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Pyrene-fused Bisphenazinothiadiazoles with Red to NIR Electroluminescence

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Supporting Information

B3LYP 6-311+g(2d,p)	LUMO+2	LUMO+1	LUMO	HOMO	HOMO-1	HOMO-2	gap
1 (alternate)	-2.12	-3.47	-3.48	-5.72	-5.76	-6.27	2.24
1 (parallel)	-2.12	-3.47	-3.48	-5.77	-5.82	-6.29	2.29
2 (UD-DU-UD)	-2.25	-3.77	-3.8	-5.86	-5.9	-6.33	2.06
2 (DD-UU-DD)	-2.25	-3.76	-3.8	-5.86	-5.91	-6.33	2.06
Experimental			LUMO				Opt. gap
1			-3.81				1.94
2			-4.07				1.96

Table S1. Frontier orbitals computed with the B3LYP and BMK Hamiltonians with the 6-311+g(2d,p) basis set in dichloromethane on B3LYP-CH_2Cl_2-6-31g(d,p) geometries. All values in eV.

B3LYP 6-311+g(2d,p)	LUMO(EA)	HOMO(IP)	GAP (EA+IP)
1 (alternate)	-3.52	5.66	2.13
1 (parallel)	-3.53	5.70	2.18
2 (UD-DU-UD)	-3.82	5.79	1.97
2 (DD-UU-DD)	-3.82	5.79	1.97
Experimental	LUMO		Opt. gap
1	-3.81		1.94
2	-4.07		1.96

Table S2. Vertical ionization potentials (IP) and electron affinities (EA), gap (EA+IP) at the B3LYP level in CH_2Cl_2 from B3LYP-CH2Cl2-6-31g(d,p) geometries. All values in eV.

B3LYP 6-311+g(2d,p)	eV	nm	Osc. Strength	Major contribs
1 (alternate)	1.82	680	0.0811	H-1->LUMO (14%), HOMO->LUMO (15%), HOMO->L+1 (65%)
1 (alternate)	**1.83**	**676**	**0.2306**	**H-1->LUMO (18%), H-1->L+1 (28%), HOMO->LUMO (46%)**
1 (parallel)	1.87	664	0.0066	H-1->LUMO (23%), HOMO->L+1 (75%)
1 (parallel)	**1.87**	**662**	**0.2873**	**H-1->L+1 (31%), HOMO->LUMO (67%)**
2 (UD-DU-UD)	**1.73**	**716**	**0.3575**	**HOMO->LUMO (90%)**
2 (UD-DU-UD)	1.74	714	0.017	HOMO->L+1 (90%)
2 (UD-DU-UD)	1.80	688	0.0044	H-1->LUMO (90%)
2 (UD-DU-UD)	1.83	677	0.0657	H-1->L+1 (92%)
2 (DD-UU-DD)	**1.73**	**716**	**0.2036**	**HOMO->LUMO (68%), HOMO->L+1 (22%)**
2 (DD-UU-DD)	**1.74**	**713**	**0.1598**	**HOMO->LUMO (24%), HOMO->L+1 (72%)**
2 (DD-UU-DD)	1.81	685	0.0149	H-1->LUMO (91%)
2 (DD-UU-DD)	1.84	674	0.0632	H-1->L+1 (92%)

Table S3. TD-DFT transitions involving frontier orbitals at the B3LYP-CH_2Cl_2-6311+g(2d,p)/B3LYP-CH_2Cl_2-6-31(d,p) level (strongest transitions are in bold).

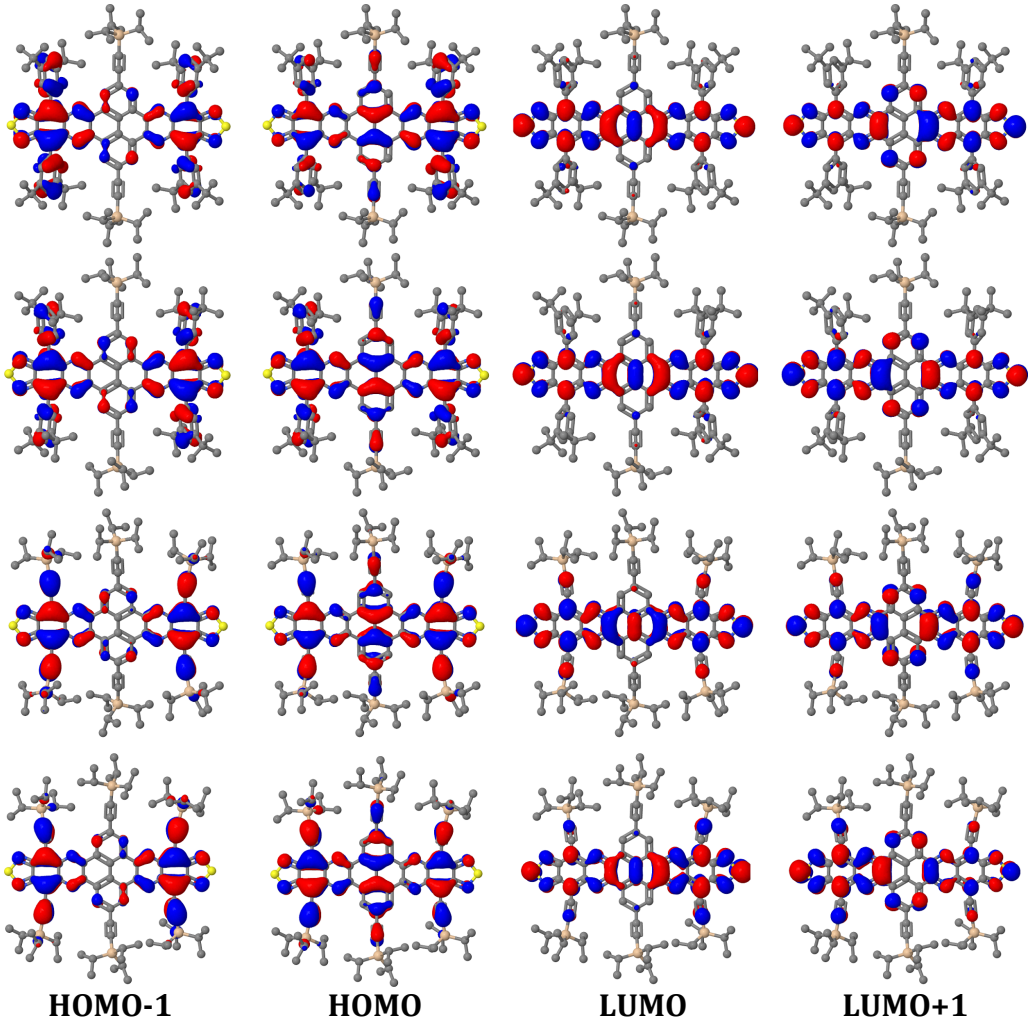

Figure S1. B3LYP-CH_2Cl_2-6311+g(2d,p)/B3LYP-CH_2Cl_2-6-31(d,p) level frontier orbitals from top to bottom: **1** alternate and parallel and **2** UD-DU-UD and DD-UU-DD.