Supporting Information

Tuning of the Electronic and Photophysical Properties of Ladder-Type Quaterphenyl by Selective Methylene-Bridge Fluorination

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Table S1: Most effective coupling ground state vibrational modes in the calculated emission spectra of L4P and L4P-F_2: frequencies and corresponding Huang-Rhys parameters (HR).

L4P			L4P-F_2		
Mode	ν/cm^{-1}	HR	Mode	ν/cm^{-1}	HR
a(F_0)	159	0.34	a(F_2)	159	0.64
b(F_0)	744	0.09	b(F_2)	413	0.50
c(F_0)	1640	0.25	c(F_2)	1370	0.25

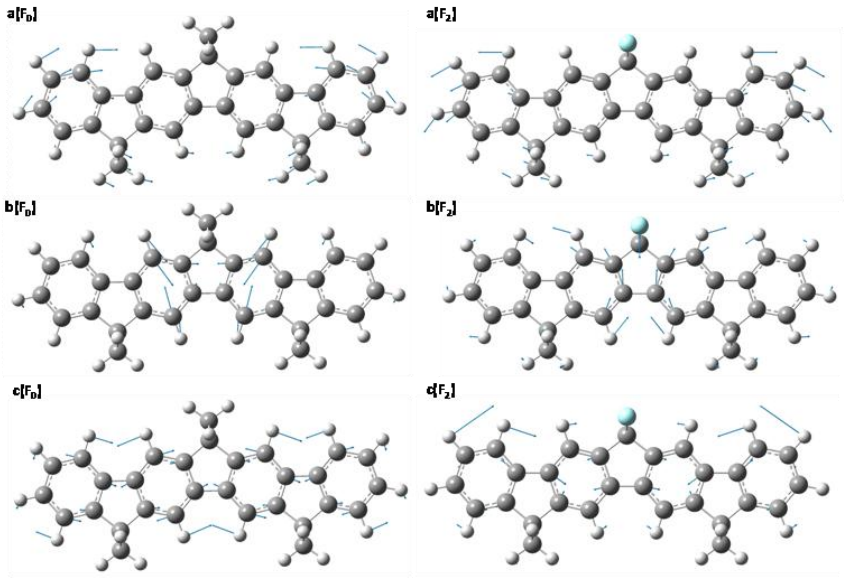

Figure S1: Displacements of the vibrational modes of of L4P and L4P-F_2 listed in Table S1

Table S2: Calculated low frequency modes in S_0 of the compounds under study

no	**L4P**	**L4P-F_2**	**L4P-F_4**	**L4P-F_6**	Description
1	21.84	20.65	21.08	19.77	Torsion
2	33.15	32.91	29.13	28.95	Torsion
3	58.00	55.15	56.96	54.45	Butterfly
4	63.94	62.31	62.61	61.02	Butterfly
5	66.20	65.40	63.82	63.05	Torsion
6	89.11	88.02	86.63	85.14	Torsion

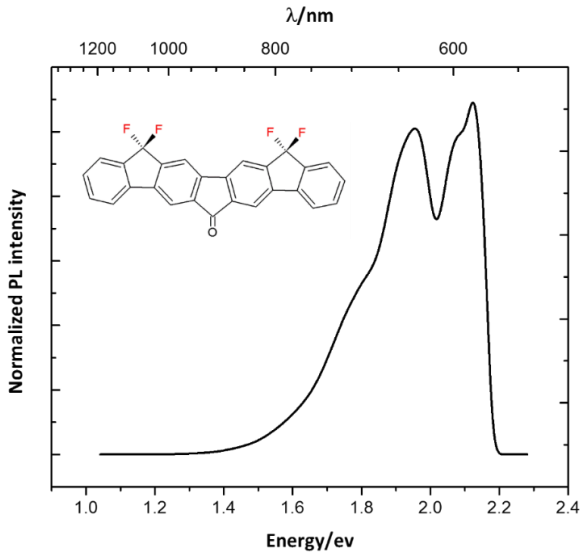

Figure S2: Calculated emission spectra of oxidized L4P-F_4 (half-width 135 cm^{-1})

Table S3: Calculated electronic transitions of dimer complexes constructed from x-ray analysis (see Experimental): Relevant electronic transition energies (E) with oscillator strength (f), configuration interaction and (CI) description (with contributions ≥ 5%) for different functionals.

System	functional	state	E/eV	*f*	Main CI configuration	
L4P	wB97XD	S_1	4.80	0.08	H-1	→ L (47%)
					H	→ L+1 (42%)
		S_2	4.91	2.79	H-1	→ L (42%)
					H	→ L+1 (48%)
	CAM-B3LYP	S_1	4.71	0.08	H-1	→ L (48%)
					H	→ L+1(43%)
		S_2	4.83	2.77	H-1	→ L (43%)
					H	→ L+1(49%)
	B3LYP	S_1	3.13	0.00	H	→ L (100%)
		S_2	3.36	0.09	H-1	→ L (56%)
					H	→ L+1(43%)
		S_3	3.50	2.14	H-1	→ L (41%)
					H	→ L+1(56%)
L4P-F_2	wB97XD	S_1	4.77	2.73	H-1	→ L (49%)
					H	→ L+1(43%)
		S_2	4.81	0.01	H-1	→ L (43%)
					H	→ L+1(49%)
	CAM-B3LYP	S_1	4.71	2.70	H-1	→ L (48%)
					H	→ L+1(45%)
		S_2	4.72	0.00	H-1	→ L (43%)
					H	→ L+1(48%)
	B3LYP	S_1	3.35	0.13	H	→ L(88%)
					H	→ L+1(09%)
		S_2	3.37	1.71	H-1	→ L(25%)
					H	→ L(07%)
					H	→ L+1(61%)
L4P-F_4	wB97XD	S_1	4.78	2.74	H-1	→ L(47%)
					H	→ L+1(42%)
		S_2	4.81	0.05	H-1	→ L(06%)
					H-1	→ L+1(35%)
					H	→ L(42%)
					H	→ L+1(07%)
	CAM-B3LYP	S_1	4.69	2.70	H-1	→ L(49%)
					H	→ L+1(43%)
		S_2	4.73	0.05	H-1	→ L(06%)
					H	→ L+1(37%)
					H	→ L(44%)
					H	→ L+1(07%)
	B3LYP	S_1	3.33	1.60	H-1	→ L(90%)
					H	→ L+1(06%)
		S_2	3.36	0.14	H	→ L(93%)
		S_3	3.41	0.29	H-1	→ L(06%)
					H	→ L+1(83%)