Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Computational predictions of adaptive aromaticity for the design of singlet fission materials

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Table S1. SOCs between the S_1 and T_n states of key species (using S_0-geomtries, unit: cm^{-1}).

	$\langle S_1\|H_{SO}\|T_2\rangle$	$\langle S_1\|H_{SO}\|T_3\rangle$	$\langle S_1\|H_{SO}\|T_4\rangle$	$\langle S_1\|H_{SO}\|T_5\rangle$
16.Os.F	314.65	325.26	17.92	131.21
16.Os.Cl	287.98	42.05	364.32	800.94
16.Os.OH	31.30	358.85	19.83	50.30
16.Re.SnCl$_3$	308.98	107.89	181.03	625.89
16.Os.SnCl$_3$	10.87	72.90	114.19	388.43
16.Ir.SnCl$_3$	320.09	84.07	376.25	329.71
***p*-CN**	19.89	2.10	7.64	18.68
***p*-NO$_2$**	0.14	19.98	0.21	2.45

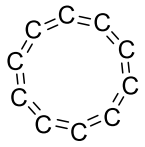
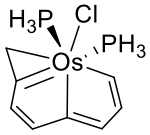
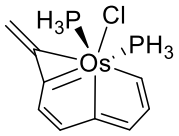
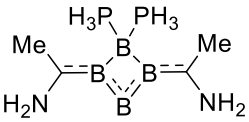
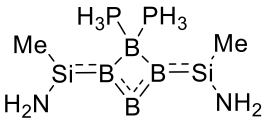
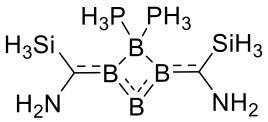
			
	C10	**1-Os**	**C-Os**
$E(S_1)_v$	3.73	2.48	2.48
$E(T_1)_a$	2.15	1.59	1.40
$E(T_2)_v$	3.08	2.07	2.02
$E(S_1)_v/E(T_1)_a$	1.73	1.56	1.77
$E(T_2)_v/E(T_1)_a$	1.43	1.30	1.44
			
	TB1-1	**TB1-Si**	**TB1-Si-2**
$E(S_1)_v$	2.76	2.53	2.52
$E(T_1)_a$	1.11	1.00	0.84
$E(T_2)_v$	2.13	2.67	2.13
$E(S_1)_v/E(T_1)_a$	2.49	2.53	3.00
$E(T_2)_v/E(T_1)_a$	1.92	2.67	2.54
$NICS(0)_{zz}$ (ppm)			
S_0	-45.5	-40.2	-44.3
T_1	-38.8	-37.5	-41.2

Fig. S1. Excitation energies (unit: eV) and excitation energy ratios of cyclo[10]carbon, unsaturated three-membered ring, and tetraatomic boron species. The adiabatic excitation energy of T_1 state is labelled as $E(T_1)_a$ whereas the vertical excitation energy of S_1 and T_2 states is labelled as $E(S_1)_v$ and $E(T_2)_v$, respectively.

Table S2. Coefficients of the major configurations and oscillator strengths from Gaussian output for the S_1 transition of key species.

16.Os.F	Excited State 1:	Singlet-A	2.3604 eV	525.26 nm	f=0.0005
	<S**2>=0.000				
	53 -> 56	0.29019			
	54 -> 55	0.11843			
	54 -> 56	0.62876			
16.Os.Cl	Excited State 1:	Singlet-A	2.1624 eV	573.36 nm	f=0.0000
	<S**2>=0.000				
	57 -> 59	0.13849			
	58 -> 59	0.68932			
16.Os.OH	Excited State 1:	Singlet-A	2.5657 eV	483.24 nm	f=0.0001
	<S**2>=0.000				
	53 -> 56	0.32782			
	54 -> 56	0.62252			
16.Os.$SnCl_3$	Excited State 1:	Singlet-A	2.0356 eV	609.09 nm	f=0.0078
	<S**2>=0.000				
	86 -> 87	0.70370			
16.Re.$SnCl_3$	Excited State 1:	Singlet-A	2.3715 eV	522.81 nm	f=0.0003
	<S**2>=0.000				
	84 -> 87	0.17470			
	85 -> 87	0.43984			
	86 -> 87	0.52013			
16.Ir.$SnCl_3$	Excited State 1:	Singlet-A	2.6736 eV	463.73 nm	f=0.0360
	<S**2>=0.000				
	85 -> 87	0.18047			
	86 -> 87	0.64369			
	86 -> 88	0.14116			
Ph.NO	Excited State 1:	Singlet-A"	1.1746 eV	1055.52 nm	f=0.0002
	<S**2>=0.000				
	28 -> 29	0.68927			
	28 -> 31	0.24134			
	28 <- 29	-0.18080			
***p*-CN**	Excited State 1:	Singlet-A"	1.1172 eV	1109.75 nm	f=0.0002
	<S**2>=0.000				
	34 -> 35	0.66325			
	34 -> 37	-0.30469			
	34 <- 35	-0.17842			
	34 <- 37	0.10287			
***p*-NO_2**	Excited State 1:	Singlet-A"	1.0992 eV	1128.00 nm	f=0.0002
	<S**2>=0.000				
	39 -> 40	0.61680			
	39 -> 41	-0.34064			
	39 -> 42	0.13305			

	39 -> 43	0.15746
	39 <- 40	-0.16605
	39 <- 41	0.10757

Table S3. The occupation numbers (n_i) of the UHF natural orbitals (UNOs) and multiple diradical character (y_i).

	n_{LUNO+1}	n_{LUNO}	n_{HONO}	n_{HONO-1}	y_0	y_1
16.Os.F	0.035	0.245	1.755	1.965	0.038	0.001
16.Os.Cl	0.035	0.241	1.759	1.965	0.037	0.001
16.Os.OH	0.038	0.262	1.738	1.962	0.044	0.001
16.Os.$SnCl_3$	0.035	0.229	1.771	1.965	0.033	0.001
16.Re.$SnCl_3$	0.221	0.305	1.695	1.779	0.063	0.030
16.Ir.$SnCl_3$	0.092	0.375	1.625	1.908	0.101	0.005
***p*-CN**	0.131	0.274	1.726	1.869	0.049	0.010
***p*-NO_2**	0.198	0.290	1.710	1.802	0.056	0.024