Supporting Information

Pericyclic Transition-State-Like Aromaticity in Inorganic Ions $\text{Se}_2\text{I}_4^{2+}$ and $\text{S}_2\text{O}_4^{2-}$

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$\text{Se}_2\text{I}_4^{2+}(\text{C}_{2v})$			$\text{S}_8^{2+}(\text{C}_s)$		
MPW1PW91/SDB-cc-pVTZ			MPW1PW91/6-311+G(3df)		
LUMO	b_2		a''	LUMO	
(-0.48486 au)				(-0.51366 au)	
HOMO	a_2		a''	HOMO-2	
(-0.58497 au)				(-0.62673 au)	
HOMO-1	a_1		a''	HOMO-4	
(-0.58904 au)				(-0.67937 au)	
HOMO-6	b_2		a'	HOMO-6	
(-0.63753 au)				(-0.69290 au)	
HOMO-7	b_1		a'	HOMO-9	
(-0.63758 au)				(-0.76261 au)	
HOMO-11	a_1		a'	HOMO-12	
(-0.73796 au)				(-0.81572 au)	

Fig. S1 Selected molecular orbitals of $\text{Se}_2\text{I}_4^{2+}$ and S_8^{2+} that show the 10π conjugation within them. For S_8^{2+} , the lone-pair electrons of the S1 and S5 atoms contribute to HOMO-6, HOMO-9, and HOMO-12, showing the involvement of these electrons in the through-space conjugation of the two S_3^+ subunits.

Cartesian coordinates, total energies, and electronic state for $\text{Se}_2\text{I}_4^{2+}$ predicted at the MPW1PW91/ SDB-cc-pVTZ level of theory and those for $\text{S}_2\text{O}_4^{2-}$, $\text{S}_2\text{Cl}_2^{2+}$, S_8^{2+} , Se_8^{2+} predicted at the MPW1PW91/6-311+G(3df) level.

$\text{Se}_2\text{I}_4^{2+}$ (C_{2v}): $E_{\text{tot}} = -63.8383144$ hartree; $^1\text{A}_1$;
 Se,0,-0.628991784,0.8347002898,-1.4880302753
 Se,0,-0.628991784,0.8347002898,1.4880302753
 I,0,1.791426355,0.9301714319,-1.9193003196
 I,0,-1.3879221917,-1.4656395423,-1.9193003196
 I,0,1.791426355,0.9301714319,1.9193003196
 I,0,-1.3879221917,-1.4656395423,1.9193003196

$\text{S}_2\text{O}_4^{2-}$: $E_{\text{tot}} = -1097.3269393$ hartree; $^1\text{A}_1$;
 O 1.657167 1.232966 0.442826
 O 1.709738 -1.251803 0.282740
 O -1.689507 1.255608 0.280130
 O -1.676314 -1.229540 0.444709
 S -1.265135 -0.032895 -0.362819
 S 1.264593 0.029280 -0.362384

$\text{S}_2\text{Cl}_4^{2+}$ (C_{2v}): $E_{\text{tot}} = -2636.5535943$ hartree; $^1\text{A}_1$;
 S,0.,1.3046670453,-0.7380884728
 S,0.,-1.3046670453,-0.7380884728
 Cl,-1.5617202791,1.6528490732,0.3473357519
 Cl,1.5617202791,1.6528490732,0.3473357519
 Cl,-1.5617202791,-1.6528490732,0.3473357519
 Cl,1.5617202791,-1.6528490732,0.3473357519

S_8^{2+} (C_s): $E_{\text{tot}} = -3185.0947719$ hartree; $^1\text{A}'$;
 S,-0.4234591761,2.1092290845,0.
 S,0.8826631499,1.6030515115,-1.5056918682
 S,0.8891078172,-0.4282686978,-1.4262791592
 S,-1.0632437244,-1.0153189947,-1.4928031944
 S,-0.9935953092,-2.4281567224,0.
 S,-1.0632437244,-1.0153189947,1.4928031944
 S,0.8891078172,-0.4282686978,1.4262791592
 S,0.8826631499,1.6030515115,1.5056918682

Se_8^{2+} (C_s): $E_{\text{tot}} = -19213.0850939$ hartree; $^1\text{A}'$;
 Se,-0.9011351315,-2.2353264731,-0.0254265452
 Se,-2.1042002124,-0.8233696167,-1.4309822286
 Se,-0.7951200945,1.0975748959,-1.2766931346
 Se,1.3329347725,0.3892832757,-1.8793643709
 Se,2.4634774708,1.6492612874,-0.2792311257
 Se,1.8744117379,0.133820081,1.3888627859
 Se,-0.316074322,0.871566088,1.6147140781
 Se,-1.5542942208,-1.0828095381,1.888120541