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

Heteroatom-bridged Heterofluorenes: A Theoretical Study on Molecular Structures and Optoelectronic Properties

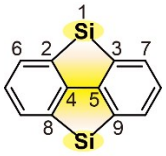
Yuanyuan Qi, Cailin Chen, Chao Zheng*, Yuting Tang, Yifang Wan, He Jiang, Ting Chen, Ye Tao, Runfeng Chen*

Key Laboratory for Organic Electronics and Information Displays & Jiangsu Key Laboratory for Biosensors, Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China.

*E-mail: iamczheng@njupt.edu.cn

*E-mail: iamrfchen@njupt.edu.cn. Phone: +86-025-85866826. Fax: +86-025-85866826.

Table S1 Bond lengths (L in Å), angles (A in deg) and dihedral angles (H in deg) of **BSiF** suggested by different calculation methods.



BSiF

Structural parameter	HF				B3LYP				Exp[1]
	3-21G	6-31G	6-31G(d)	6-31G(d,p)	3-21G	6-31G	6-31G(d)	6-31G(d,p)	
L_{45}	1.470	1.466	1.470	1.470	1.470	1.465	1.466	1.465	1.462
L_{12}	1.903	1.932	1.903	1.903	1.905	1.935	1.905	1.905	1.888
L_{24}	1.392	1.392	1.392	1.392	1.405	1.407	1.405	1.405	1.396
L_{26}	1.390	1.391	1.390	1.390	1.400	1.402	1.400	1.400	1.396
A_{213}	92.132	91.038	92.132	92.126	92.483	91.291	92.483	92.487	92.754
A_{124}	106.765	106.878	106.765	106.761	106.508	106.796	106.508	106.502	106.580
A_{245}	117.169	117.603	117.169	117.176	117.251	117.559	117.251	117.254	116.842
H_{6245}	180.000	180.000	180.000	180.000	180.000	180.000	180.000	180.000	179.260
H_{6213}	180.000	180.000	180.000	180.000	180.000	180.000	180.000	179.999	179.162

Table S2 HOMO, LUMO and band gap (E_g) of **BXF** and **XF** (in eV).

	BCF	**BSiF**	**BGeF**	**BNF**	**BPF**	**BAsF**	**BOF**	**BSF**	**BSeF**
HOMO	-5.41	-5.61	-5.63	-4.91	-5.86	-5.86	-6.04	-5.80	-5.60
LUMO	-0.45	-0.80	-0.76	-0.10	-0.95	-0.96	-0.99	-0.89	-0.90
E_g	4.96	4.81	4.87	4.81	4.91	4.9	5.05	4.91	4.7
	CF	**SiF**	**GeF**	**NF**	**PF**	**AsF**	**OF**	**SF**	**SeF**
HOMO	-5.73	-5.78	-5.78	-5.32	-5.93	-5.92	-6.01	-5.82	-5.65
LUMO	-0.74	-0.92	-0.87	-0.62	-0.98	-0.97	-0.92	-0.95	-0.95
E_g	4.99	4.85	4.92	4.70	4.95	4.95	5.09	4.87	4.70

Table S3 Simulated electronic transition, absorption peak, oscillator strength (f) and main transition configuration for **BXF** by TD-DFT/B3LYP/6-31G(d)

BXF	Electronic transitions	Wavelength/nm	f	Main Configurations
BCF	$S_0 \rightarrow S_{10}$	189	0.73	HOMO - 1 → LUMO + 2 (61%)
	$S_0 \rightarrow S_{11}$	188	0.26	HOMO - 3 → LUMO + 1 (61%)
				HOMO - 2 → LUMO (23%)
				HOMO - 1 → LUMO (10%)
	$S_0 \rightarrow S_2$	270	0.25	HOMO → LUMO (82%)
BSiF	$S_0 \rightarrow S_{13}$	201	0.45	HOMO - 4 → LUMO + 1 (54%)
				HOMO - 2 → LUMO (13%)
	$S_0 \rightarrow S_{15}$	192	0.43	HOMO - 2 → LUMO + 2 (79%)
	$S_0 \rightarrow S_6$	228	0.31	HOMO - 2 → LUMO + 2 (10%)
				HOMO - 1 → LUMO + 1 (79%)
BGeF	$S_0 \rightarrow S_{16}$	192	0.48	HOMO - 1 → LUMO + 2 (79%)
	$S_0 \rightarrow S_{13}$	201	0.44	HOMO - 5 → LUMO + 1 (63%)
				HOMO - 2 → LUMO + 3 (14%)
	$S_0 \rightarrow S_8$	224	0.26	HOMO - 2 → LUMO + 1 (79%)
				HOMO - 1 → LUMO + 2 (13%)
BNF	$S_0 \rightarrow S_6$	232	0.92	HOMO - 1 → LUMO (42%)
				HOMO → LUMO + 1 (32%)
	$S_0 \rightarrow S_{12}$	193	0.22	HOMO - 3 → LUMO + 3 (13%)
				HOMO - 2 → LUMO + 2 (74%)
BPF	$S_0 \rightarrow S_{12}$	213	0.48	HOMO - 3 → LUMO + 1 (61%)
				HOMO - 1 → LUMO + 3 (14%)
BAsF	$S_0 \rightarrow S_2$	281	0.13	HOMO → LUMO (93%)
	$S_0 \rightarrow S_7$	235	0.11	HOMO - 5 → LUMO (10%)
				HOMO → LUMO + 2 (61%)
				HOMO → LUMO + 3 (18%)
	$S_0 \rightarrow S_{13}$	210	0.48	HOMO - 3 → LUMO + 1 (59%)
				HOMO - 1 → LUMO + 2 (27%)
	$S_0 \rightarrow S_{21}$	194	0.31	HOMO - 5 → LUMO (21.83%)
				HOMO - 4 → LUMO + 1 (53.84%)
				HOMO - 3 → LUMO + 4 (11.49%)
				HOMO - 2 → LUMO + 3 (23%)
BOF	$S_0 \rightarrow S_6$	230	0.50	HOMO – 1 → LUMO (10%)
				HOMO → LUMO + 2 (67%)
	$S_0 \rightarrow S_{10}$	199	0.23	HOMO - 2 → LUMO + 1 (85%)
	$S_0 \rightarrow S_{19}$	169	0.26	HOMO – 5 → LUMO (41%)
				HOMO – 2 → LUMO +3 (23%)
BSF	$S_0 \rightarrow S_8$	233	0.76	HOMO - 1 → LUMO (41%)
	$S_0 \rightarrow S_{16}$	199	0.30	HOMO - 2 → LUMO + 3 (79%)
BSeF	$S_0 \rightarrow S_9$	238	0.64	HOMO - 1 → LUMO (56%)
				HOMO → LUMO + 2 (38%)

$S_0 \rightarrow S_{14}$	214	0.32	HOMO - 2 → LUMO + 3 (77%)
			HOMO - 1 → LUMO + 2 (11%)
$S_0 \rightarrow S_{26}$	186	0.21	HOMO - 3 → LUMO + 3 (25%)
			HOMO - 2 → LUMO + 5 (71%)
$S_0 \rightarrow S_{28}$	184	0.19	HOMO - 3 → LUMO + 3 (68%)
			HOMO - 2 → LUMO + 5 (26%)

Table S4 Simulated electronic transition, absorption peak, oscillator strength (f) and main transition configuration for **XF** by TD-DFT/B3LYP/6-31G(d).

XF	Electronic transitions	Wavelength/nm	f	Main Configurations
CF	$S_0 \rightarrow S_1$	268	0.27	HOMO - 2 → LUMO (12%)
				HOMO → LUMO (72%)
				HOMO → LUMO + 1 (13%)
	$S_0 \rightarrow S_{10}$	187	0.75	HOMO - 2 → LUMO + 1 (22%)
				HOMO - 1 → LUMO + 2 (72%)
	$S_0 \rightarrow S_{23}$	161	0.45	HOMO - 2 → LUMO + 1 (22%)
				HOMO - 7 → LUMO (37%)
				HOMO - 2 → LUMO + 3 (37%)
	$S_0 \rightarrow S_{27}$	158	0.34	HOMO - 7 → LUMO (61%)
				HOMO - 2 → LUMO + 3 (20%)
SiF	$S_0 \rightarrow S_4$	230	0.28	HOMO - 1 → LUMO (63%)
				HOMO → LUMO + 1 (30%)
	$S_0 \rightarrow S_{15}$	187	0.55	HOMO - 2 → LUMO + 2 (87%)
	$S_0 \rightarrow S_{29}$	162	0.69	HOMO - 3 → LUMO + 1 (12%)
				HOMO - 1 → LUMO + 3 (63%)
GeF	$S_0 \rightarrow S_4$	229	0.18	HOMO - 2 → LUMO (67%)
				HOMO → LUMO + 1 (27%)
	$S_0 \rightarrow S_8$	213	0.19	HOMO - 2 → LUMO + 1 (85%)
	$S_0 \rightarrow S_{15}$	188	0.58	HOMO - 2 → LUMO + 1 (10%)
				HOMO - 1 → LUMO + 2 (85%)
NF	$S_0 \rightarrow S_3$	236	0.46	HOMO - 1 → LUMO (13%)
				HOMO - 1 → LUMO + 2 (15%)
				HOMO → LUMO + 1 (54%)
	$S_0 \rightarrow S_7$	208	0.46	HOMO - 1 → LUMO + 2 (14%)
				HOMO → LUMO + 3 (65%)
	$S_0 \rightarrow S_{13}$	175	0.26	HOMO - 2 → LUMO + 2 (92%)
	$S_0 \rightarrow S_{28}$	153	0.51	HOMO - 3 → LUMO + 2 (54%)
				HOMO - 2 → LUMO + 3 (20%)
PF	$S_0 \rightarrow S_7$	225	0.24	HOMO - 2 → LUMO (41%)
				HOMO - 1 → LUMO + 2 (27%)
				HOMO → LUMO + 1 (17%)
	$S_0 \rightarrow S_7$	208	0.35	HOMO - 3 → LUMO + 29%)
				HOMO - 2 → LUMO + 1 (74%)
	$S_0 \rightarrow S_{13}$	200	0.26	HOMO - 1 → LUMO + 3 (87%)
AsF	$S_0 \rightarrow S_{10}$	207	0.33	HOMO - 3 → LUMO + 2 (11%)
				HOMO - 2 → LUMO + 1 (67%)
				HOMO - 1 → LUMO + 2 (12%)
	$S_0 \rightarrow S_{20}$	181	0.18	HOMO - 5 → LUMO + 1 (26%)
				HOMO - 3 → LUMO + 2 (58%)
	$S_0 \rightarrow S_{27}$	170	0.12	HOMO - 3 → LUMO + 3 (54%)
				HOMO - 3 → LUMO + 4 (23%)

OF	$S_0 \rightarrow S_5$	216	0.36	HOMO - 2 → LUMO (11%)
				HOMO - 1 → LUMO + 1 (70%)
	$S_0 \rightarrow S_6$	204	0.32	HOMO - 2 → LUMO (23%)
				HOMO - 1 → LUMO + 1 (16%)
				HOMO → LUMO + 2 (44%)
	$S_0 \rightarrow S_{11}$	178	0.46	HOMO - 2 → LUMO + 2 (92%)
	$S_0 \rightarrow S_{24}$	152	0.49	HOMO - 6 → LUMO (37%)
				HOMO - 3 → LUMO + 2 (34%)
				HOMO - 2 → LUMO + 3 (17%)
SF	$S_0 \rightarrow S_6$	232	0.62	HOMO - 1 → LUMO (23%)
				HOMO → LUMO + 1 (61%)
	$S_0 \rightarrow S_{13}$	189	0.47	HOMO - 2 → LUMO + 2 (90%)
	$S_0 \rightarrow S_{28}$	158	0.25	HOMO - 3 → LUMO (10%)
				HOMO - 3 → LUMO + 2 (10%)
				HOMO - 3 → LUMO + 2 (27%)
				HOMO - 2 → LUMO + 4 (29%)
SeF	$S_0 \rightarrow S_7$	238	0.52	HOMO - 1 → LUMO (29%)
				HOMO → LUMO + 2 (54%)
	$S_0 \rightarrow S_{14}$	191	0.44	HOMO - 2 → LUMO + 1 (90%)
	$S_0 \rightarrow S_{26}$	165	0.16	HOMO - 3 → LUMO + 2 (85%)

Table S5 NICS (0), NICS (1), and MCBO values of **CNF, CSiF** and **SNF**.[a]

Comp.	NICS(0)			NICS(1)			MCBO		
	A	B	C	A	B	C	A	B	C
CNF	2.97	-8.88	-11.37	-2.06	-9.74	-12.73	0.01	0.03	0.06
CSiF	2.44	1.19	-7.59	-1.49	0.43	-9.80	0.01	0.01	0.07
SNF	-5.99	-8.48	-12.96	-5.25	-8.08	-12.65	0.02	0.03	0.05

[a] Component A is the penta-heterocycle containing C or S atom, B is the penta-heterocycle containing N or Si atom, and C is the phenyl-ring unit.

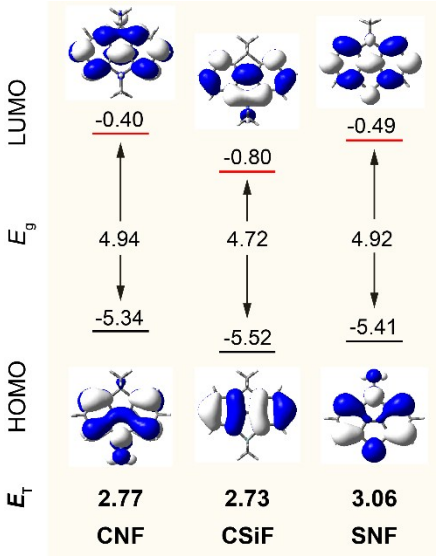


Figure S1 LUMO and HOMO energy levels, energy bandgaps (E_g) and triplet energies (E_T) of mix-heteroatom-bridged heterofluorenes (in eV).

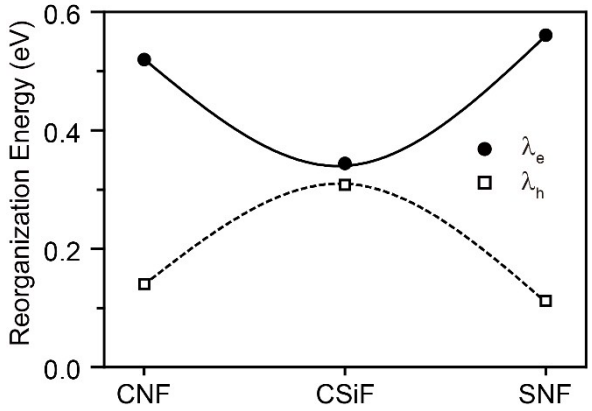


Figure S2 Hole (λ_h) and electron (λ_e) reorganization energies of mix-heteroatom-bridged heterofluorenes (in eV).

Table S6 Simulated electronic transition, absorption peak, oscillator strength (f) and main transition configuration for **BSiF** oligomers by TD-DFT/B3LYP/6-31G(d).

BXF	Electronic transitions	Wavelength/nm	f	Main Configurations
$(BSiF)_2$	$S_0 \rightarrow S_5$	290	0.11	HOMO - 1 → LUMO (22%)
				HOMO → LUMO + 2 (48%)
				HOMO → LUMO + 3 (6%)
	$S_0 \rightarrow S_6$	290	0.11	HOMO - 1 → LUMO + 1 (22%)
				HOMO → LUMO + 3 (48%)
	$S_0 \rightarrow S_{19}$	239	0.18	HOMO - 3 → LUMO (32%)
				HOMO - 3 → LUMO + 2 (5%)
				HOMO - 3 → LUMO + 3 (5%)
				HOMO - 3 → LUMO + 1 (30%)
				HOMO - 3 → LUMO + 2 (5%)
				HOMO - 3 → LUMO + 3 (5%)
				HOMO → LUMO + 4 (9%)
$(BSiF)_3$	$S_0 \rightarrow S_{11}$	290	0.22	HOMO - 2 → LUMO (18%)
				HOMO - 1 → LUMO + 4 (20%)
				HOMO → LUMO + 5 (30%)
$(BSiF)_4$	$S_0 \rightarrow S_{15}$	291	0.2	HOMO - 3 → LUMO (9%)
				HOMO - 2 → LUMO (9%)
				HOMO - 1 → LUMO + 6 (20%)
				HOMO → LUMO + 6 (18%)
	$S_0 \rightarrow S_{16}$	291	0.12	HOMO - 3 → LUMO + 1 (9%)
				HOMO - 2 → LUMO + 1 (9%)
				HOMO - 1 → LUMO + 7 (20%)
				HOMO → LUMO + 7 (18%)
$(BSiF)_5$	$S_0 \rightarrow S_{20}$	291	0.17	HOMO - 3 → LUMO (20%)
				HOMO - 1 → LUMO (11%)
				HOMO - 1 → LUMO + 9 (19%)
				HOMO → LUMO + 8 (15%)

Table S7 Simulated electronic transition, absorption peak, oscillator strength (f) and main transition configuration for **BGeF** oligomers by TD-DFT/B3LYP/6-31G(d).

BXF	Electronic transitions	Wavelength/nm	f	Main Configurations
$(BGeF)_2$	$S_0 \rightarrow S_5$	283	0.13	HOMO - 1 → LUMO (29%)
				HOMO - 1 → LUMO + 1 (8%)
				HOMO - 1 → LUMO + 2 (6%)
				HOMO → LUMO + 2 (34%)
	$S_0 \rightarrow S_6$	283	0.13	HOMO - 1 → LUMO (8%)
				HOMO - 1 → LUMO + 1 (29%)
				HOMO → LUMO + 3 (34%)
	$S_0 \rightarrow S_{17}$	237	0.14	HOMO - 3 → LUMO + 1 (8%)
				HOMO - 3 → LUMO + 2 (15%)
				HOMO - 3 → LUMO + 3 (14%)
				HOMO - 2 → LUMO (8%)
				HOMO - 2 → LUMO + 2 (13%)
				HOMO - 2 → LUMO + 3 (13%)
$(BGeF)_3$	$S_0 \rightarrow S_{11}$	283	0.25	HOMO - 2 → LUMO (18%)
				HOMO - 1 → LUMO + 3 (19%)
				HOMO - 1 → LUMO + 5 (12%)
				HOMO → LUMO + 4 (26%)
	$S_0 \rightarrow S_{20}$	258	0.21	HOMO - 6 → LUMO + 3 (10%)
				HOMO - 3 → LUMO + 2 (35%)
				HOMO - 3 → LUMO (20%)
				HOMO → LUMO + 6 (13%)
$(BGeF)_4$	$S_0 \rightarrow S_{13}$	285	0.15	HOMO - 3 → LUMO (16%)
				HOMO - 3 → LUMO + 5 (8%)
				HOMO - 2 → LUMO + 2 (10%)
				HOMO - 1 → LUMO + 5 (11%)
				HOMO → LUMO + 4 (19%)
	$S_0 \rightarrow S_{14}$	285	0.15	HOMO - 3 → LUMO + 1 (17%)
				HOMO - 3 → LUMO + 4 (8%)
				HOMO - 2 → LUMO + 3 (9%)
				HOMO - 1 → LUMO + 4 (11%)
				HOMO → LUMO + 5 (18%)
$(BGeF)_5$	$S_0 \rightarrow S_{15}$	286	0.15	HOMO - 3 → LUMO (30%)
				HOMO - 3 → LUMO + 4 (19%)
				HOMO - 3 → LUMO + 5 (9%)
				HOMO - 2 → LUMO + 3 (25%)
	$S_0 \rightarrow S_{19}$	284	0.18	HOMO - 3 → LUMO + 2 (44%)
				HOMO - 3 → LUMO + 6 (9%)
				HOMO → LUMO + 6 (14%)

Reference

1. M. Shimizu, H. Tatsumi, K. Mochida, K. Oda and T. Hiyama, *Chem. Asian J.*, 2008, **3**, 1238-1247.