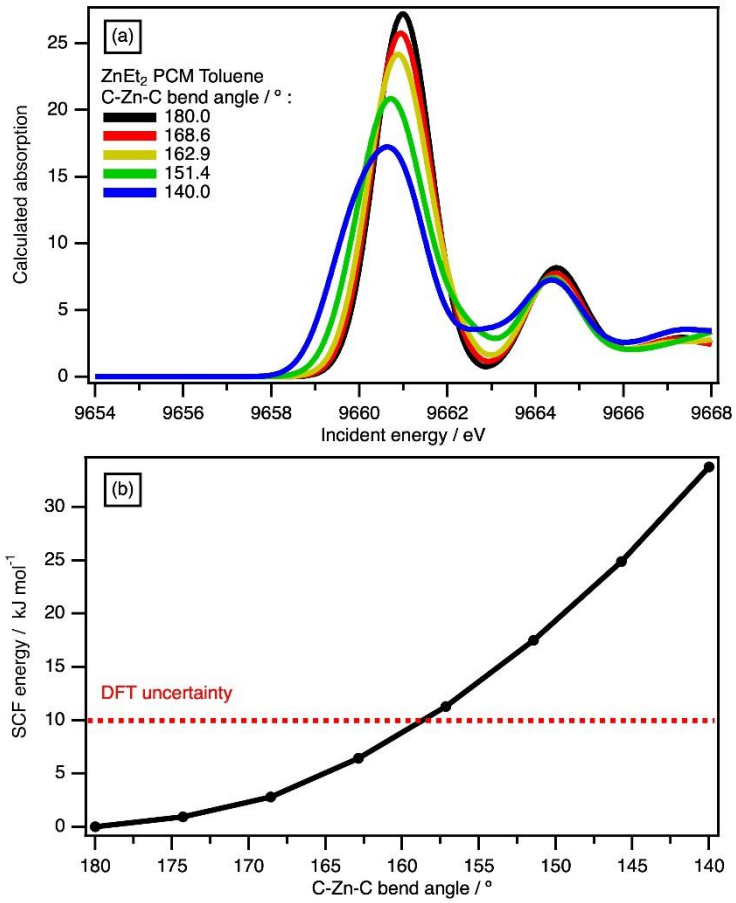
Supplementary Figures



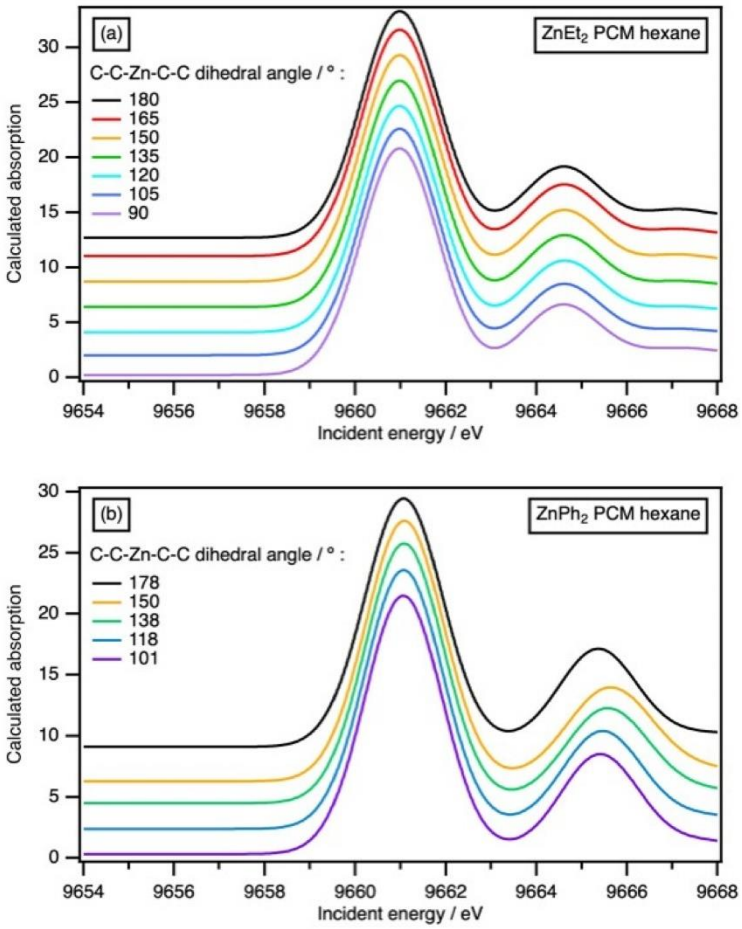
Supplementary Figure 1. Zn 1s HERFD-XAS (y intensities normalised) spectra of organozinc compounds ZnR_2 (R = Me, Et, *i*-Pr, Ph, C_6F_5, concentration 0.1 M for all apart from C_6F_5 which was 0.033 M), $[ZnCl_4]^{2-}$ (*x* = 0.33 $ZnCl_2$ in $[C_8C_1Im]Cl$), $ZnCl_2(THF)_2$ (0.1 M $ZnCl_2$ in THF), $[Zn(NCMe)_6]^{2+}$ (0.1 M $Zn(OTf)_2$ in MeCN) and $[Zn(OH_2)_6]^{2+}$ (0.1 M $ZnCl_2$ in H_2O).



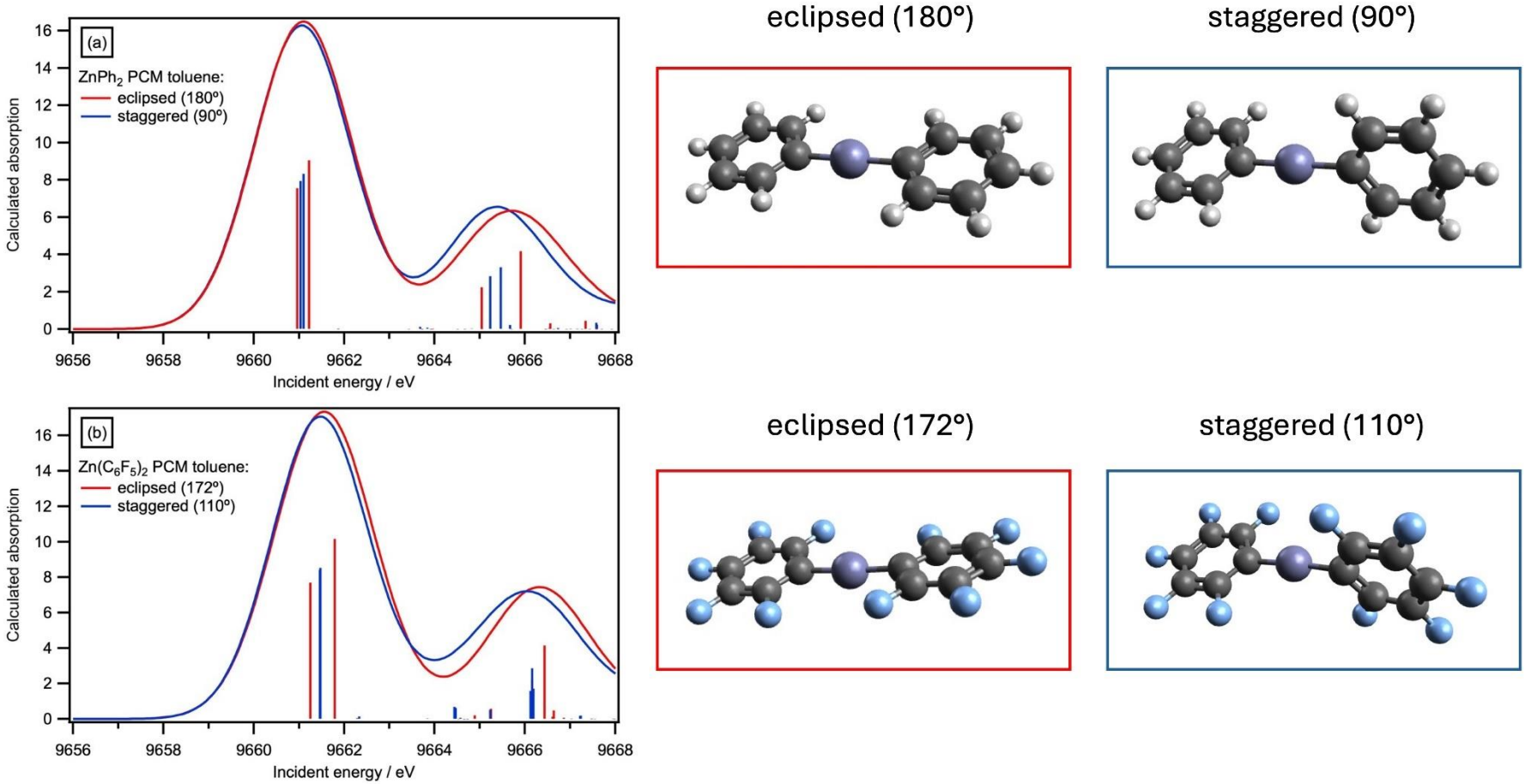
Supplementary Figure 2. Zn 1s XA spectra (y-intensities normalised) of 0.1 M $ZnEt_2$ in *n*-hexanes and toluene.



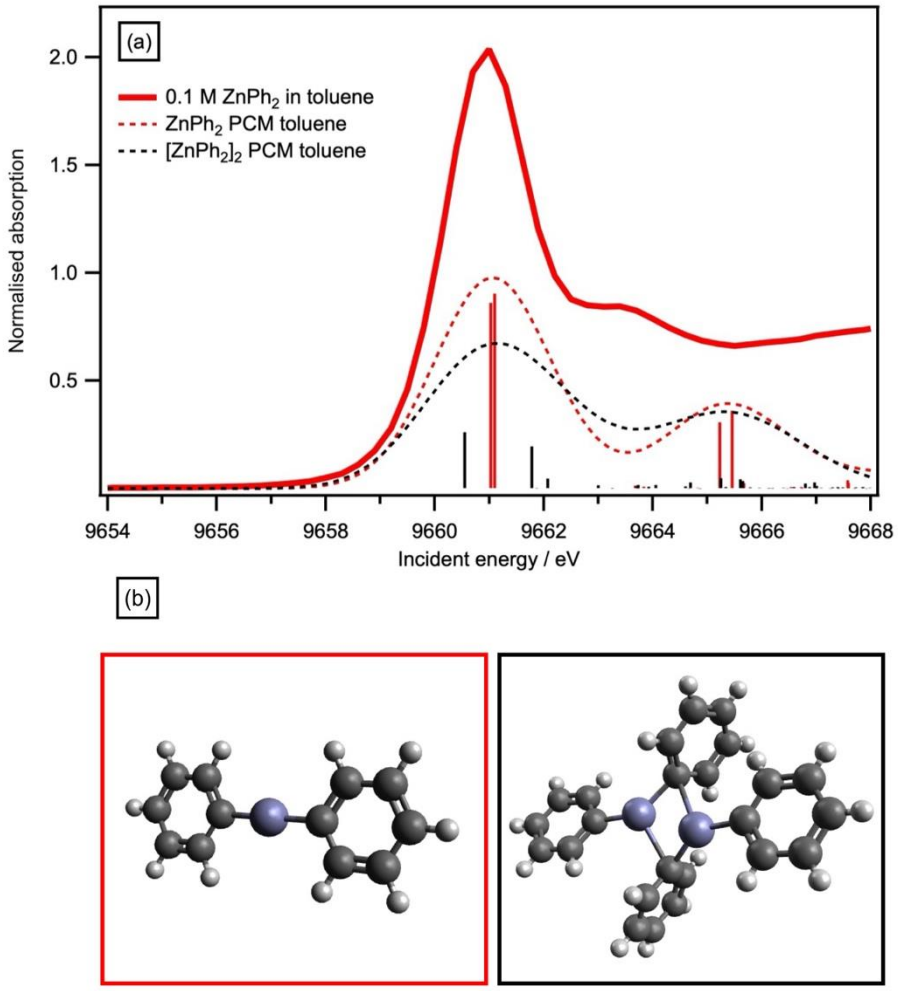
Supplementary Figure 3. (a) Calculated Zn 1s XA spectra of $ZnEt_2$ (PCM toluene) at different bend angles (FWHM: 2.5 eV, applied shift of -8.90 eV); (b) calculated SCF energy as a function of $ZnEt_2$ bend angle. The red line highlights the error of the DFT uncertainty.



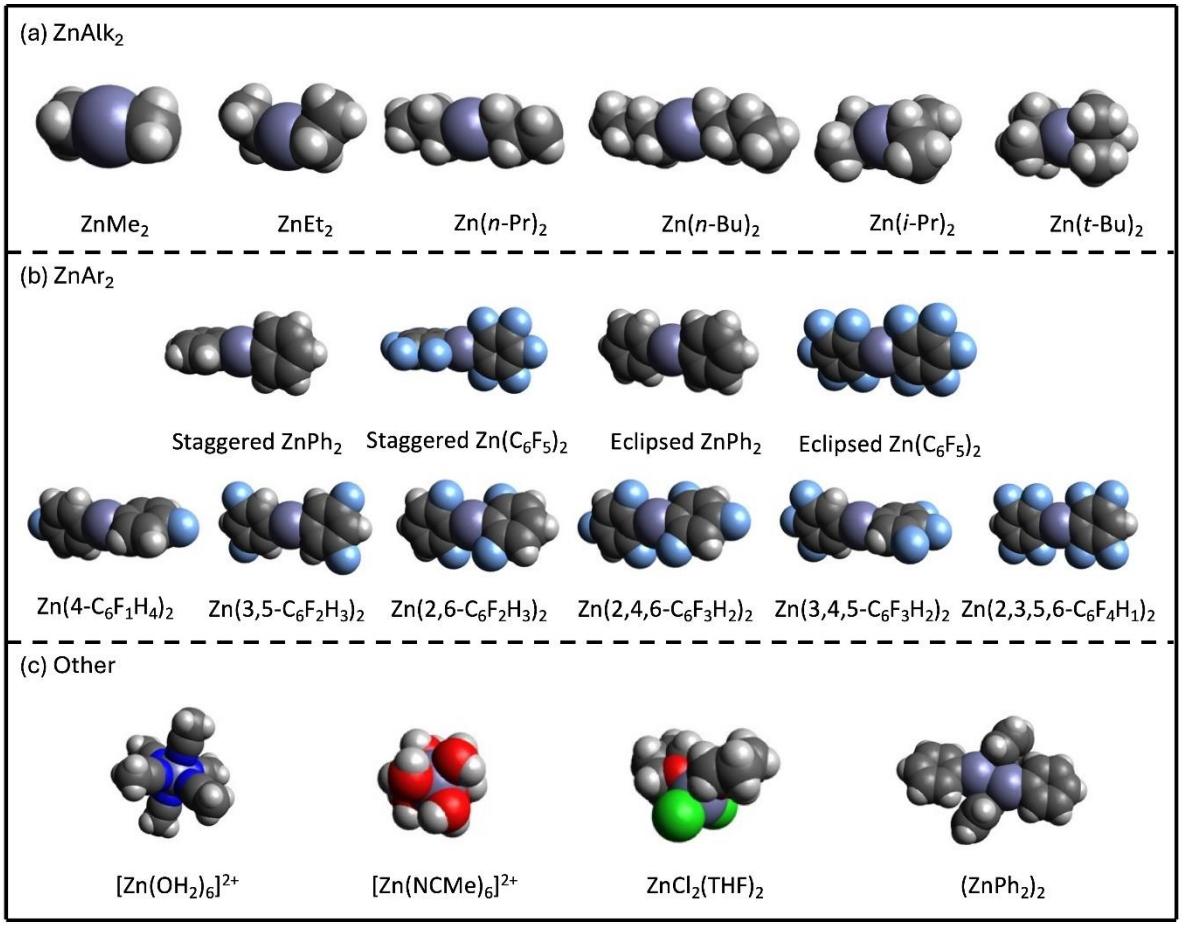
Supplementary Figure 4. Calculated Zn 1s XA spectra as a function of dihedral angle: (a) $ZnEt_2$ (PCM hexane, FWHM 2.5 eV, applied shift of -8.90 eV), (b) $ZnPh_2$ (PCM hexane, FWHM 2.5 eV, applied shift of -8.90 eV).



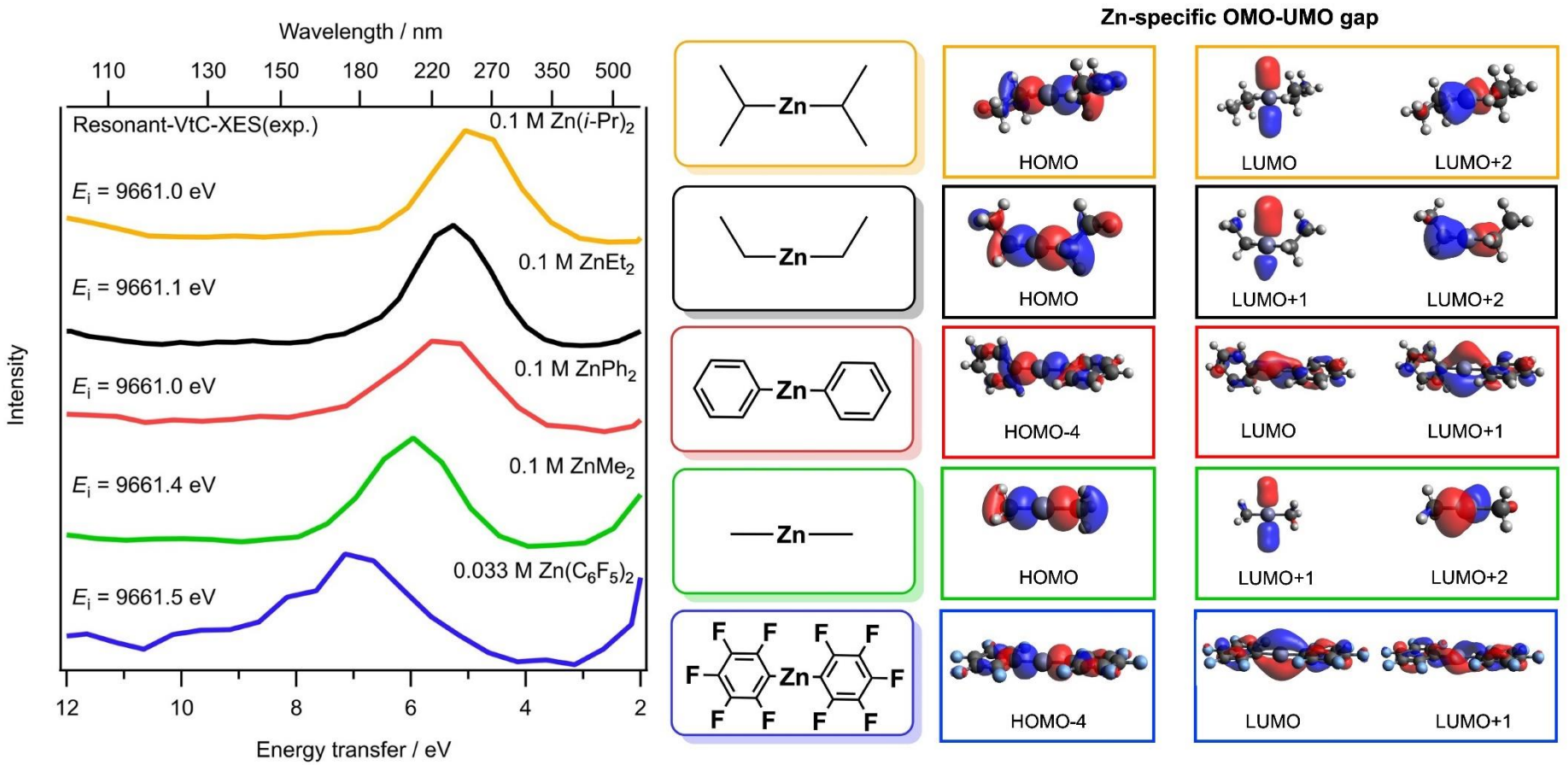
Supplementary Figure 5. Calculated Zn 1s XA spectra of staggered and eclipsed conformers of (a) $ZnPh_2$ (PCM toluene, FWHM 2.5 eV, applied shift of -8.9 eV) and (b) $Zn(C_6F_5)_2$ (PCM toluene, FWHM 2.5 eV, applied shift of -8.90 eV).



Supplementary Figure 6. (a) Zn 1s XA spectra of 0.1 M $ZnPh_2$ in toluene, calculated $ZnPh_2$ and $(ZnPh_2)_2$ (PCM toluene, FWHM 2.5 eV, applied shift of -8.90 eV; (b) Calculated structures for $ZnPh_2$ (left, red box) and $(ZnPh_2)_2$ (right, black box). Coordinates for $(ZnPh_2)_2$ were taken from the solid-state $(ZnPh_2)_2$ structure in reference [2].

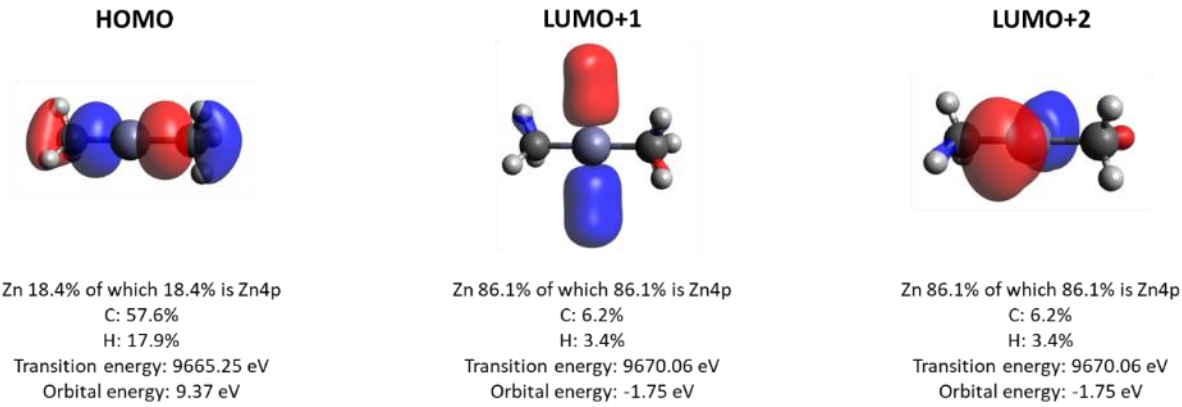


Supplementary Figure 7. Calculated ZnR_2 structures with a van der Waals space-filling model applied.



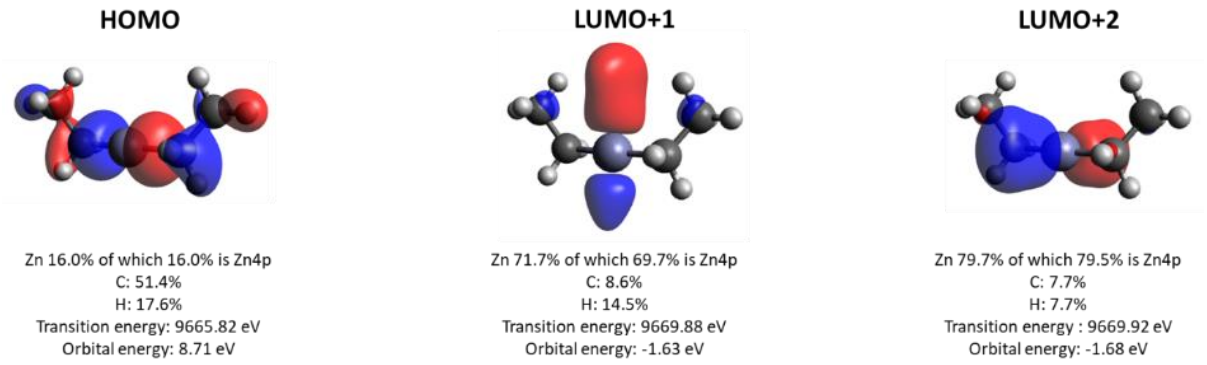
Supplementary Figure. 8. Left: Experimental R-VtC-XE spectra for ZnR_2 (R = Me, Et, *i*-Pr, Ph, C_6F_5, concentration 0.1 M for all apart from C_6F_5 which was 0.033 M). Right: Visual representations of key Zn p-based OMOs and UMOs; for ZnR_2 the UMO shown here is degenerate (or near-degenerate).

$ZnMe_2$ PCM toluene



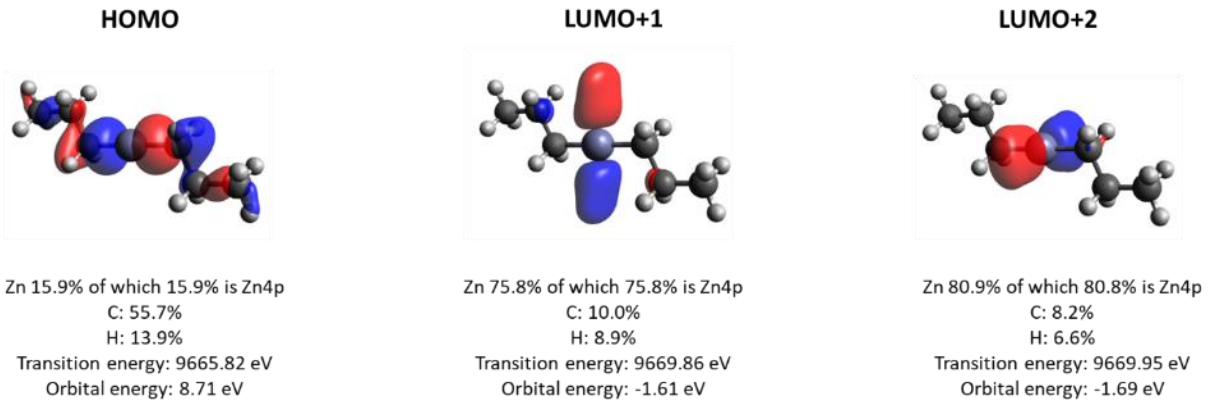
Supplementary Figure 9. Calculated molecular orbitals of $ZnMe_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.

$ZnEt_2$ PCM toluene



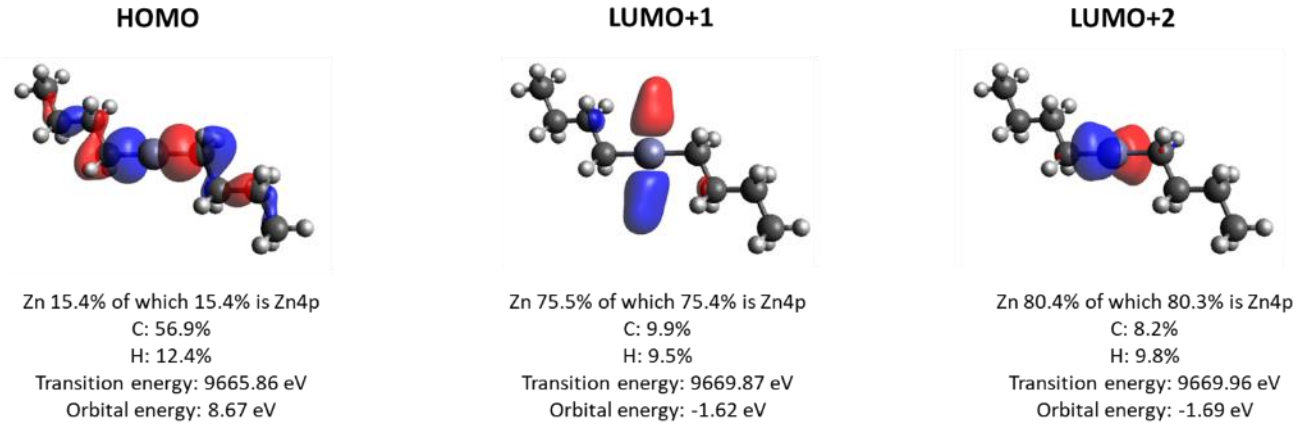
Supplementary Figure 10. Calculated molecular orbitals of $ZnEt_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.

Zn(*n*-Pr)$_2$ PCM toluene



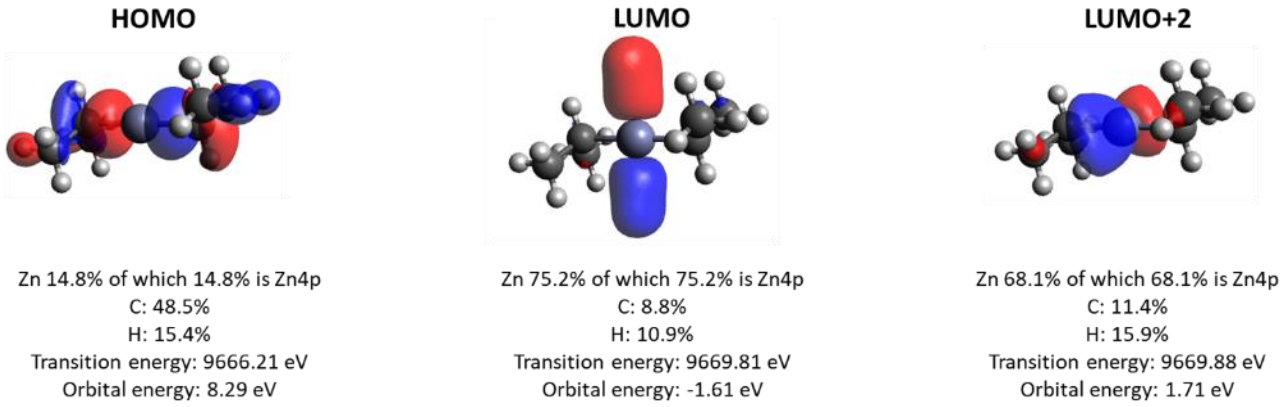
Supplementary Figure 11. Calculated molecular orbitals of Zn(*n*-Pr)$_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.

Zn(*n*-Bu)$_2$ PCM toluene



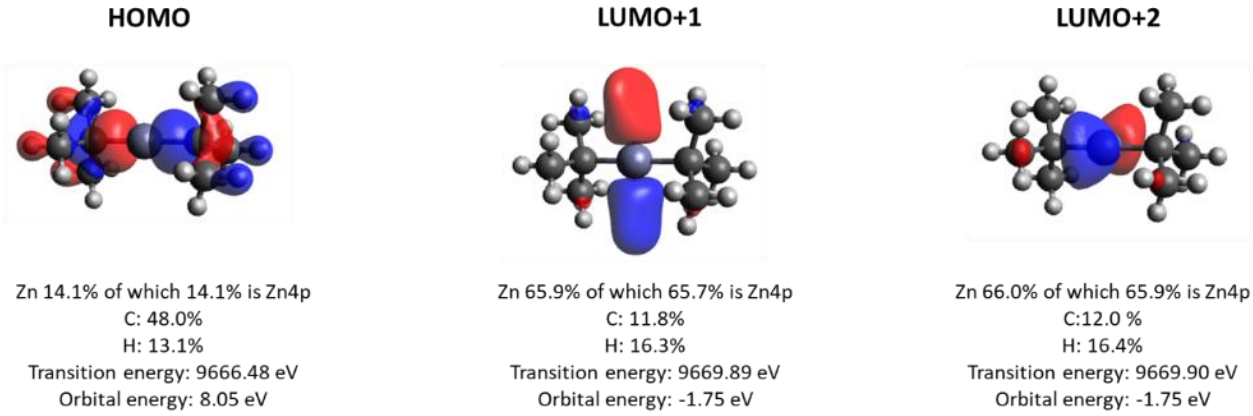
Supplementary Figure 12. Calculated molecular orbitals of Zn(*n*-Bu)$_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.

Zn(*i*-Pr)$_2$ PCM toluene

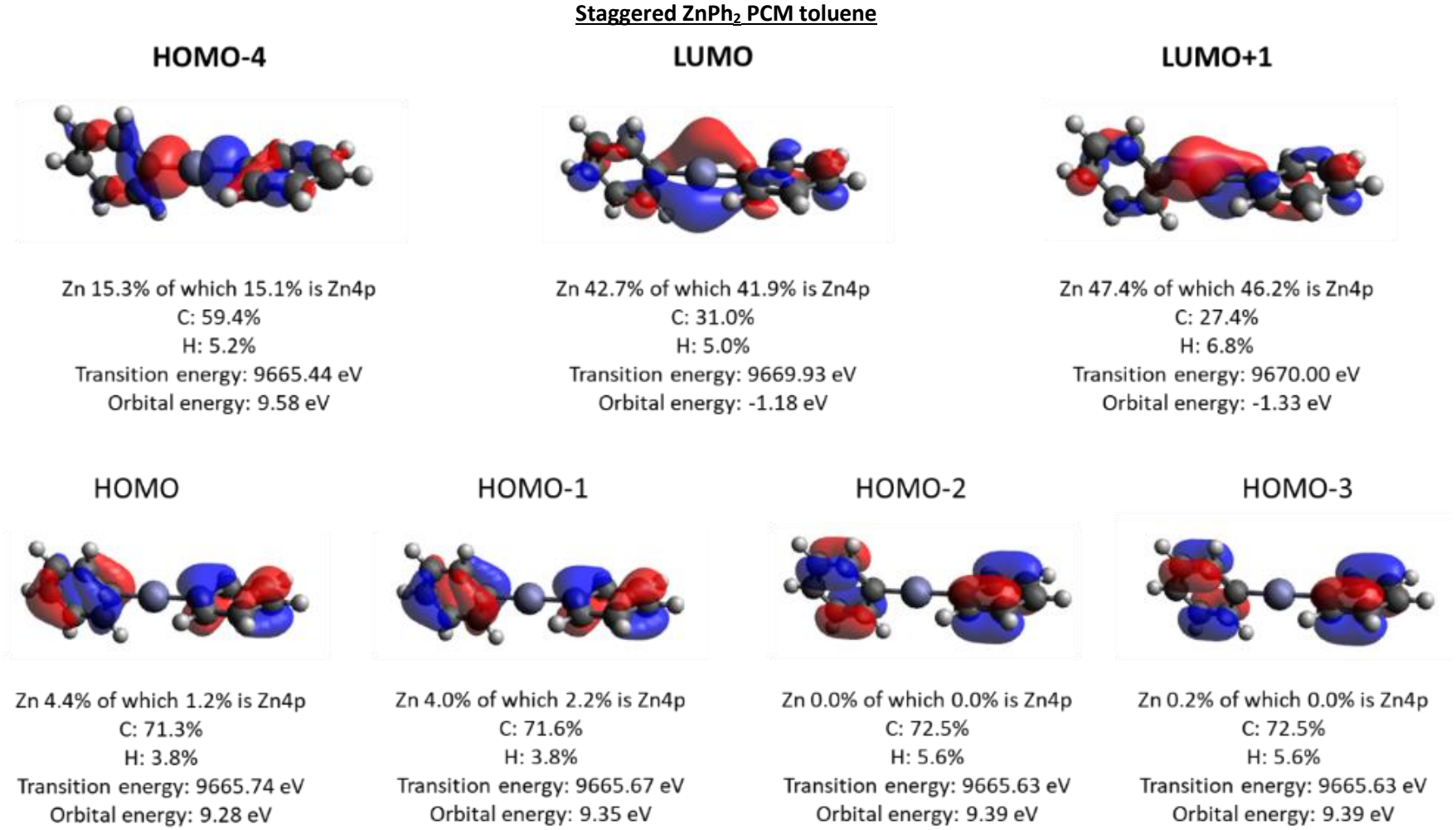


Supplementary Figure 13. Calculated molecular orbitals of Zn(*i*-Pr)$_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.

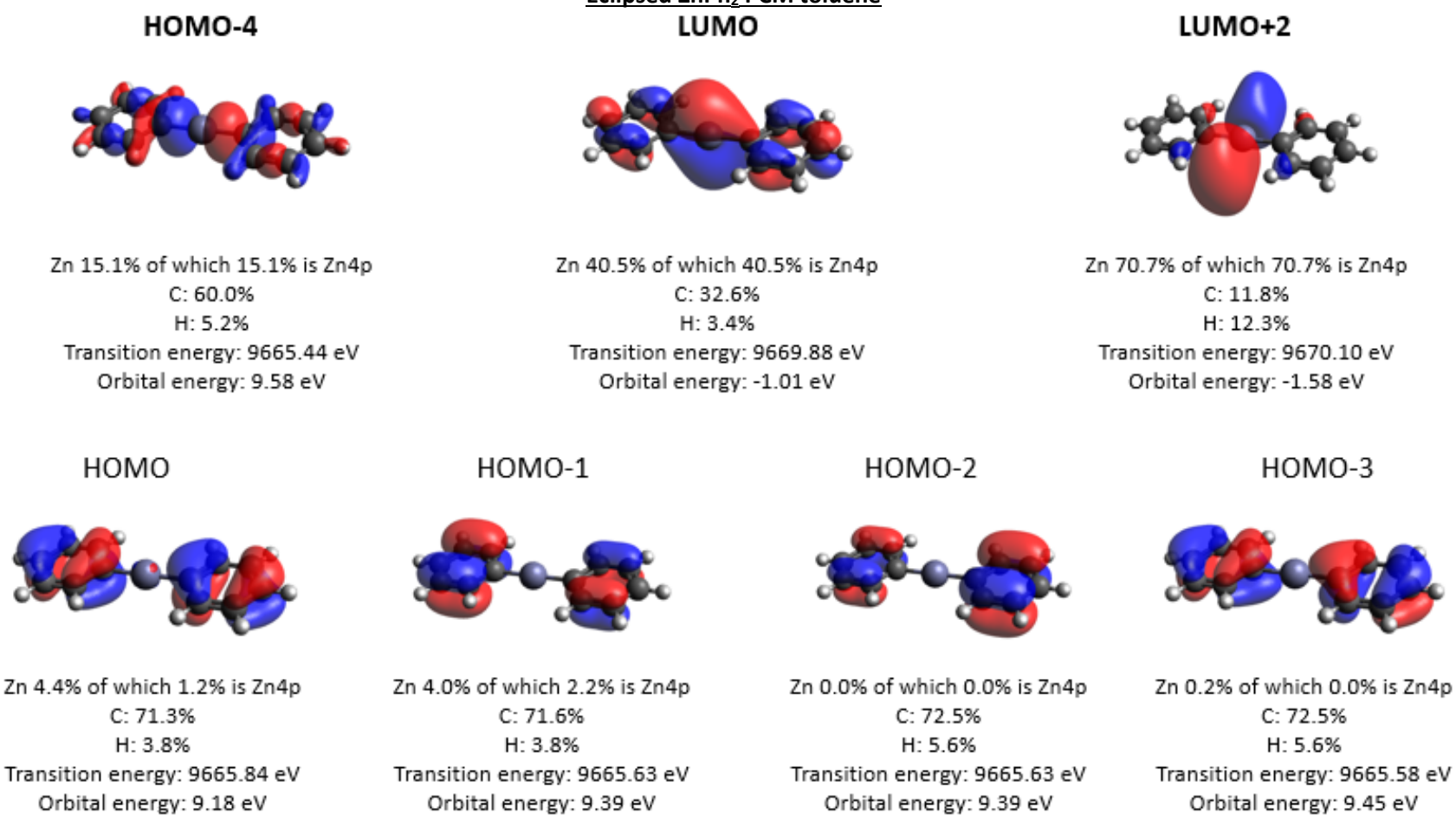
Zn(*t*-Bu)$_2$ PCM toluene



Supplementary Figure 14. Calculated molecular orbitals of Zn(*t*-Bu)$_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.

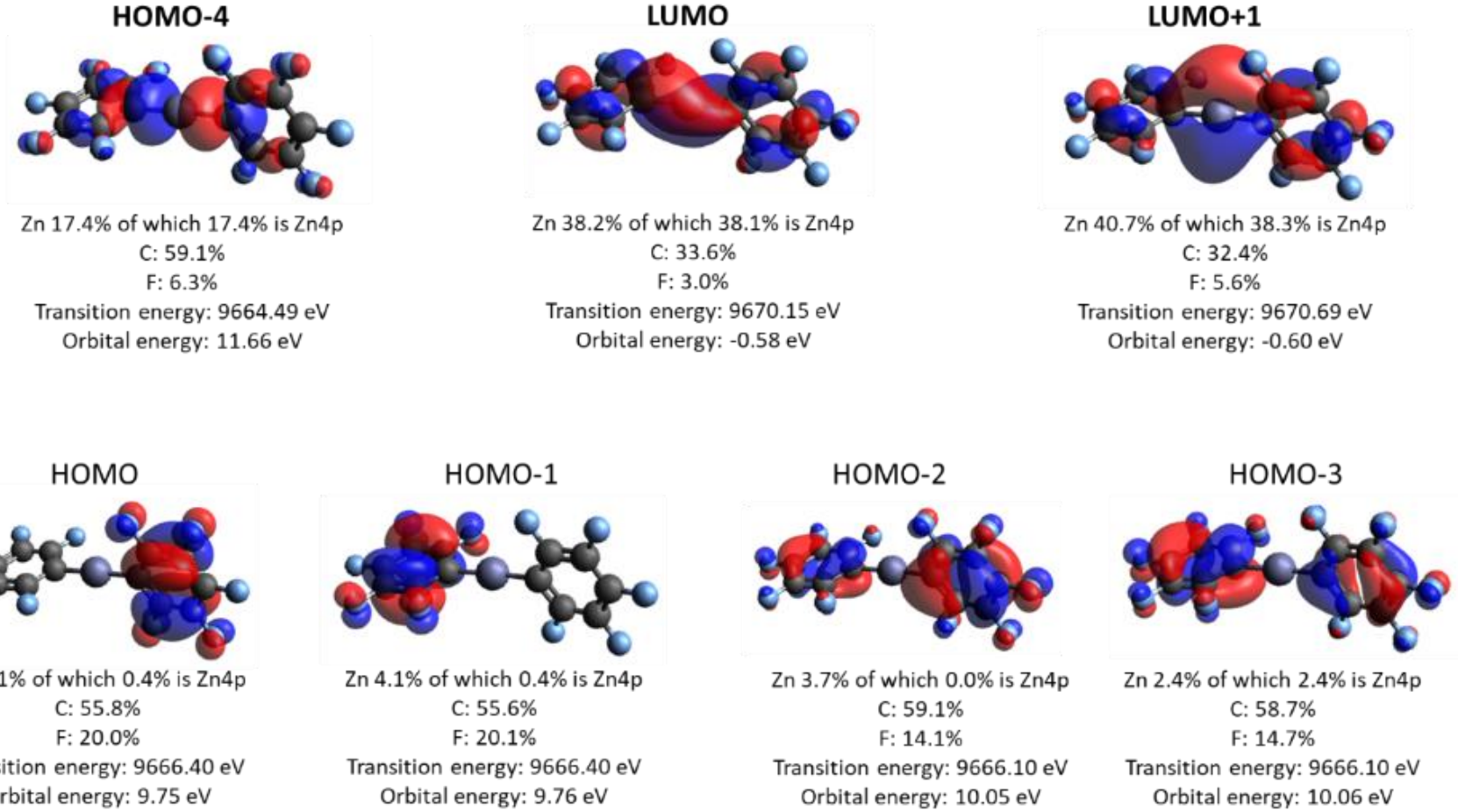


Supplementary Figure 15. Calculated molecular orbitals of staggered $ZnPh_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.



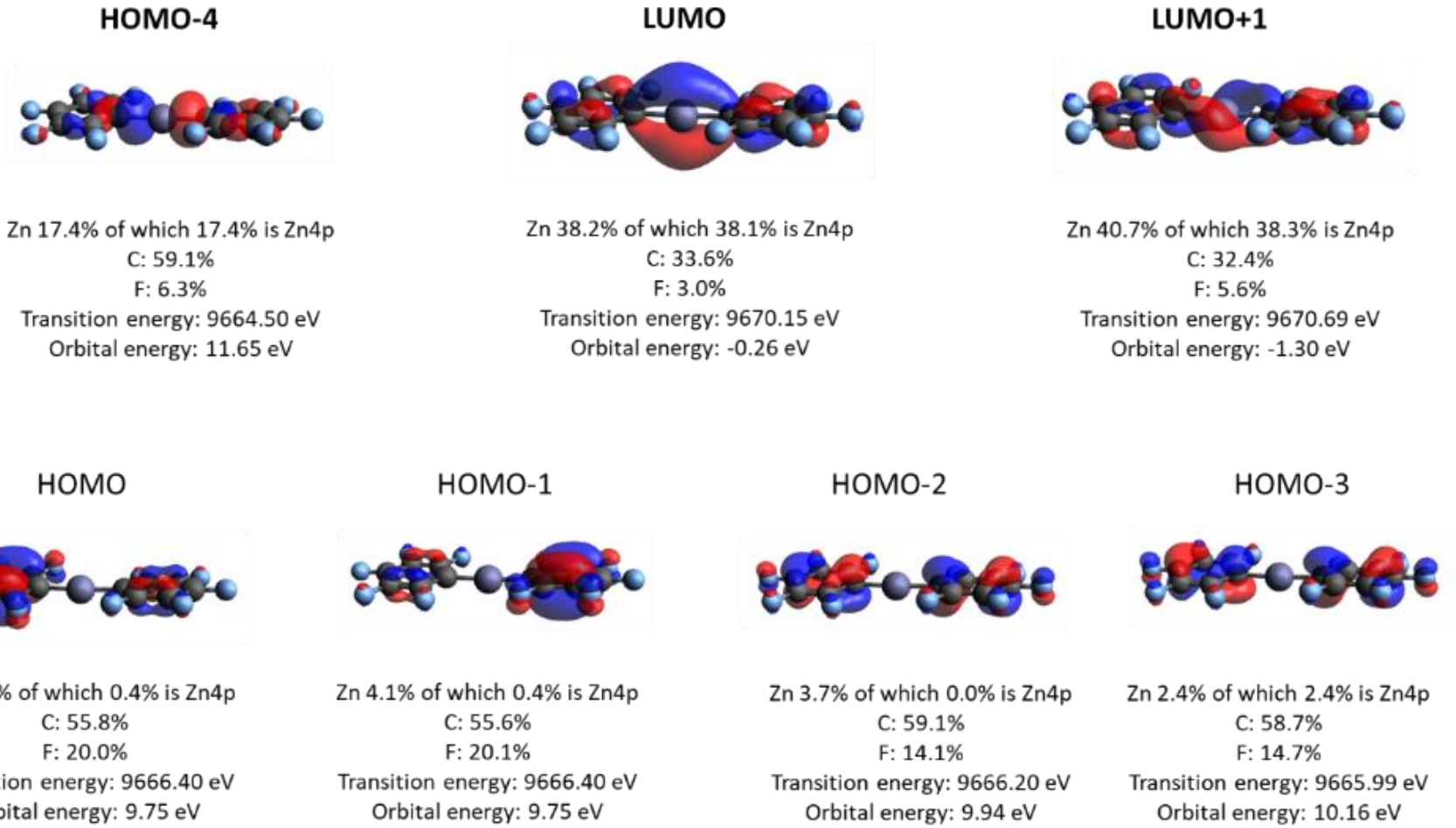
Supplementary Figure 16. Calculated molecular orbitals of eclipsed $ZnPh_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.

Staggered $Zn(C_6F_5)_2$ PCM toluene

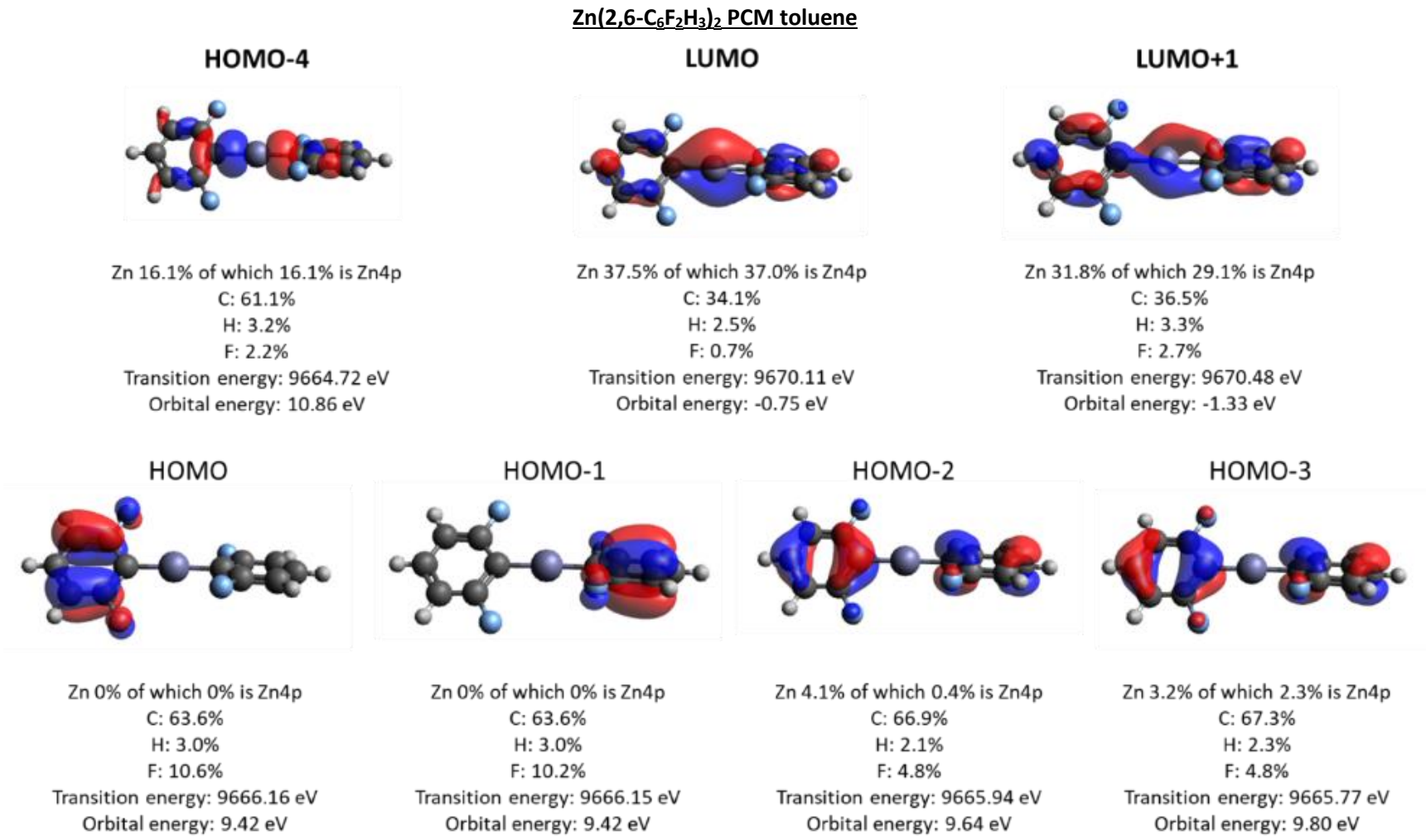


Supplementary Figure 17. Calculated molecular orbitals of staggered $Zn(C_6F_5)_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.

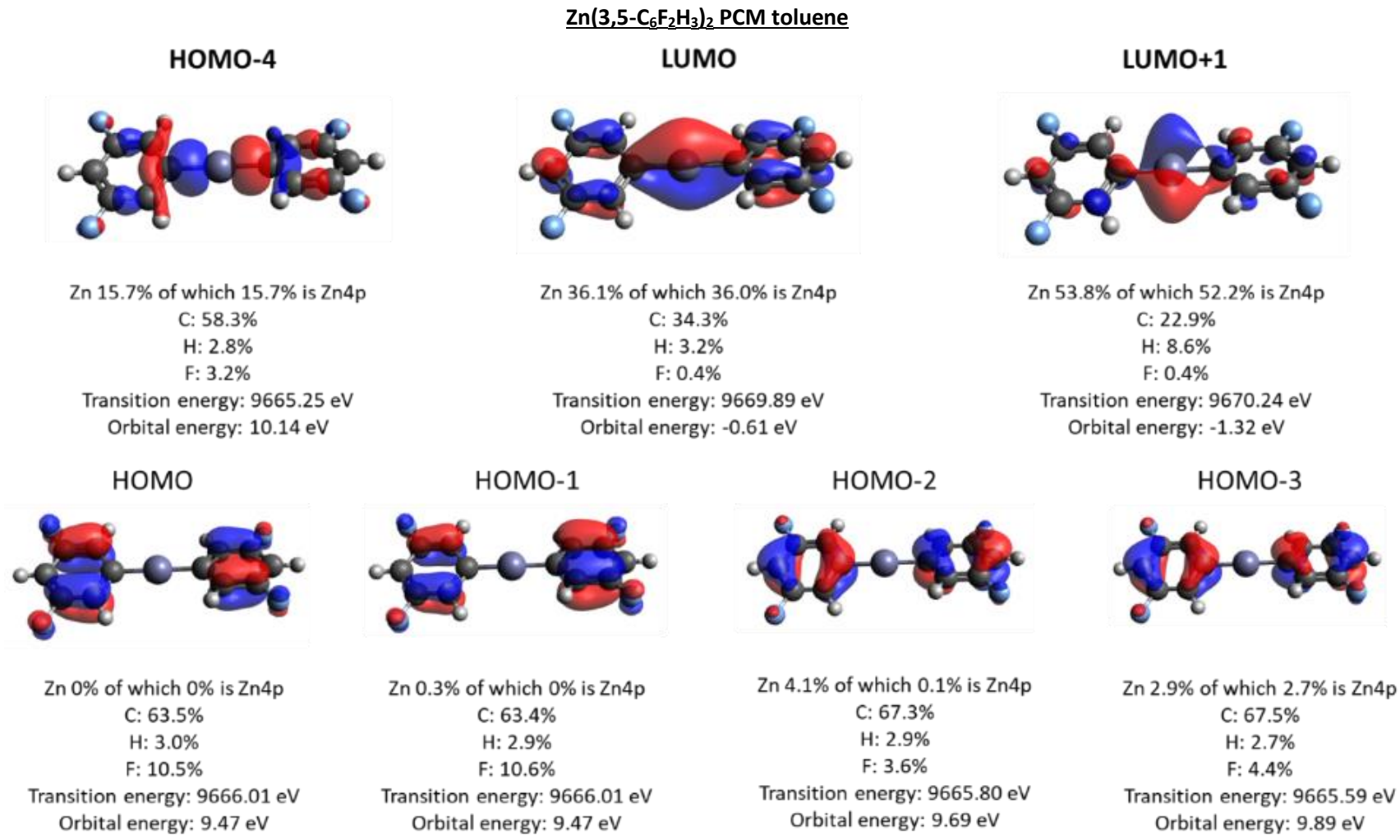
Eclipsed $Zn(C_6F_5)_2$ PCM toluene



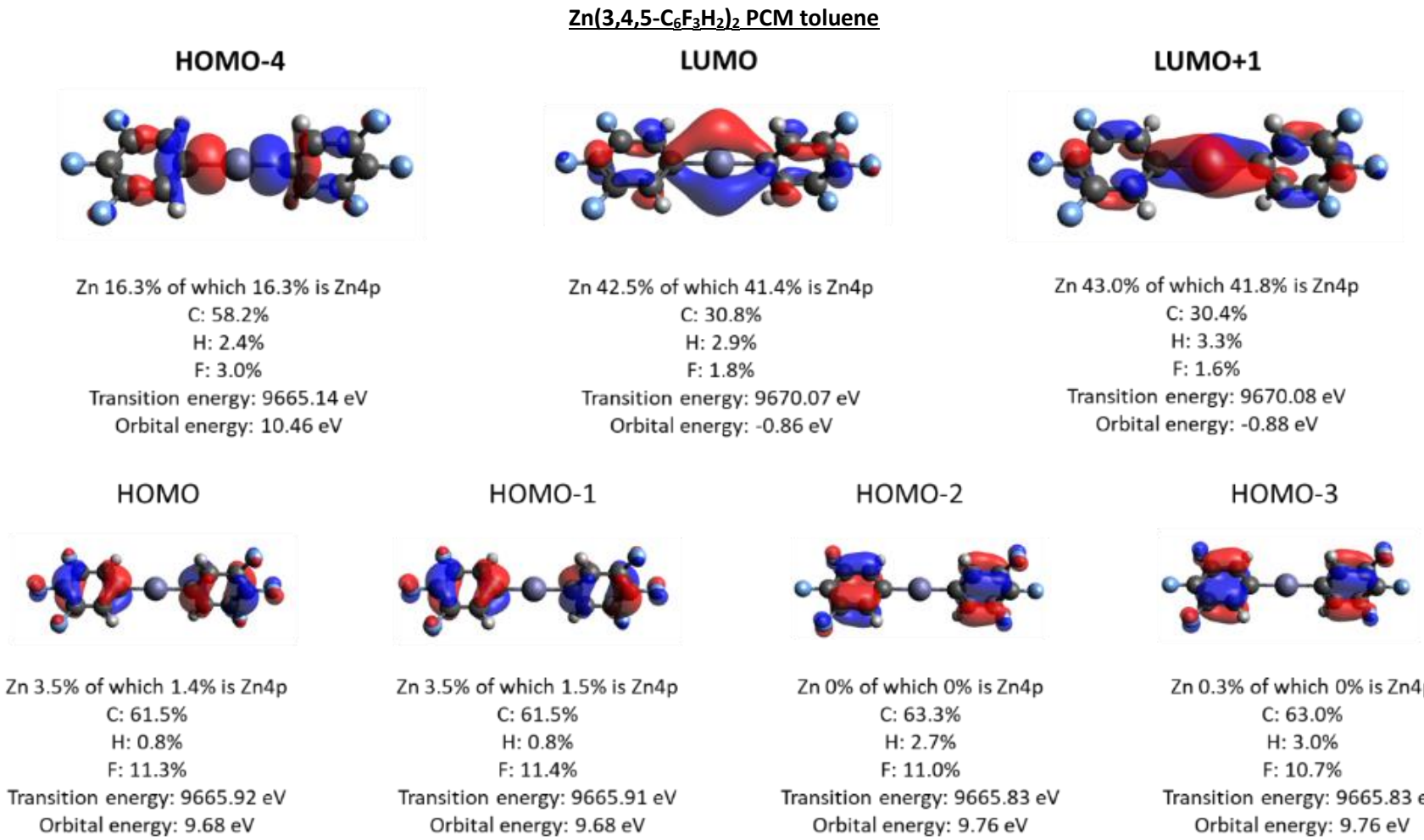
Supplementary Figure 18. Calculated molecular orbitals of eclipsed $Zn(C_6F_5)_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.



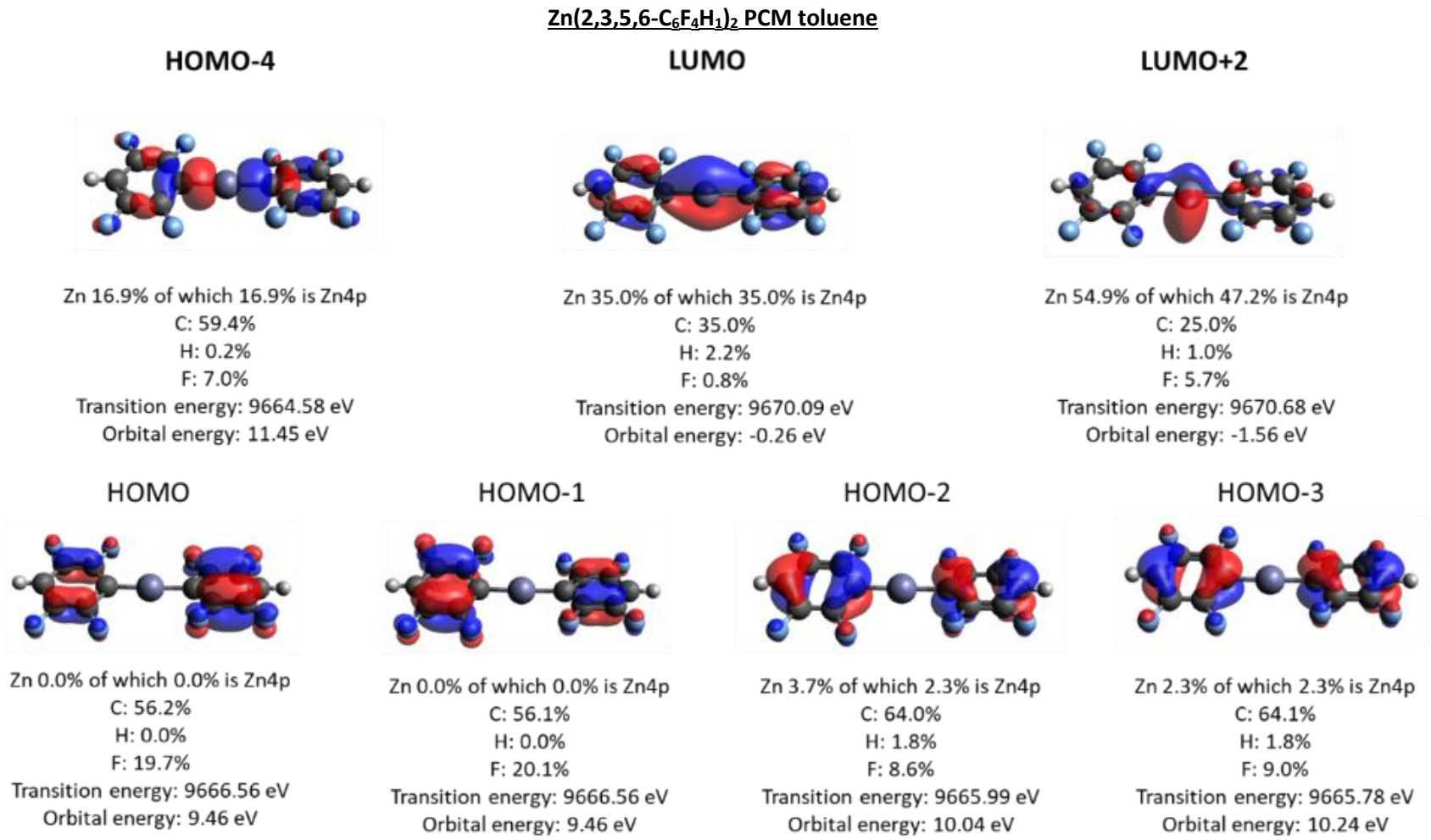
Supplementary Figure 19. Calculated molecular orbitals of eclipsed Zn(2,6-$C_6F_2H_3$)$_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.



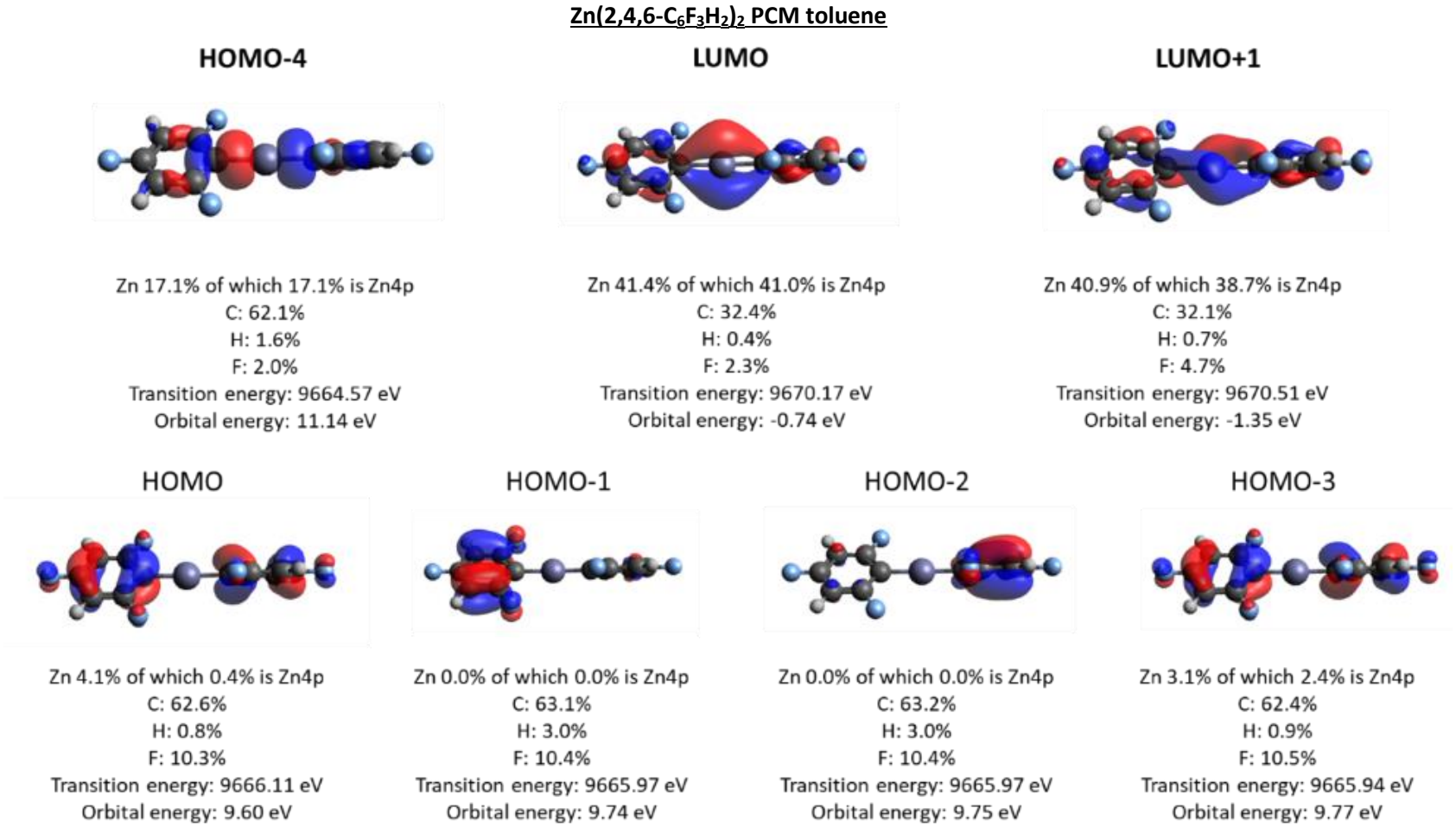
Supplementary Figure 20. Calculated molecular orbitals of eclipsed $Zn(3,5\text{-}C_6F_2H_3)_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.



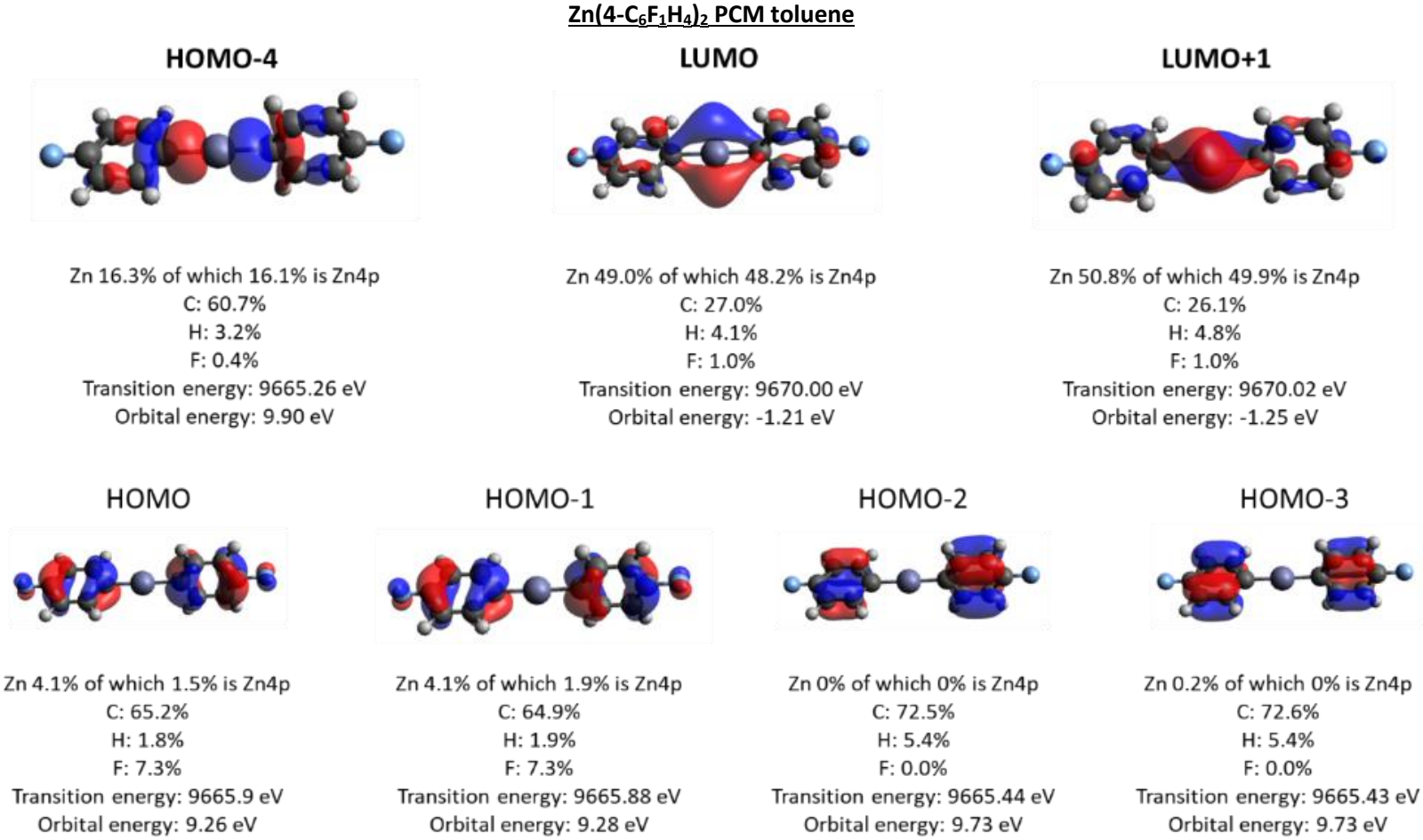
Supplementary Figure 21. Calculated molecular orbitals of eclipsed Zn(3,4,5-$C_6F_3H_2$)$_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.



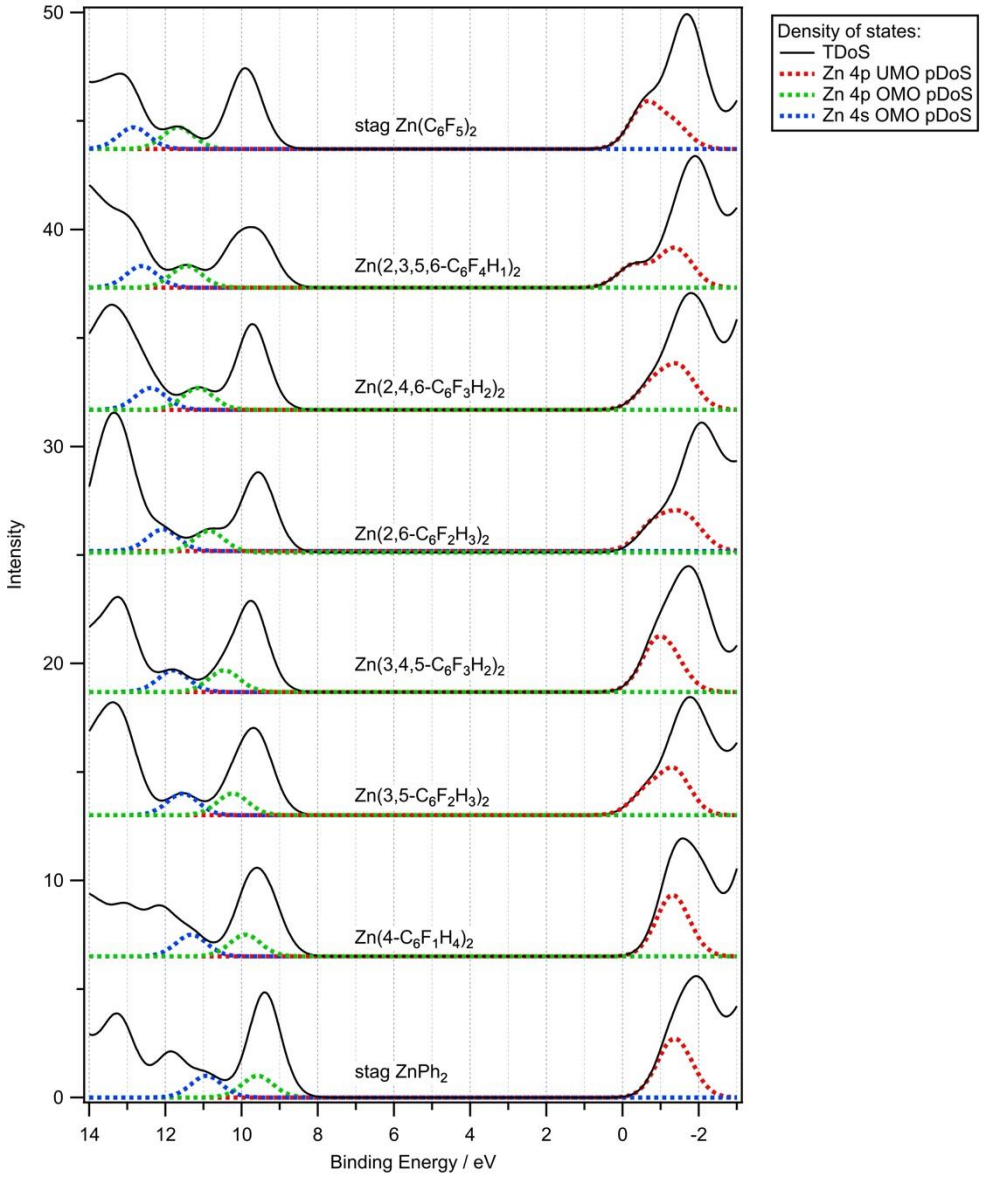
Supplementary Figure 22. Calculated molecular orbitals of eclipsed Zn(2,3,5,6-$C_6F_4H_1)_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.



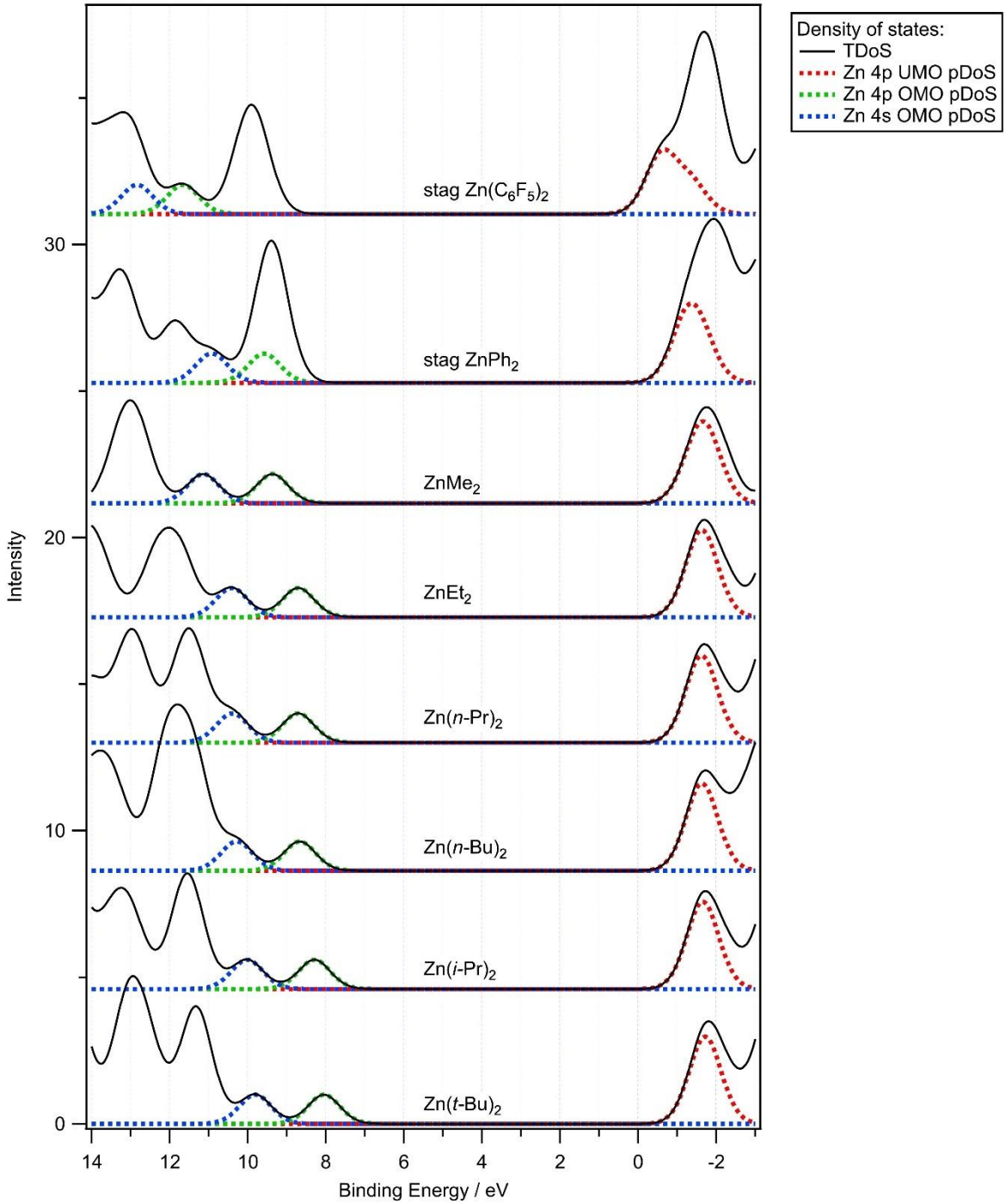
Supplementary Figure 23. Calculated molecular orbitals of eclipsed Zn(2,4,6-$C_6F_3H_2$)$_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.



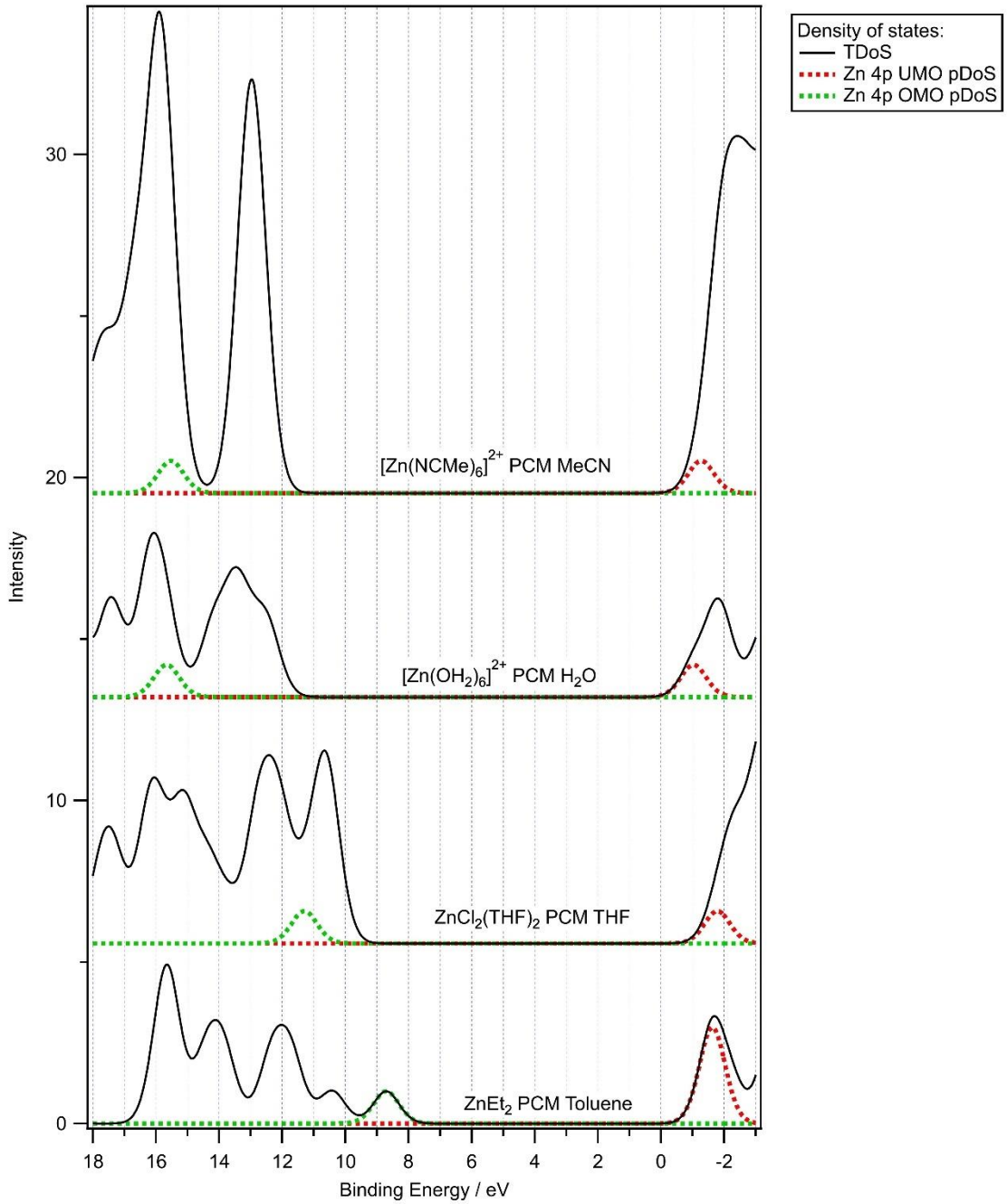
Supplementary Figure 24. Calculated molecular orbitals of eclipsed Zn(4-$C_6F_1H_4$)$_2$. The percentage of Zn 4p character has been listed for all key orbitals involved in both XAS and XES alongside the calculated transition energy (from KS-DFT XES (OMOs) and TDDFT (UMOs)) and orbital energy.



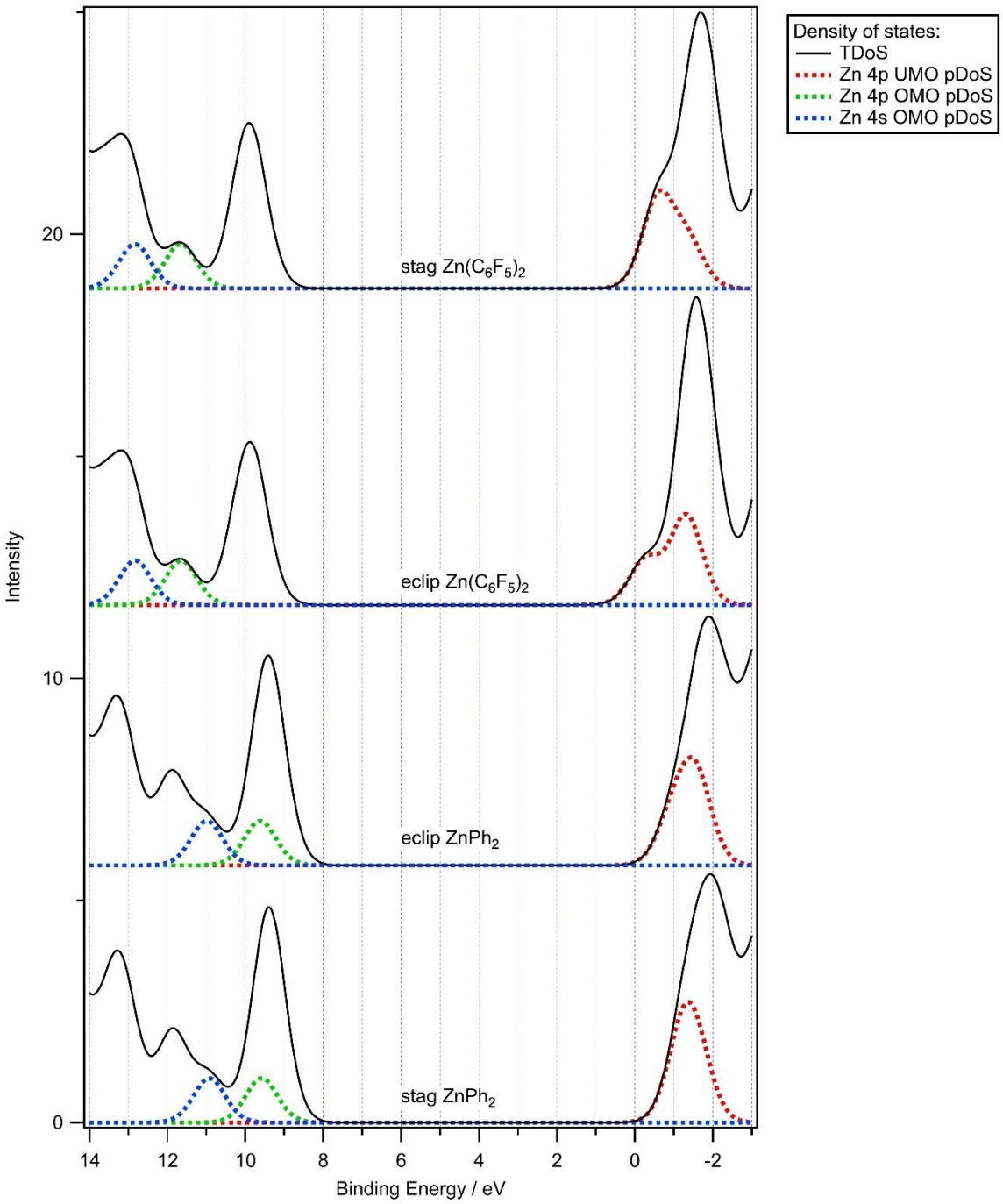
Supplementary Figure 25. Calculated total density-of-states (tDoS) and Zn 4p/Zn 4s (dotted line) partial density-of-states (pDoS) of ZnR_2 complexes (where R = aryl) showing the energy gap of the valence occupied and unoccupied molecular orbitals.



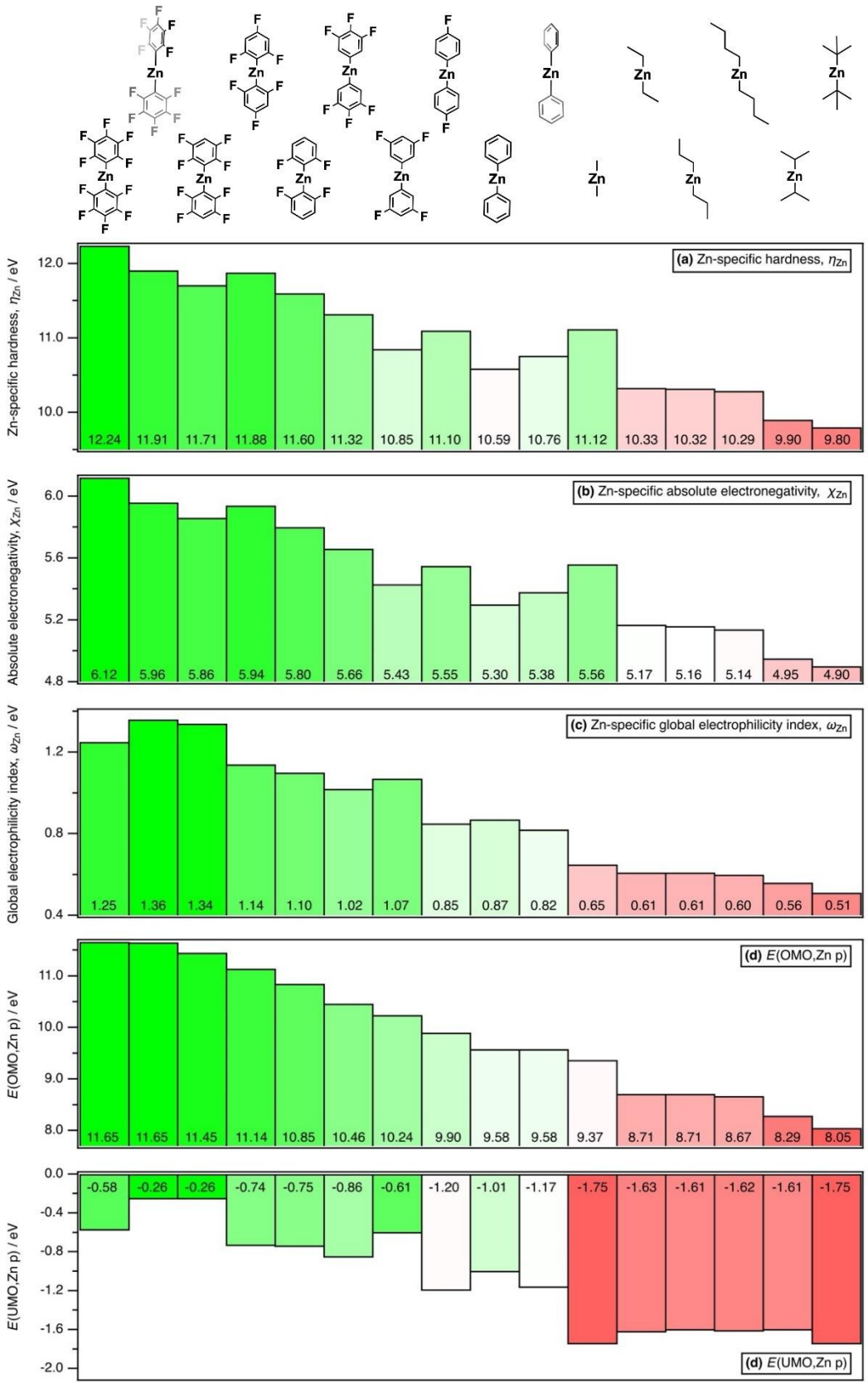
Supplementary Figure 26. Calculated total density-of-states (tDoS) and Zn 4p/Zn 4s (dotted line) partial density-of-states (pDoS) of ZnR_2 (including staggered $ZnPh_2$ and $Zn(C_6F_5)_2$) complexes showing the energy gap and identity of the valence occupied and unoccupied molecular orbitals.



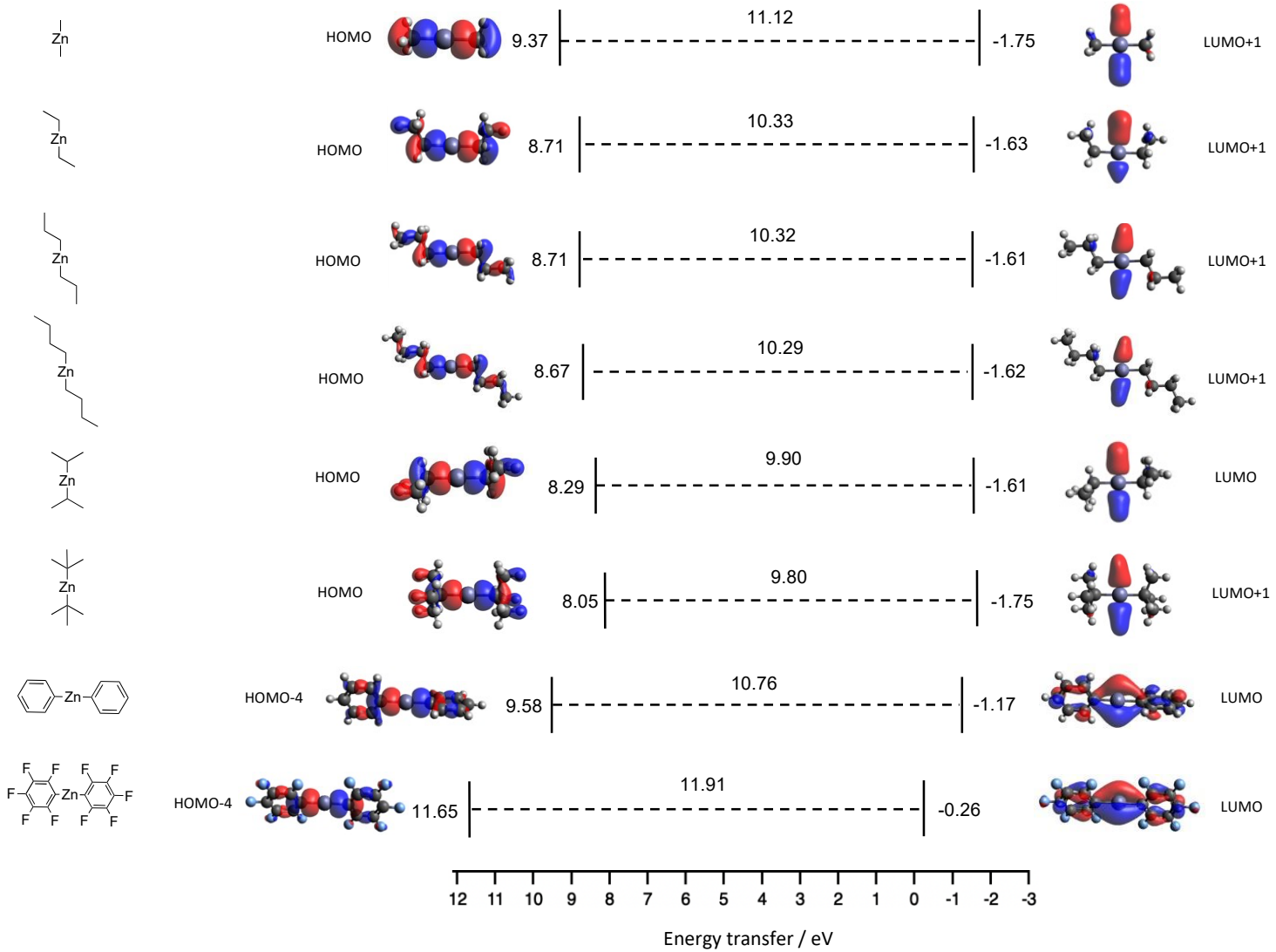
Supplementary Figure 27. Calculated total density-of-states (tDoS) and Zn 4p (dotted line) partial density-of-states (pDoS) of organozinc complexes showing the energy gap and identity of the valence occupied and unoccupied molecular orbitals.



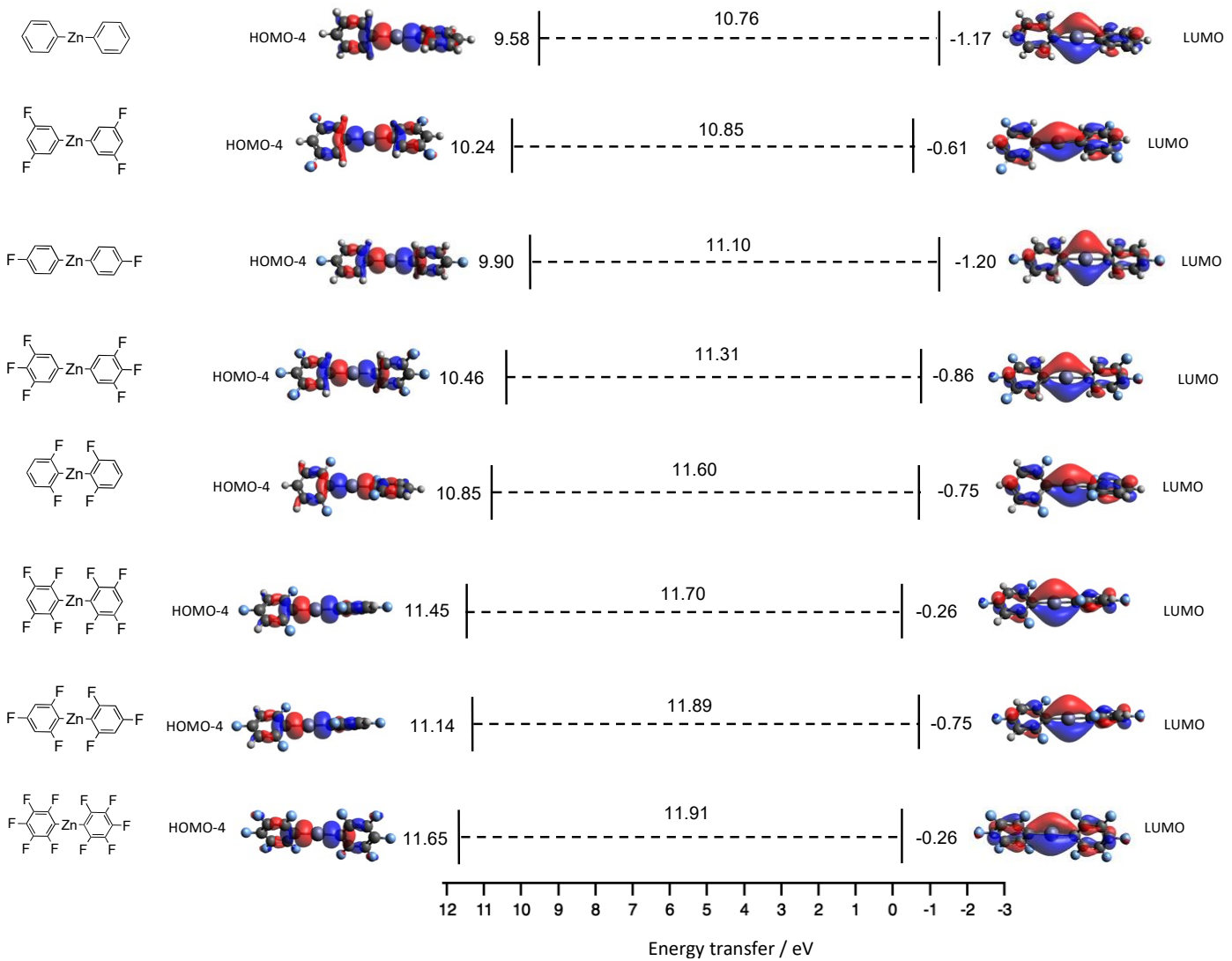
Supplementary Figure 28. Calculated total density-of-states (tDoS) and Zn 4p/Zn 4s (dotted line) partial density-of-states (pDoS) of the staggered and eclipsed $ZnPh_2$ and $Zn(C_6F_5)_2$ complexes showing the energy gap and identity of the valence occupied and unoccupied molecular orbitals.



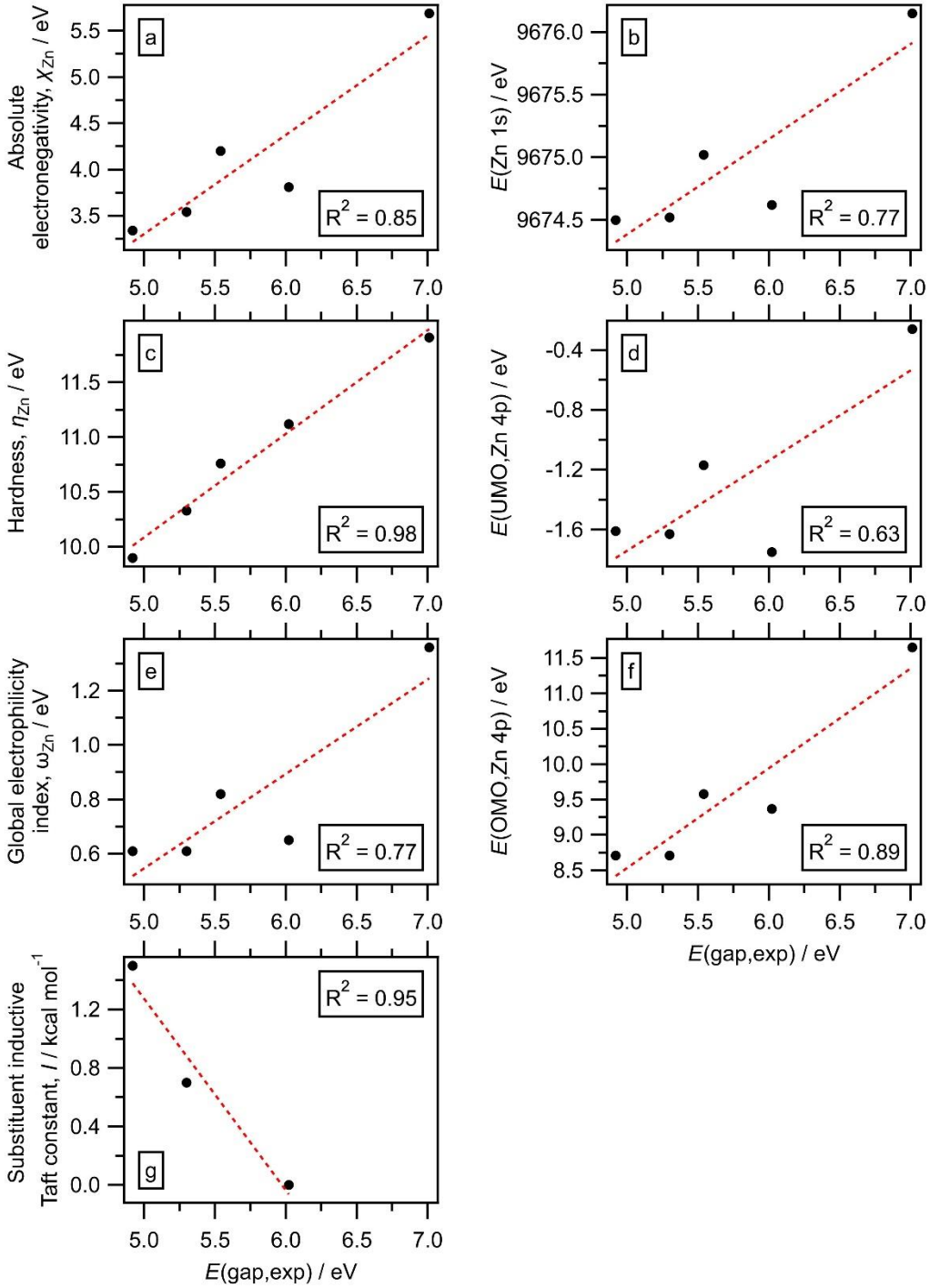
Supplementary Figure 29. Electronic structure properties for ZnR_2: (a) zinc-specific hardness (μ_{Zn}), (b) zinc-specific absolute electronegativity (χ_{Zn}), (c) global electrophilicity index (ω_{Zn}), (d) *E*(OMO,Zn p), (e) *E*(UMO,Zn p).



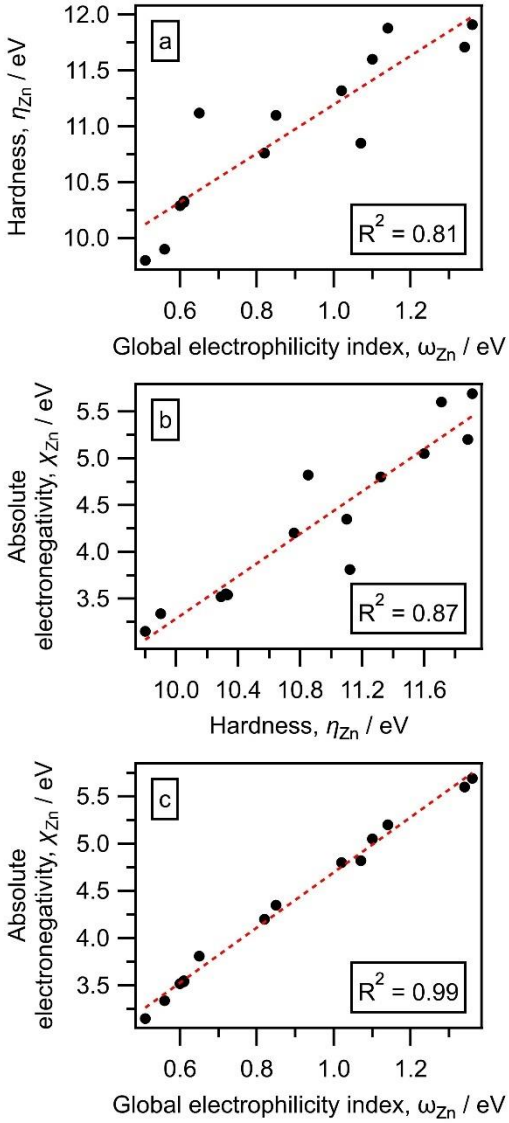
Supplementary Figure 30. Calculated Zn-specific occupied to unoccupied molecular orbital gap, *i.e.* Zn-specific hardness, η_{Zn}, for ZnR_2 compounds (R = Me, Et, *n*-Pr, *n*-Bu, *i*-Pr, *t*-Bu, Ph, C_6F_5).



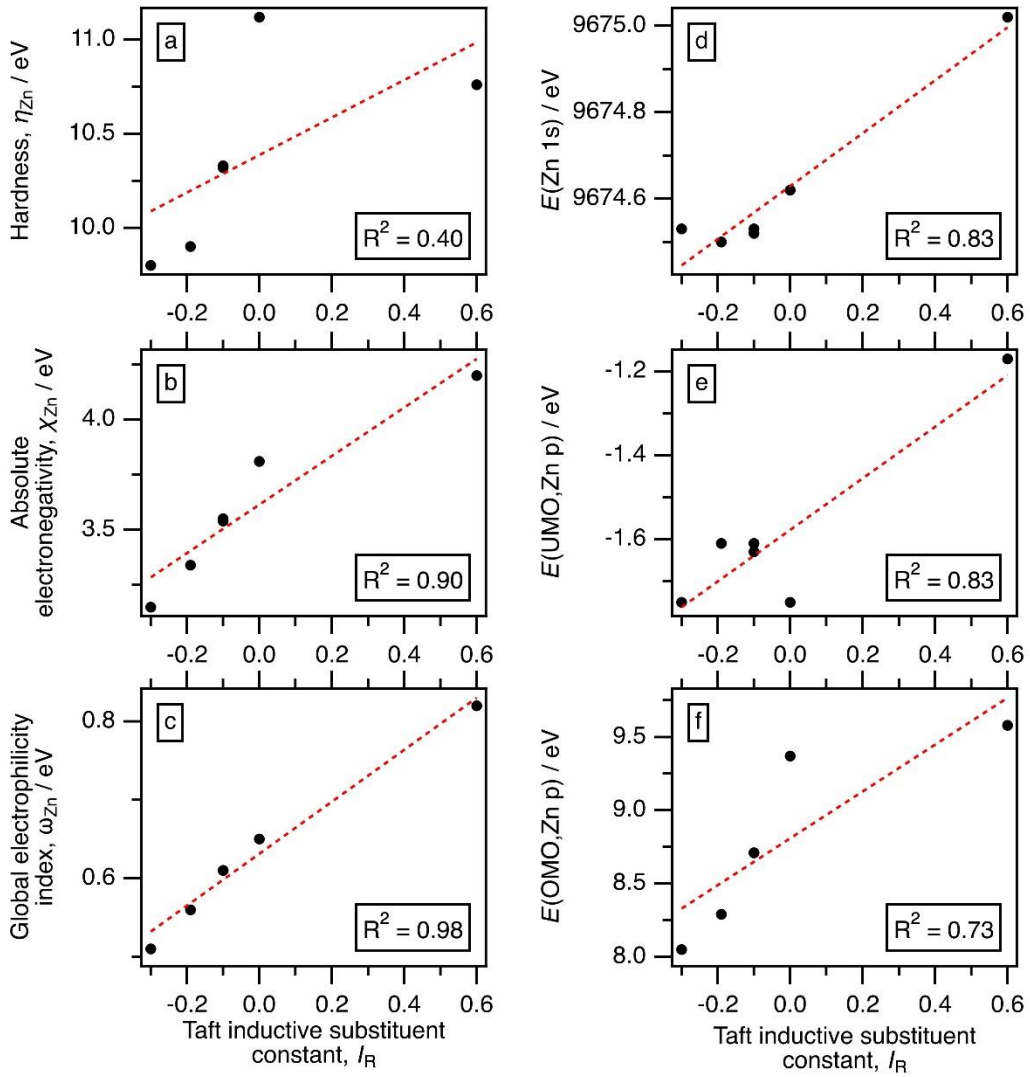
Supplementary Figure 31. Calculated Zn-specific occupied to unoccupied molecular orbital gap, *i.e.* Zn-specific hardness, η_{Zn}, for ZnR_2 compounds (R = Ph, 3,5-$C_6F_2H_3$, 4-$C_6F_1H_4$, 3,4,5-$C_6F_3H_2$, 2,6-$C_6F_2H_3$, 2,3,5,6-$C_6F_4H_1$, 2,4,6-$C_6F_3H_2$, C_6F_5).



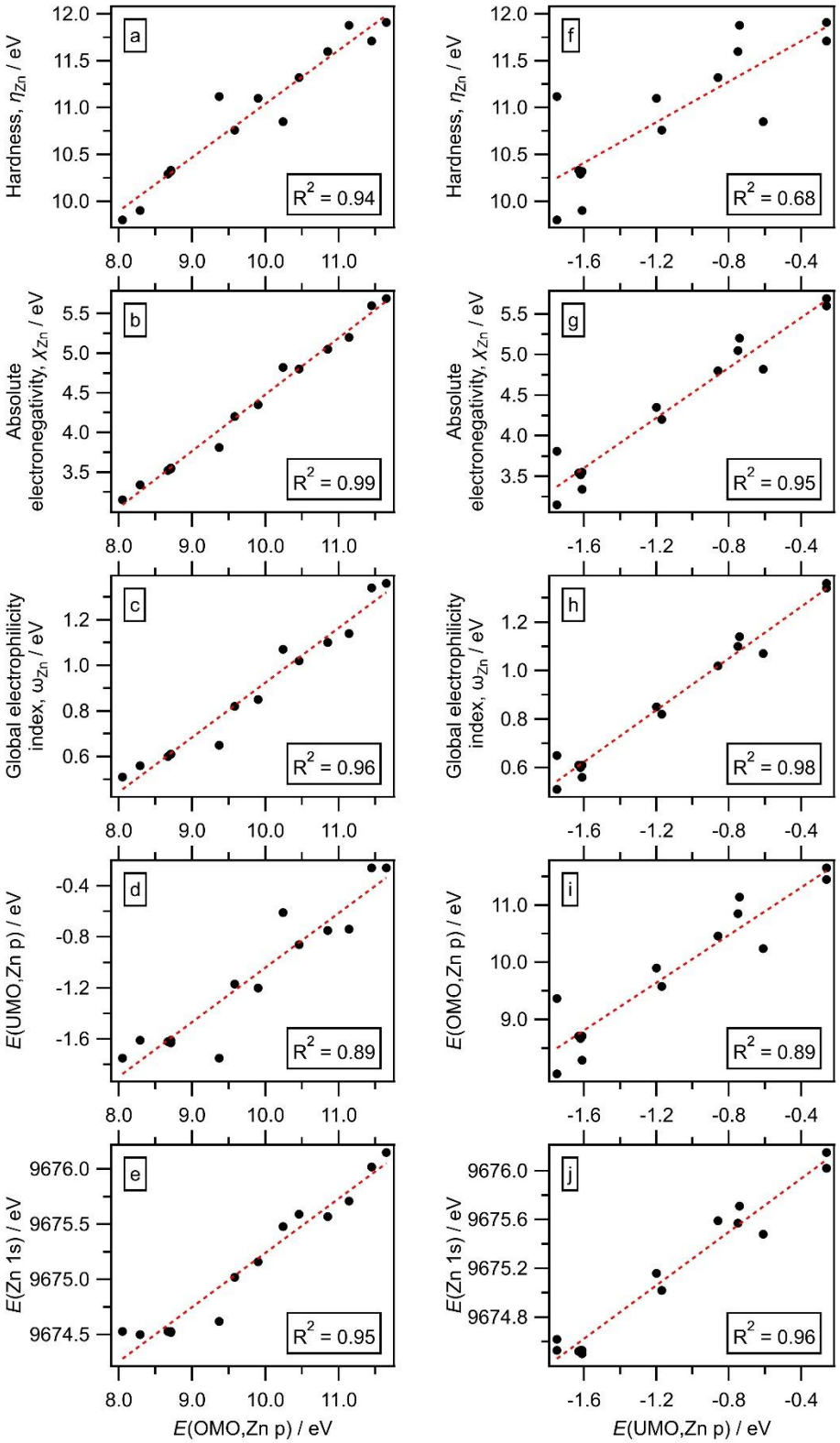
Supplementary Figure 32. Linear correlation fits for calculated descriptors against experimental R-VtC-XES gap size, E(gap,exp), for ZnR_2 complexes: (a) Zn-specific hardness (μ_{Zn}) versus E(gap,exp); (b) Zn-specific absolute electronegativity (χ_{Zn}) versus E(gap,exp), (c) zinc-specific global electrophilicity index (ω_{Zn}) versus E(gap,exp), (d) Taft inductive substituent constant (I_R) versus E(gap,exp), (e) E(Zn 1s) versus E(gap,exp), (f) E(UMO,Zn p) versus E(gap,exp), and (g) E(OMO,Zn p) versus E(gap,exp). Data for I_R taken from reference [1].



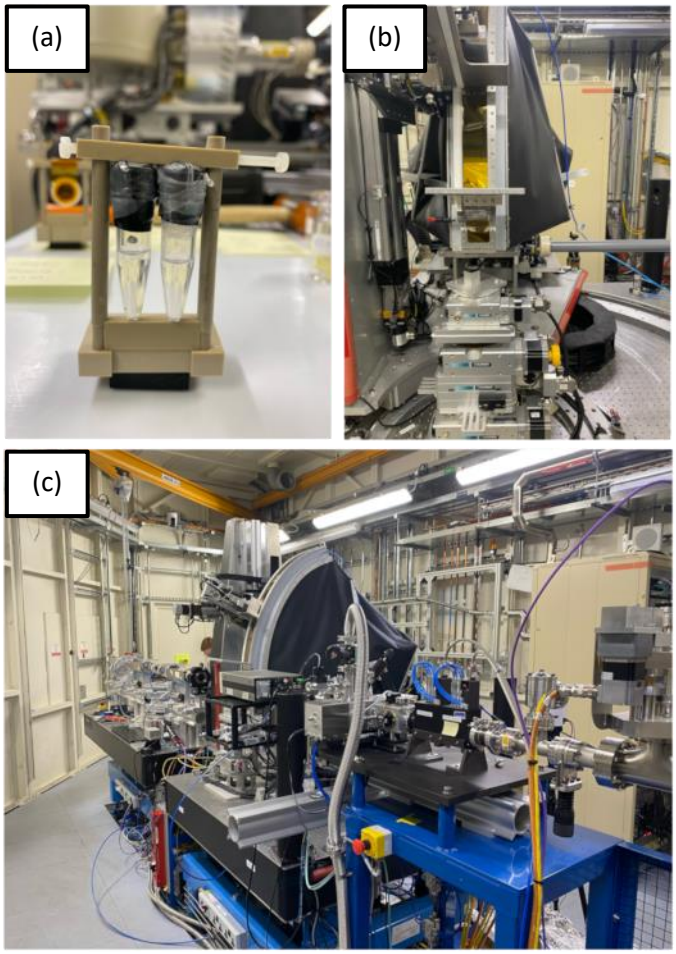
Supplementary Figure 33. Linear correlation fits for calculated descriptors for ZnR_2 complexes: (a) Zn-specific hardness (μ_{Zn}) versus zinc-specific global electrophilicity index (ω_{Zn}); (b) Zn-specific absolute electronegativity (χ_{Zn}) versus Zn-specific hardness (μ_{Zn}); (c) Zn-specific absolute electronegativity (χ_{Zn}) versus zinc-specific global electrophilicity index (ω_{Zn}).



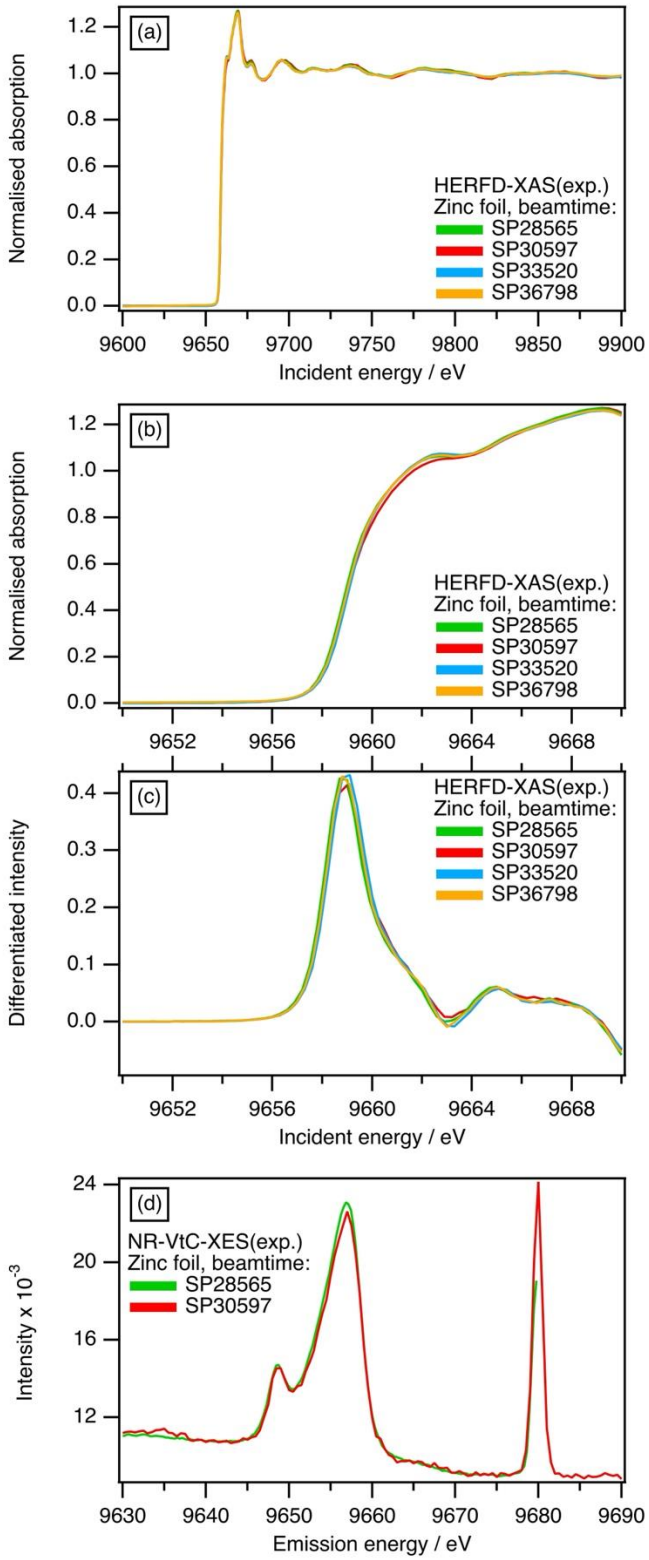
Supplementary Figure 34. Linear correlation fits for calculated descriptors against Taft inductive substituent constant (I_R) for ZnR_2 complexes: (a) Zn-specific hardness (μ_{Zn}) versus I_R; (b) Zn-specific absolute electronegativity (χ_{Zn}) versus I_R; (c) zinc-specific global electrophilicity index (ω_{Zn}) versus I_R; (d) E(Zn 1s) versus I_R; (e) E(UMO,Zn p) versus I_R; (f) E(OMO,Zn p) versus I_R. Data for I_R taken from reference[1].



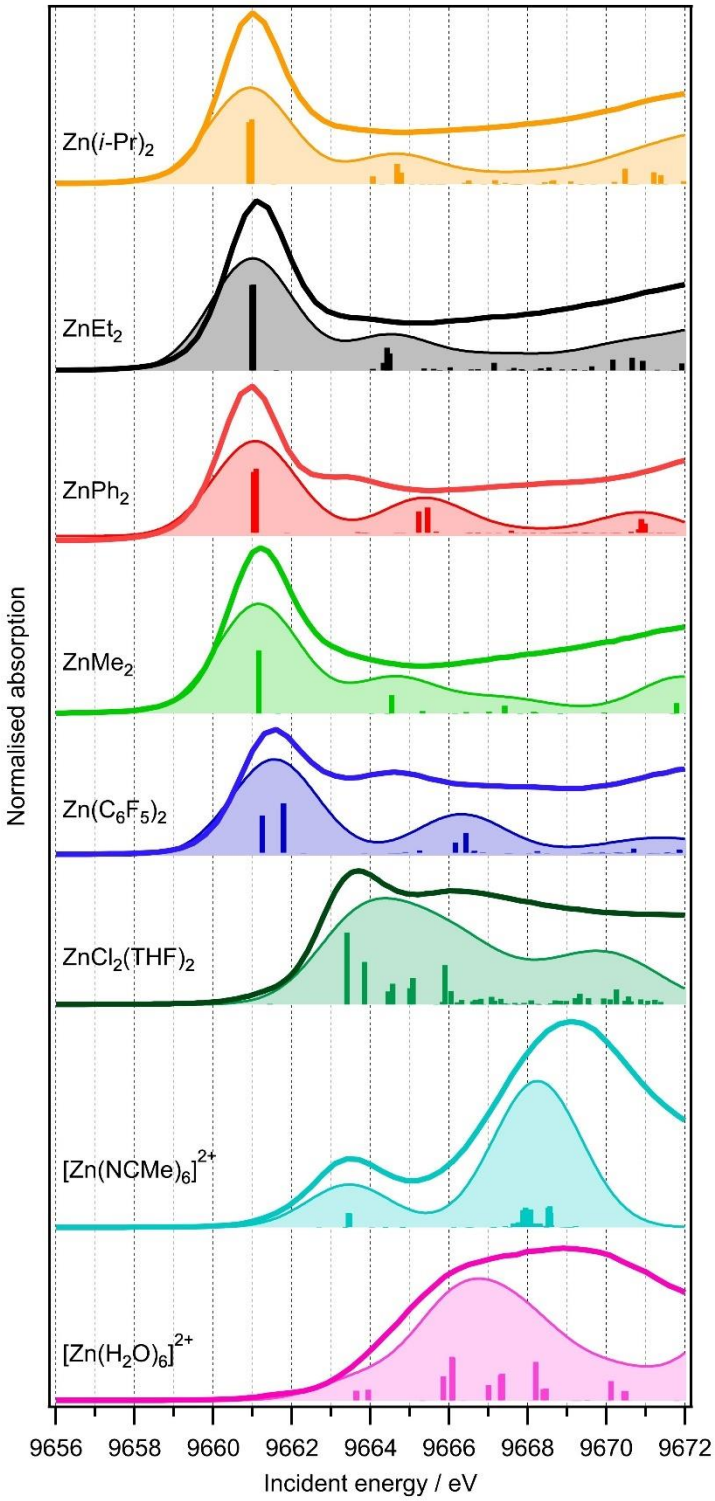
Supplementary Figure 35. Linear correlation fits for calculated descriptors against *E*(OMO,Zn p) (a-e) and *E*(UMO,Zn p) (f-j) for ZnR_2 complexes: (a) Zn-specific hardness (μ_{Zn}) versus *E*(OMO,Zn p) (b) Zn-specific absolute electronegativity (χ_{Zn}) versus *E*(OMO,Zn p); (c) zinc-specific global electrophilicity index (ω_{Zn}) versus *E*(OMO,Zn p); (f) *E*(UMO,Zn p) versus *E*(OMO,Zn p); (e) *E*(Zn 1s) versus *E*(OMO,Zn p); (f) Zn-specific hardness (μ_{Zn}) versus *E*(UMO,Zn p) (g) Zn-specific absolute electronegativity (χ_{Zn}) versus *E*(UMO,Zn p); (h) zinc-specific global electrophilicity index (ω_{Zn}) versus *E*(UMO,Zn p); (i) *E*(OMO,Zn p) versus *E*(UMO,Zn p); (j) *E*(Zn 1s) versus *E*(UMO,Zn p).



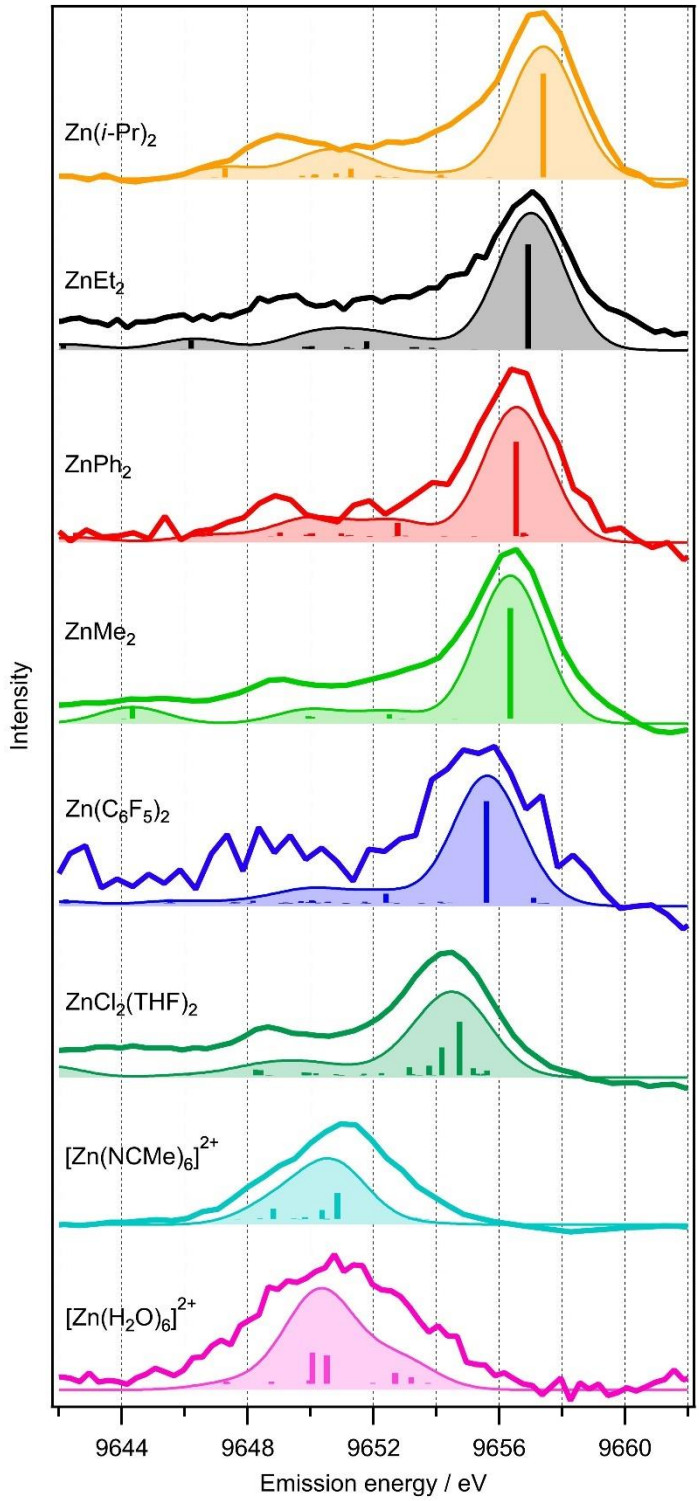
Supplementary Figure 36. Photographs of the experimental setup at I20-Scanning Diamond Lightsource.[3] (a) Small plastic vice containing two centrifuge vials used during the experiment, (b) Sample holder in line with the incident X-ray beam, samples are placed on the small rectangle platform and aligned with the incident X-rays, (c) full setup of the I20-Scanning spectrometer.[4]



Supplementary Figure 37. Zinc foil reference data from each I20 beamtime (separate beamtimes denoted by naming scheme SPxxxxx): (a) normalised Zn 1s edge HERFD-XA spectra (b) normalised Zn 1s edge HERFD-XA spectra zoomed into the XANES region, (c) derivative plot of Zn 1s XANES region showing the first inflection and (d) NR-VtC-XE spectra of Zn foil (E_i = 9680.0 eV). The energy of the monochromator was calibrated to E_i = 9659.0 eV at the beginning of each beamtime to ensure cross-beamtime data comparability.



Supplementary Figure 38. Zn 1s HERFD-XA (y intensities normalised) and calculated TDDFT Zn 1s XA spectra of organozinc compounds ZnR_2 (R = Me, Et, *i*-Pr, Ph, C_6F_5, concentration 0.1 M for all apart from C_6F_5 which was 0.033 M), $ZnCl_2(THF)_2$ (0.1 M $ZnCl_2$ in THF), $[Zn(NCMe)_6]^{2+}$ (0.1 M $Zn(OTf)_2$ in MeCN) and $[Zn(OH_2)_6]^{2+}$ (0.1 M $ZnCl_2$ in H_2O). To achieve the best agreement with the experimental data, a Gaussian broadening with a full width at half maximum (FWHM) of 2.5 eV and an energy shift of -8.90 eV were applied.



Supplementary Figure 39. Zn 1s NR-VtC-XE and calculated KS-DFT Zn 1s NR-VtC-XE spectra of organozinc compounds ZnR_2 (R = Me, Et, *i*-Pr, Ph, C_6F_5, concentration 0.1 M for all apart from C_6F_5 which was 0.033 M), $ZnCl_2(THF)_2$ (0.1 M $ZnCl_2$ in THF), $[Zn(NCMe)_6]^{2+}$ (0.1 M $Zn(OTf)_2$ in MeCN) and $[Zn(OH_2)_6]^{2+}$ (0.1 M $ZnCl_2$ in H_2O). To achieve the best agreement with the experimental data, a Gaussian broadening with a full width at half maximum (FWHM) of 2.5 eV and an energy shift of -8.90 eV were applied.

Supplementary Notes

Cartesian coordinates for all calculated structures (TDDFT, XES, RASPT2)

$[Zn(OH_2)_6]^{2+}$ CPCM water

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-1.84109	0.12925	0.49999
2	O	-0.74904	-1.41264	-0.43321
3	H	-0.92649	-2.31444	-0.14190
4	O	-1.16356	-0.41012	2.42331
5	H	-1.17409	0.30111	3.07425
6	O	-2.51861	0.66861	-1.42334
7	H	-2.50809	-0.04262	-2.07428
8	O	-2.93314	1.67115	1.43317
9	H	-3.89135	1.56545	1.41596
10	O	-3.50294	-1.12761	0.81875
11	H	-3.37618	-1.82654	1.47070
12	O	-0.17923	1.38611	0.18124
13	H	0.19437	1.80998	0.96249
14	H	0.20917	-1.30694	-0.41600
15	H	-0.29429	-0.82222	2.48811
16	H	-3.87655	-1.55146	0.03749
17	H	-2.75569	2.57295	1.14186
18	H	-3.38787	1.08072	-1.48815
19	H	-0.30598	2.08504	-0.47072

$[Zn(NCMe)_6]^{2+}$ CPCM MeCN

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-3.44958	0.03696	0.18915
2	N	-3.63638	1.80356	1.39077
3	N	-4.91154	0.82959	-1.16768
4	N	-1.89009	0.97978	-0.94175
5	N	-1.98801	-0.74976	1.54614
6	N	-3.27345	-1.72030	-1.02389
7	N	-5.00658	-0.90246	1.32444
8	C	-5.82903	-1.40026	1.94492
9	C	-5.70671	1.25854	-1.86979
10	C	-3.75854	2.76669	1.99631
11	C	-1.06227	1.48412	-1.54967
12	C	-1.19632	-1.16984	2.25746
13	C	-3.18222	-2.65745	-1.67395
14	C	-3.06678	-3.84803	-2.49951
15	H	-2.84360	-4.70417	-1.86266
16	H	-2.26273	-3.70513	-3.22164
17	H	-4.00856	-4.01260	-3.02311
18	C	-0.18984	-1.70241	3.16071
19	H	0.35743	-2.49822	2.65527
20	H	-0.68040	-2.09862	4.04980
21	H	0.49621	-0.90344	3.44203
22	C	-0.01020	2.12377	-2.32183
23	H	0.95882	1.79929	-1.94247
24	H	-0.10203	3.20548	-2.22378
25	H	-0.11160	1.83791	-3.36884
26	C	-3.91716	3.99200	2.76179
27	H	-3.10913	4.67864	2.50929
28	H	-3.88292	3.75682	3.82560
29	H	-4.87755	4.44451	2.51414
30	C	-6.71724	1.80259	-2.76161
31	H	-7.21852	2.63477	-2.26719
32	H	-7.44161	1.02329	-2.99859
33	H	-6.23731	2.15144	-3.67600
34	C	-6.87331	-2.03054	2.73519
35	H	-6.42846	-2.47316	3.62652
36	H	-7.35522	-2.80559	2.13923
37	H	-7.60661	-1.27727	3.02340

$ZnCl_2(THF)_2$ CPCM THF

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-1.12403	5.59037	0.46907
2	Cl	-0.74483	3.99365	-1.02534
3	Cl	-1.72512	5.46728	2.60734
4	O	-2.28059	7.05282	-0.36733
5	O	0.57913	6.76432	0.40646
6	C	-3.36467	7.70214	0.34548
7	C	-4.04477	8.56876	-0.70108
8	H	-2.92893	8.25736	1.17476
9	H	-4.02950	6.92908	0.73522
10	C	-3.85466	7.74403	-1.97596
11	H	-3.53367	9.52997	-0.78898
12	H	-5.09131	8.74950	-0.45801
13	C	0.57948	8.03760	1.10630
14	C	1.87591	6.12123	0.52917
15	C	2.80420	7.21229	1.03439
16	H	2.13809	5.72183	-0.44898
17	H	1.78466	5.30196	1.24647
18	C	1.86891	8.04698	1.91157
19	H	-0.32163	8.08762	1.71664
20	H	0.55836	8.82788	0.35326
21	H	1.71505	7.55712	2.87553
22	H	2.23126	9.05953	2.08629
23	H	3.18031	7.80859	0.20025
24	H	3.65201	6.80024	1.58071
25	C	-2.44479	7.20294	-1.80176
26	H	-2.27753	6.23033	-2.26128
27	H	-1.68767	7.90870	-2.15022
28	H	-3.95332	8.33220	-2.88767
29	H	-4.57387	6.92283	-2.00852

$[ZnCl_4]^{2-}$ CPCM Ionic liquid (dielectric constant = 11.40)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	0.02652	1.69032	0.1098
2	Cl	-0.84475	3.75417	-0.38794
3	Cl	-1.03949	0.10766	-1.17472
4	Cl	-0.31217	1.24883	2.33679
5	Cl	2.2746	1.65581	-0.35624

$ZnMe_2$ CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.16678	1.33925	0.00119
2	C	-2.10159	1.37855	0.00023
3	H	-2.49282	1.54702	-1.00721
4	H	-2.48203	2.17816	0.64224
5	H	-2.51732	0.43456	0.36400
6	C	1.76798	1.29956	0.00002
7	H	2.14240	0.28554	-0.16713
8	H	2.17188	1.64925	0.95442
9	H	2.17675	1.93875	-0.78776

$ZnEt_2$ CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.18088	1.89935	-0.29275
2	C	-2.11277	1.71664	-0.17847
3	C	1.75056	2.10353	-0.37415
4	C	2.27925	3.35762	0.34022
5	H	2.06084	2.12200	-1.42532
6	H	2.22118	1.21111	0.05415
7	H	1.85828	4.27220	-0.08721
8	H	3.36957	3.44420	0.27544
9	H	2.01953	3.35545	1.40274
10	C	-2.63972	1.52258	1.25249
11	H	-2.42844	0.87334	-0.80340
12	H	-2.57994	2.60234	-0.62422
13	H	-2.22380	0.62358	1.71643
14	H	-3.73064	1.42603	1.28438
15	H	-2.37271	2.36449	1.89771

Zn(*i*-Pr)$_2$ CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	0.28391	0.81220	-1.31546
2	C	-1.09184	0.98784	0.05924
3	C	-1.94389	2.24741	-0.14187
4	H	-2.70479	2.34655	0.64402
5	H	-2.47674	2.22077	-1.09818
6	H	-1.34083	3.15986	-0.13165
7	C	-1.98824	-0.25464	0.13210
8	H	-0.57559	1.08435	1.02290
9	H	-2.52170	-0.41813	-0.81020
10	H	-2.75050	-0.15410	0.91650
11	H	-1.41771	-1.16359	0.34367
12	C	1.65837	0.63769	-2.69162
13	C	2.54367	1.88738	-2.77651
14	H	3.30369	1.78796	-3.56323
15	H	3.07943	2.06175	-1.83747
16	H	1.96461	2.79000	-2.99191
17	C	2.52194	-0.61279	-2.48312
18	H	1.14073	0.52931	-3.65329
19	H	3.05631	-0.57456	-1.52803
20	H	3.28226	-0.71081	-3.26973
21	H	1.92700	-1.53059	-2.48563

Zn(*n*-Pr)$_2$ CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.51314	1.03177	0.02773
2	C	-2.45628	1.00723	0.04511
3	C	1.43001	1.05589	0.02582
4	C	2.04652	2.46161	-0.01733
5	H	1.80011	0.47454	-0.82813
6	H	1.79535	0.53039	0.91737
7	C	3.57550	2.44691	-0.01188
8	H	1.69368	3.05086	0.83648
9	H	1.69920	2.99484	-0.90936
10	H	3.95280	1.95367	0.88871
11	H	3.99398	3.45713	-0.04412
12	H	3.95852	1.89498	-0.87523
13	C	-3.07277	-0.39568	-0.04075
14	H	-2.83697	1.61860	-0.78278
15	H	-2.81072	1.50004	0.95952
16	C	-4.60130	-0.38192	-0.01385
17	H	-2.70834	-1.01537	0.78629
18	H	-2.73749	-0.89581	-0.95629
19	H	-4.96616	0.07679	0.90983
20	H	-5.02030	-1.39040	-0.07850
21	H	-4.99599	0.20209	-0.85044

Zn(*n*-Bu)$_2$ CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.50346	1.05215	0.02787
2	C	-2.44534	1.09010	0.04075
3	C	1.43847	1.01042	0.02920
4	C	2.10415	2.39288	0.00400
5	H	1.78750	0.42672	-0.83192
6	H	1.78330	0.46105	0.91439
7	C	3.63202	2.33653	0.01171
8	H	1.77336	2.98713	0.86462
9	H	1.78082	2.95138	-0.88301
10	C	-3.10617	-0.29442	0.00024
11	H	-2.80251	1.68479	-0.80938
12	H	-2.78626	1.62515	0.93619
13	C	-4.63408	-0.24417	0.02034
14	H	-2.76676	-0.90005	0.84950
15	H	-2.78760	-0.83855	-0.89737
16	C	-5.27730	-1.62804	-0.01959
17	H	-4.98067	0.35066	-0.83220
18	H	-4.95934	0.29010	0.92012
19	H	-4.98494	-2.16773	-0.92506
20	H	-6.36824	-1.56722	-0.00427
21	H	-4.96359	-2.22884	0.83902
22	C	4.28040	3.71836	-0.01237
23	H	3.96984	1.75328	-0.85229
24	H	3.96208	1.78751	0.90079
25	H	3.98309	4.27292	-0.90719
26	H	5.37118	3.65303	-0.00666
27	H	3.97590	4.30726	0.85772

Zn(*t*-Bu)$_2$ CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	C	-5.28643	1.91540	0.08240
2	C	-6.00733	3.03870	0.83459
3	H	-5.88146	4.00712	0.34046
4	H	-5.64497	3.14102	1.86232
5	H	-7.08813	2.83645	0.88783
6	C	-5.85998	1.82167	-1.33520
7	H	-6.94133	1.61892	-1.30124
8	H	-5.39642	1.01509	-1.91162
9	H	-5.72082	2.75164	-1.89495
10	C	-5.54332	0.59058	0.80826
11	H	-6.62195	0.37525	0.84786
12	H	-5.17836	0.61204	1.83969
13	H	-5.06203	-0.25301	0.30390
14	C	-1.43308	2.62098	-0.06589
15	C	-0.94175	3.16398	1.27981
16	H	-1.43663	4.10257	1.54761
17	H	0.13998	3.36387	1.24312
18	H	-1.11349	2.45381	2.09454
19	C	-1.12932	3.65366	-1.15633
20	H	-1.63847	4.60471	-0.97177
21	H	-1.43111	3.30266	-2.14815
22	H	-0.04945	3.86325	-1.19916
23	C	-0.67556	1.32777	-0.38448
24	H	0.40709	1.51759	-0.43925
25	H	-0.97937	0.90192	-1.34560
26	H	-0.83291	0.56260	0.38178
27	Zn	-3.36132	2.27345	0.00801

$[ZnPh_2]_2$ CPCM Toluene. XYZ coordinates taken from crystal structure.[2]

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	0.47169	2.27883	2.75604
2	Zn	0.72579	4.81753	1.91871
3	C	0.87891	6.27955	0.63640
4	C	1.05016	7.56512	1.14973
5	C	1.11659	8.68036	0.33321
6	C	1.03511	8.53525	-1.03966
7	C	0.91900	7.28098	-1.57600
8	C	0.84008	6.17144	-0.75348
9	C	0.27435	4.45292	3.84944
10	C	1.30724	4.33517	4.77803
11	C	1.06055	4.38896	6.13789
12	C	-0.20848	4.56500	6.61419
13	C	-1.25027	4.68337	5.72863
14	C	-1.01446	4.63481	4.36276
15	C	-0.04035	0.78759	3.88746
16	C	0.06928	-0.48407	3.37414
17	C	-0.11450	-1.61328	4.15763
18	C	-0.42791	-1.47708	5.49548
19	C	-0.56318	-0.22940	6.03482
20	C	-0.37047	0.89720	5.25433
21	C	1.65430	2.76236	1.20977
22	C	1.34663	2.47888	-0.12208
23	C	2.30758	2.49475	-1.10670
24	C	3.59193	2.79628	-0.80951
25	C	3.95011	3.07837	0.49732
26	C	2.98339	3.06148	1.47093
27	H	1.12635	7.68703	2.11834
28	H	1.21858	9.57385	0.72446
29	H	1.06162	9.32199	-1.62303
30	H	0.88888	7.16674	-2.54961
31	H	0.75533	5.28298	-1.15773
32	H	2.22864	4.22769	4.46183
33	H	1.80429	4.28613	6.76829
34	H	-0.37130	4.60906	7.57980
35	H	-2.16408	4.80163	6.05984
36	H	-1.76560	4.73622	3.74237
37	H	0.28574	-0.59989	2.42554
38	H	-0.02642	-2.50668	3.76438
39	H	-0.55730	-2.27217	6.05383
40	H	-0.78992	-0.12992	6.98242
41	H	-0.46840	1.78520	5.65758
42	H	0.42193	2.26180	-0.36223
43	H	2.06053	2.28649	-2.03129

44	H	4.26922	2.81165	-1.51896
45	H	4.88087	3.29018	0.72146
46	H	3.24707	3.27091	2.39151

$ZnPh_2$ CPCM toluene (eclipsed)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	1.57090	4.00064	0.00134
2	C	-2.36654	3.10431	-1.22375
3	C	-3.02311	2.80367	-0.03633
4	C	-2.32576	2.85940	1.16463
5	C	-0.98062	3.21483	1.17221
6	C	-1.02151	3.45948	-1.20415
7	C	-0.29204	3.52276	-0.00906
8	H	-0.53655	3.69037	-2.14828
9	H	-2.90328	3.06218	-2.16577
10	H	-4.07206	2.52827	-0.04670
11	H	-2.83042	2.62516	2.09623
12	H	-0.46270	3.25015	2.12661
13	C	6.16457	5.20070	0.03481
14	C	5.46621	5.14317	-1.16536
15	C	5.50938	4.90073	1.22313
16	C	4.16450	4.54419	1.20522
17	C	4.12128	4.78637	-1.17134
18	C	3.43412	4.47872	0.01085
19	H	5.97004	5.37665	-2.09790
20	H	3.60247	4.74972	-2.12525
21	H	7.21320	5.47724	0.04394
22	H	3.68037	4.31385	2.15035
23	H	6.04692	4.94465	2.16458

$ZnPh_2$ CPCM toluene (staggered)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	1.57176	3.99869	-0.00855
2	C	-2.58027	3.69713	-0.71669
3	C	-2.95498	2.56965	0.00447
4	C	-1.99516	1.86465	0.72094
5	C	-0.67017	2.28953	0.71315
6	C	-1.25227	4.11257	-0.71785
7	C	-0.26282	3.42232	-0.00464
8	H	-0.98955	4.99706	-1.29141
9	H	-3.32339	4.25298	-1.27887
10	H	-3.98892	2.24215	0.00790
11	H	-2.27925	0.98323	1.28632
12	H	0.05743	1.71845	1.28306
13	C	6.09585	5.43615	0.00386
14	C	5.72329	4.30800	-0.71737
15	C	5.13476	6.13905	0.72067
16	C	3.81064	5.71144	0.71316
17	C	4.39615	3.88983	-0.71826
18	C	3.40545	4.57793	-0.00471
19	H	6.46742	3.75378	-1.27982
20	H	4.13513	3.00488	-1.29190
21	H	7.12911	5.76580	0.00708
22	H	3.08200	6.28094	1.28333
23	H	5.41716	7.02098	1.28611

$Zn(C_6F_5)_2$ CPCM toluene (eclipsed)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	1.58682	3.99292	-0.11693
2	C	-2.63162	3.92286	-0.04373
3	C	-2.92925	2.56899	-0.00597
4	C	-1.90494	1.63430	-0.00893
5	C	-0.59365	2.07923	-0.04964
6	C	-1.30341	4.31569	-0.08307
7	C	-0.25199	3.41801	-0.08640
8	C	6.10111	5.41751	0.06077
9	C	5.78571	4.08101	0.25344
10	C	5.09405	6.33762	-0.18943
11	C	3.78170	5.89633	-0.24230
12	C	4.45769	3.69145	0.19110
13	C	3.42303	4.57435	-0.05498
14	F	-1.04984	5.63961	-0.11828
15	F	-3.62240	4.81924	-0.04122
16	F	-4.19827	2.16681	0.03310
17	F	-2.19588	0.33093	0.02778
18	F	0.37898	1.14498	-0.05113
19	F	4.18565	2.38469	0.38332
20	F	6.75810	3.19722	0.49507
21	F	2.82795	6.81742	-0.48855
22	F	5.40226	7.62462	-0.37324
23	F	7.37028	5.81727	0.11656

$Zn(C_6F_5)_2$ CPCM toluene (staggered)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	1.61668	3.89509	0.13359
2	C	-2.41234	3.55699	-0.96850
3	C	-2.93020	2.60897	-0.09872
4	C	-2.11449	2.03118	0.86273
5	C	-0.78571	2.41798	0.93542
6	C	-1.07863	3.91061	-0.85125
7	C	-0.23104	3.36314	0.09347
8	C	6.06915	5.48100	-0.09744
9	C	5.69960	4.34865	-0.80798
10	C	5.14277	6.12834	0.70557
11	C	3.85279	5.62777	0.77326
12	C	4.39750	3.88747	-0.70351
13	C	3.43901	4.50979	0.07390
14	F	-0.59980	4.83234	-1.71368
15	F	-3.19822	4.10675	-1.89815
16	F	-4.21067	2.25403	-0.18722
17	F	-2.61815	1.11750	1.69756
18	F	-0.02328	1.83528	1.88233
19	F	4.06819	2.78709	-1.41132
20	F	6.59707	3.72913	-1.57922
21	F	2.97565	6.28199	1.56140
22	F	5.50243	7.21590	1.39336
23	F	7.31376	5.94606	-0.18822

Zn(2,6-$C_6F_2H_3$) CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	1.61947	3.94706	-0.05298
2	C	-2.59380	3.92984	0.32837
3	C	-2.94377	2.64367	-0.06449
4	C	-1.96967	1.73151	-0.45203
5	C	-0.65048	2.14865	-0.43278
6	C	-1.25128	4.26461	0.31817
7	C	-0.22621	3.41160	-0.05530
8	C	6.13291	5.40779	0.03212
9	C	5.79396	4.19746	0.62508
10	C	5.16486	6.18848	-0.58834
11	C	3.86353	5.71879	-0.59306
12	C	4.46853	3.80283	0.57596
13	C	3.45115	4.52599	-0.02307
14	F	-0.91473	5.52517	0.70347
15	F	0.29801	1.25068	-0.81294
16	F	4.14263	2.61802	1.15945
17	F	2.91943	6.48608	-1.20207
18	H	-2.21987	0.72497	-0.76177
19	H	-3.98642	2.34881	-0.06838
20	H	-3.33573	4.65611	0.63443
21	H	5.40609	7.13466	-1.05560
22	H	7.16188	5.74615	0.05370
23	H	6.53178	3.57345	1.11298

$Zn(3,5\text{-}C_6F_2H_4)_2$ CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	1.58228	3.97315	-0.01573
2	C	-2.61019	3.91296	0.06110
3	C	-2.96940	2.58372	-0.06387
4	C	-1.92983	1.67872	-0.17437
5	C	-0.59824	2.05399	-0.16357
6	C	-1.29456	4.34026	0.07891
7	C	-0.25814	3.40601	-0.03497
8	C	6.11616	5.41932	0.01478
9	C	5.76123	4.12872	0.36104
10	C	5.07980	6.26298	-0.33927
11	C	3.75504	5.86466	-0.35496
12	C	4.45237	3.68040	0.36226
13	C	3.41891	4.55258	-0.00025
14	H	-1.10242	5.40225	0.18179
15	F	-3.59651	4.83059	0.17003
16	F	-2.23910	0.36867	-0.29857
17	H	0.15347	1.27842	-0.25659
18	H	4.26275	2.65209	0.64844
19	F	6.74669	3.27333	0.71315
20	H	3.00490	6.59105	-0.64647
21	F	5.38527	7.53339	-0.68492
22	H	-4.00453	2.26963	-0.07490
23	H	7.14622	5.74969	0.02058

$Zn(4\text{-}C_6F_3H_2)_2$ CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	1.60840	3.98171	-0.06183
2	C	-2.54269	3.75025	0.67242
3	C	-2.90618	2.63147	-0.05193
4	C	-1.99326	1.89467	-0.78147
5	C	-0.66403	2.30581	-0.77710
6	C	-1.20611	4.13670	0.65746
7	C	-0.23255	3.43136	-0.06250
8	C	6.10703	5.38105	0.02881
9	C	5.69318	4.40789	0.91775
10	C	5.24930	5.95742	-0.88808
11	C	3.92445	5.53256	-0.90551
12	C	4.36238	4.00393	0.87658
13	C	3.44368	4.54988	-0.02989
14	H	-0.92853	5.01675	1.22961
15	H	0.04728	1.72136	-1.35280
16	H	4.04479	3.23893	1.57870
17	H	3.25665	5.99036	-1.62906
18	H	-2.32138	1.02340	-1.33569
19	F	-4.20342	2.24298	-0.04647
20	H	-3.29123	4.29925	1.23116
21	H	5.61566	6.71801	-1.56722
22	F	7.39949	5.78438	0.05735
23	H	6.39935	3.98225	1.62065

$Zn(2,3,5,6\text{-}C_6F_4H_1)_2$ CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	1.56168	4.03712	-0.00304
2	C	-2.65526	3.90037	0.00215
3	C	-2.95346	2.55250	-0.06840
4	C	-1.90351	1.65462	-0.11657
5	C	-0.59335	2.10523	-0.09352
6	C	-1.33716	4.32899	0.02332
7	C	-0.27253	3.44840	-0.02398
8	C	6.12207	5.38175	0.00073
9	C	5.76156	4.08137	0.29949
10	C	5.11761	6.28521	-0.29197
11	C	3.78988	5.88796	-0.28397
12	C	4.42741	3.70595	0.30242
13	C	3.40713	4.59237	0.01109
14	F	-1.10087	5.65769	0.09198
15	F	-3.64938	4.80180	0.04988
16	F	-2.15380	0.33721	-0.18675
17	F	0.39767	1.18759	-0.14142
18	F	4.12775	2.42270	0.60148
19	F	6.70944	3.17505	0.58792
20	F	2.84761	6.81091	-0.57821
21	F	5.43055	7.55704	-0.58771
22	H	-3.97974	2.20991	-0.08648
23	H	7.16086	5.68482	-0.00479

$Zn(3,4,5\text{-}C_6F_3H_2)_2$ CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	1.60569	3.99010	-0.04415
2	C	-2.51958	3.71975	0.68205
3	C	-2.92847	2.62329	-0.05949
4	C	-1.97812	1.93608	-0.79708
5	C	-0.65210	2.32690	-0.79934
6	C	-1.19809	4.12599	0.69246
7	C	-0.23511	3.43413	-0.05133
8	C	6.13173	5.38183	0.01967
9	C	5.66697	4.43532	0.91825
10	C	5.23971	5.91165	-0.89855
11	C	3.91619	5.51330	-0.92475
12	C	4.34717	4.02360	0.90722
13	C	3.44299	4.55723	-0.01859
14	H	-0.94665	4.99202	1.29473
15	H	0.03917	1.74508	-1.39858
16	H	4.05001	3.27928	1.63753
17	H	3.27195	5.96824	-1.66876
18	F	-2.37961	0.87364	-1.51555
19	F	-4.20879	2.23766	-0.06331
20	F	-3.44497	4.38357	1.39545
21	F	5.69595	6.82722	-1.77003
22	F	7.41001	5.77391	0.03730
23	F	6.53621	3.92259	1.80579

$Zn(2.4.6\text{-}C_6F_3H_2)_2$ CPCM toluene

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	1.61597	3.95818	-0.05908
2	C	-2.60137	3.94109	0.30794
3	C	-2.91426	2.64520	-0.06071
4	C	-1.95987	1.71362	-0.42747
5	C	-0.64483	2.14504	-0.40988
6	C	-1.25790	4.27384	0.29284
7	C	-0.22706	3.41797	-0.05834
8	C	6.10777	5.39184	0.03216
9	C	5.79502	4.17279	0.60624
10	C	5.16559	6.20641	-0.56970
11	C	3.86369	5.73668	-0.57290
12	C	4.46493	3.79345	0.55160
13	C	3.44738	4.53392	-0.02644
14	F	-0.93405	5.54066	0.65183
15	F	0.30270	1.24298	-0.76611
16	F	4.14151	2.60119	1.11072
17	F	2.92733	6.52307	-1.15910
18	H	-2.22977	0.70583	-0.71178
19	F	-4.20730	2.27304	-0.06220
20	H	-3.36575	4.65150	0.59140
21	H	5.43445	7.15615	-1.01136
22	F	7.38822	5.80445	0.06043
23	H	6.54987	3.55346	1.07086

XYZ coordinates for the relaxed scan of the $ZnEt_2$ C-Zn-C bend angle.

$ZnEt_2$ CPCM Toluene (C-Zn-C bend = 180°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.18224	1.90834	-0.28164
2	C	-2.12781	1.69818	-0.17605
3	C	1.76334	2.11850	-0.38723
4	C	2.30542	3.35481	0.34845
5	H	2.05595	2.16156	-1.44275
6	H	2.24056	1.21587	0.01120
7	H	1.88194	4.27988	-0.05305
8	H	3.39519	3.44016	0.27220
9	H	2.05920	3.33021	1.41386
10	C	-2.66425	1.53023	1.25511
11	H	-2.42321	0.83446	-0.78272
12	H	-2.60635	2.56453	-0.64681
13	H	-2.23885	0.64878	1.74352
14	H	-3.75393	1.41813	1.28159
15	H	-2.41463	2.39082	1.88237

$ZnEt_2$ CPCM Toluene (C-Zn-C bend = 174°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.21642	1.96981	-0.40511
2	C	-2.14680	1.69065	-0.20840
3	C	1.73680	2.13185	-0.41637
4	C	2.27392	3.32937	0.38440
5	H	2.09860	2.18821	-1.44915
6	H	2.15298	1.20235	-0.01048
7	H	1.90894	4.27889	-0.01729
8	H	3.36867	3.37708	0.37846
9	H	1.96036	3.28714	1.43155
10	C	-2.59438	1.56131	1.25730
11	H	-2.42910	0.78615	-0.75928
12	H	-2.69497	2.50930	-0.68784
13	H	-2.09384	0.72848	1.75978
14	H	-3.67288	1.39086	1.34951
15	H	-2.36156	2.46303	1.83095

$ZnEt_2$ CPCM Toluene (C-Zn-C bend = 168°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.16951	1.78657	-0.43903
2	C	-2.11573	1.76240	-0.19795
3	C	1.77287	2.04859	-0.37037
4	C	2.15643	3.36757	0.32226
5	H	2.20148	2.02363	-1.37818
6	H	2.23063	1.20840	0.16406
7	H	1.74804	4.23443	-0.20521
8	H	3.24184	3.50686	0.37828
9	H	1.77416	3.41221	1.34634
10	C	-2.53349	1.50119	1.25887
11	H	-2.58083	1.01760	-0.85281
12	H	-2.51309	2.73008	-0.52536
13	H	-2.19146	0.52215	1.60668
14	H	-3.62107	1.52808	1.39010
15	H	-2.10996	2.24469	1.94034

$ZnEt_2$ CPCM Toluene (C-Zn-C bend = 162°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.16438	1.69145	-0.59783
2	C	-2.09762	1.67172	-0.25444
3	C	1.76028	2.05864	-0.47028
4	C	2.02471	3.26185	0.45129
5	H	2.19526	2.24905	-1.45713
6	H	2.28201	1.17683	-0.08234
7	H	1.54801	4.17098	0.07338
8	H	3.09371	3.47834	0.55542
9	H	1.63177	3.09320	1.45826
10	C	-2.40534	1.66720	1.25281
11	H	-2.58716	0.81677	-0.73238
12	H	-2.54059	2.56133	-0.71655
13	H	-2.01508	0.76952	1.74078
14	H	-3.48125	1.70267	1.45691
15	H	-1.95402	2.52490	1.76014

$ZnEt_2$ CPCM Toluene (C-Zn-C bend = 157°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.16410	1.57621	-0.74696
2	C	-2.06518	1.45840	-0.26354
3	C	1.70277	2.17857	-0.62154
4	C	1.91756	2.95694	0.68854
5	H	1.94880	2.82066	-1.47434
6	H	2.40551	1.34033	-0.67050
7	H	1.24454	3.81613	0.76437
8	H	2.94004	3.34010	0.77951
9	H	1.73027	2.33000	1.56508
10	C	-2.27635	2.04131	1.14550
11	H	-2.43804	0.42967	-0.29798
12	H	-2.66924	2.01738	-0.98650
13	H	-1.72425	1.47690	1.90249
14	H	-3.33074	2.03434	1.44342
15	H	-1.93129	3.07752	1.21049

$ZnEt_2$ CPCM Toluene (C-Zn-C bend = 151°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.18709	1.63729	-0.89666
2	C	-2.02241	1.38228	-0.22939
3	C	1.66226	2.27505	-0.67068
4	C	1.83701	2.76275	0.77886
5	H	1.88313	3.09320	-1.36424
6	H	2.39681	1.49315	-0.88872
7	H	1.13991	3.57050	1.02049
8	H	2.84763	3.14097	0.96965
9	H	1.65198	1.96052	1.49931
10	C	-2.20105	2.22975	1.04328
11	H	-2.19999	0.32697	0.00386
12	H	-2.78305	1.65636	-0.96707
13	H	-1.47306	1.95895	1.81372
14	H	-3.19694	2.11050	1.48447
15	H	-2.06482	3.29623	0.84116

$ZnEt_2$ CPCM Toluene (C-Zn-C bend = 145°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.20500	1.68189	-1.01475
2	C	-1.98908	1.38346	-0.22566
3	C	1.64461	2.28896	-0.68370
4	C	1.74040	2.72634	0.78878
5	H	1.92764	3.12162	-1.33558
6	H	2.37269	1.49540	-0.88064
7	H	1.05638	3.55026	1.01147
8	H	2.74865	3.06298	1.05468
9	H	1.48307	1.91023	1.47056
10	C	-2.12149	2.26348	1.02922
11	H	-2.08843	0.32859	0.05315
12	H	-2.81682	1.58896	-0.91124
13	H	-1.32965	2.05480	1.75413
14	H	-3.07758	2.10966	1.54194
15	H	-2.05506	3.32785	0.78567

$ZnEt_2$ CPCM Toluene (C-Zn-C bend = 140°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	-0.22149	1.72453	-1.11319
2	C	-1.94174	1.37111	-0.20270
3	C	1.61960	2.32099	-0.69760
4	C	1.66439	2.65565	0.80371
5	H	1.92576	3.19515	-1.28056
6	H	2.35368	1.54044	-0.92285
7	H	0.98401	3.47367	1.05585
8	H	2.66669	2.95660	1.12844
9	H	1.37045	1.80005	1.41914
10	C	-2.06799	2.32447	0.99742
11	H	-1.93920	0.33356	0.14987
12	H	-2.82466	1.46522	-0.84223
13	H	-1.23670	2.20507	1.69692
14	H	-2.99206	2.15526	1.56167
15	H	-2.07043	3.37268	0.68414

XYZ coodinates for the relaxed scan of the $ZnEt_2$ C-C-Zn-C-C dihedral angle.

$ZnEt_2$ CPCM Hexane (C-C-Zn-C-C dihedral = 180°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	0.09819	0.52460	0.04718
2	C	-1.76140	0.47486	0.65383
3	H	-1.90315	-0.42744	1.25524
4	H	-1.92127	1.30948	1.34216
5	C	-2.81480	0.51967	-0.46098
6	H	-2.71558	-0.32282	-1.14686
7	H	-3.83092	0.48898	-0.06129
8	H	-2.73395	1.42840	-1.05909
9	C	1.95777	0.57434	-0.55946
10	H	2.09952	1.47664	-1.16087
11	H	2.11764	-0.26027	-1.24779
12	C	3.01118	0.52953	0.55535
13	H	2.93033	-0.37920	1.15346
14	H	4.02729	0.56023	0.15566
15	H	2.91195	1.37202	1.24122

$ZnEt_2$ CPCM Hexane (C-C-Zn-C-C dihedral = 165°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	0.10010	0.33314	0.03805
2	C	-1.76553	0.28757	0.62620
3	H	-1.98698	-0.71953	0.99038
4	H	-1.86733	0.93949	1.49831
5	C	-2.79696	0.68765	-0.43707
6	H	-2.75654	0.03226	-1.30821
7	H	-3.81751	0.64312	-0.05018
8	H	-2.63542	1.70498	-0.79624
9	C	1.96570	0.38109	-0.54999
10	H	2.05362	1.11504	-1.35593
11	H	2.20690	-0.58211	-1.00824
12	C	2.98996	0.69860	0.54752
13	H	2.96343	-0.03741	1.35228
14	H	4.01082	0.71144	0.15913
15	H	2.80853	1.67370	1.00174

$ZnEt_2$ CPCM Hexane (C-C-Zn-C-C dihedral = 150°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	0.10010	0.33314	0.03805
2	C	-1.76553	0.28757	0.62620
3	H	-1.98698	-0.71953	0.99038
4	H	-1.86733	0.93949	1.49831
5	C	-2.79696	0.68765	-0.43707
6	H	-2.75654	0.03226	-1.30821
7	H	-3.81751	0.64312	-0.05018
8	H	-2.63542	1.70498	-0.79624
9	C	1.96570	0.38109	-0.54999
10	H	2.05362	1.11504	-1.35593
11	H	2.20690	-0.58211	-1.00824
12	C	2.98996	0.69860	0.54752
13	H	2.96343	-0.03741	1.35228
14	H	4.01082	0.71144	0.15913
15	H	2.80853	1.67370	1.00174

$ZnEt_2$ CPCM Toluene (C-C-Zn-C-C dihedral = 135°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	0.10096	0.24170	0.03401
2	C	-1.77148	0.19857	0.60029
3	H	-2.03587	-0.83613	0.83573
4	H	-1.85753	0.74144	1.54571
5	C	-2.77476	0.76761	-0.41166
6	H	-2.75017	0.22363	-1.35693
7	H	-3.80049	0.71645	-0.03959
8	H	-2.56986	1.81421	-0.64121
9	C	1.97337	0.28801	-0.53212
10	H	2.04792	0.91797	-1.42293
11	H	2.25773	-0.71496	-0.86246
12	C	2.96625	0.78005	0.52925
13	H	2.95316	0.15018	1.41983
14	H	3.99244	0.78376	0.15496
15	H	2.74113	1.79658	0.85489

$ZnEt_2$ CPCM Toluene (C-C-Zn-C-C dihedral = 120°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	0.10174	0.15521	0.03037
2	C	-1.77967	0.11453	0.56627
3	H	-2.08564	-0.93045	0.66802
4	H	-1.86042	0.53871	1.57101
5	C	-2.74534	0.84298	-0.37777
6	H	-2.72592	0.42008	-1.38316
7	H	-3.77797	0.78550	-0.02628
8	H	-2.49850	1.90133	-0.47275
9	C	1.98310	0.19959	-0.50538
10	H	2.05478	0.71486	-1.46731
11	H	2.30899	-0.82573	-0.70149
12	C	2.93546	0.85759	0.50181
13	H	2.92509	0.34469	1.46455
14	H	3.96868	0.85216	0.14741
15	H	2.66842	1.89798	0.69245

$ZnEt_2$ CPCM Toluene (C-C-Zn-C-C dihedral = 105°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	0.10246	0.07508	0.02709
2	C	-1.78961	0.03687	0.52417
3	H	-2.13323	-1.00075	0.48900
4	H	-1.87592	0.33472	1.57287
5	C	-2.71053	0.91244	-0.33585
6	H	-2.68522	0.61826	-1.38602
7	H	-3.75142	0.84910	-0.01073
8	H	-2.42580	1.96465	-0.29303
9	C	1.99448	0.11737	-0.46984
10	H	2.07420	0.50929	-1.48767
11	H	2.35777	-0.91253	-0.52721
12	C	2.89936	0.92995	0.46570
13	H	2.88059	0.54271	1.48538
14	H	3.94099	0.91570	0.13707
15	H	2.59466	1.97618	0.51683

$ZnEt_2$ CPCM Toluene (C-C-Zn-C-C dihedral = 90°)

Centre number	Atom type	Coordinates (Angstroms)		
		X	Y	Z
1	Zn	0.10311	0.00243	0.02410
2	C	-1.80072	-0.03309	0.47417
3	H	-2.17585	-1.04561	0.30082
4	H	-1.90313	0.13301	1.55020
5	C	-2.67241	0.97491	-0.28639
6	H	-2.63057	0.81486	-1.36467
7	H	-3.72244	0.90667	0.00678
8	H	-2.35601	2.00297	-0.104 62
9	C	2.00689	0.04263	-0.42578
10	H	2.10525	0.30497	-1.48287
11	H	2.40115	-0.97401	-0.34220
12	C	2.86010	0.99576	0.42151
13	H	2.82217	0.74040	1.48142
14	H	3.91099	0.97343	0.12434
15	H	2.52427	2.02972	0.33095

Example input files:

Optimisation/Frequency calculation in ORCA 5.0.3

```
! wB97X-D3BJ ZORA-def2-TZVPP SARC/J RIJCOSX TightSCF SlowConv CPCM(toluene) ZORA defgrid3
! LargePrint
! Opt Freq

%SCF
        MaxIter 500
End

* xyzfile 0 1 opt.xyz
```

Zn 1s TDDFT calculation in ORCA 5.0.3

```
! wB97X-D3BJ ZORA-def2-QZVPP SARC/J RIJCOSX TightSCF CPCM(toluene) ZORA
! LargePrint

%tddft
        nroots 50
        maxdim 500
        OrbWin[0] = 0,0,-1,-1
        DoQuad True
        TDA True
end

* xyzfile 0 1 XAS.xyz
```

Zn XES KS-DFT calculation in ORCA 5.0.3

```
! wB97X-D3BJ ZORA-def2-QZVPP SARC/J RIJCOSX TightSCF CPCM(toluene) ZORA defgrid3
! LargePrint

%xes
CoreOrb 0
OrbOp 0
CoreOrbSoc 0
DOSOC True
DoQuad true
end

* xyzfile 0 1 XES.xyz
```

Relaxed scan (dihedral) calculation in ORCA 5.0.3

```
! wB97X-D3BJ ZORA-def2-TZVPP SARC/J RIJCOSX tightscf tightopt slowconv CPCM(Toluene) ZORA
! LargePrint
! Opt

%geom Scan
D 4 6 16 17 = 0, 180, 18
end
end

* xyzfile 0 1 opt.xyz
```

Relaxed scan (bend) calculation in ORCA 5.0.3

```
! wB97X-D3BJ def2-TZVPP def2/J RIJCOSX CPCM(toluene) TightSCF SlowConv
! LargePrint
! Opt

%geom Scan
A 1 0 2 = 180, 140, 8
end
end

* xyzfile 0 1 opt.xyz
```

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