SUPPORTING INFORMATION

Fluorinated Diphenylpolyenes: Crystal Structures and Emission Properties

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Preparation of 14.

Aldehyde **10** (1.18g, 6.0 mmol) and **12** (1.83g, 6.0 mmol) were dissolved in toluene (30 mL). The mixture was stirred under nitrogen atmosphere at 90 ^{o}C for 24 h. After cooling, water (350 mL) was added to the reaction mixture. The products were extracted with diethyl ether (80 mL x 3 times) and the extract was washed with water (300 mL), and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure gave **14** as brown oil in 70-80 % yield. ^{1}H NMR ($CDCl_3$) δ 9.74 (1H, d, *J* 7.3, CHO), 7.45 (1H, d, *J* 16.6, C_6F_5-CH=), 6.98 (1H, dd, *J* 16.5 and 7.3, -C*H*=CHO).

Crystal and structure refinement data.

2. Of the 8586 reflections which were collected, 5926 were independent (R_{int} = 0.0394). The structure was refined on F^2 with 361 parameters to R_1 0.0663 ($I > 2\sigma(I)$), wR_2 0.1642 (all data).

3. Of the 1904 reflections which were collected, 1453 were independent (R_{int} = 0.0170). The structure was refined on F^2 with 100 parameters to R_1 0.0605 ($I > 2\sigma(I)$), wR_2 0.1844 (all data).

4. Of the 2197 reflections which were collected, 1540 were independent (R_{int} = 0.0180). The structure was refined on F^2 with 109 parameters to R_1 0.0483 ($I > 2\sigma(I)$), wR_2 0.1352 (all data).

5. Of the 2370 reflections which were collected, 1656 were independent (R_{int} = 0.0088). The structure was refined on F^2 with 127 parameters to R_1 0.0422 ($I > 2\sigma(I)$), wR_2 0.1492 (all data).

6. Of the 4271 reflections which were collected, 3046 were independent (R_{int} = 0.0275). The structure was refined on F^2 with 208 parameters to R_1 0.0655 ($I > 2\sigma(I)$), wR_2 0.1910 (all data).

1/5. Of the 3801 reflections which were collected, 2964 were independent (R_{int} = 0.0158). The structure was refined on F^2 with 208 parameters to R_1 0.0489 ($I > 2\sigma(I)$), wR_2 0.1622 (all data).

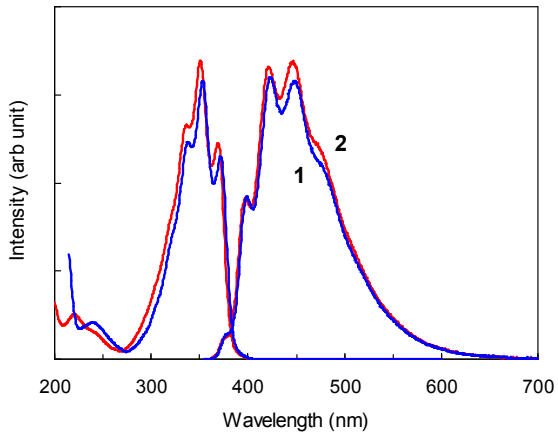


Figure S1. Absorption and fluorescence spectra of **1** and **2** in methylcyclohexane.

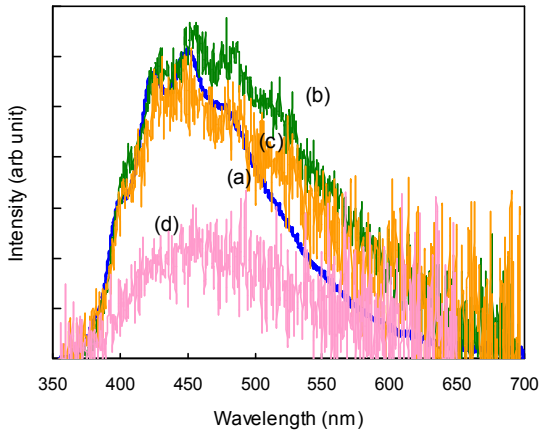
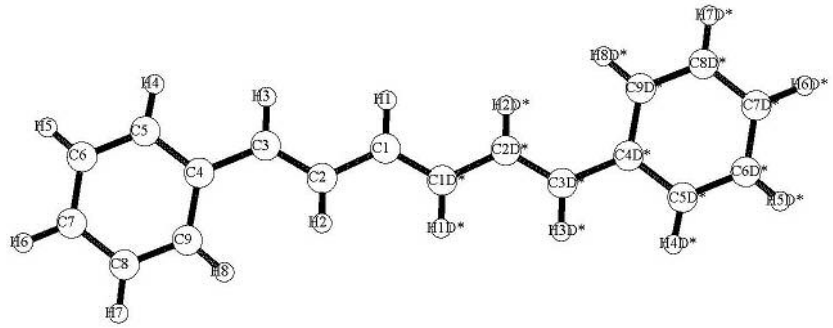


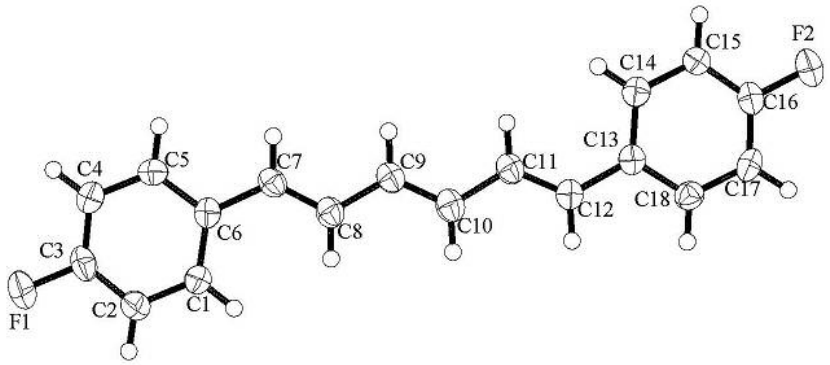
Figure S2. Fluorescence spectra of **6** in (a) methylcyclohexane (ϕ_f = 0.059), (b) toluene (ϕ_f = 0.014), (c) dichloromethane (ϕ_f = 0.006), and (d) acetonitrile (ϕ_f = 0.003). Excitation wavelength: 350 nm.

Figure S3. ORTEP representations for the molecular structures of (a) **1** (b) **2**, (c) **3**, (d) **4**, (e) **5**, (f) **6**, and (g) **1/5**.

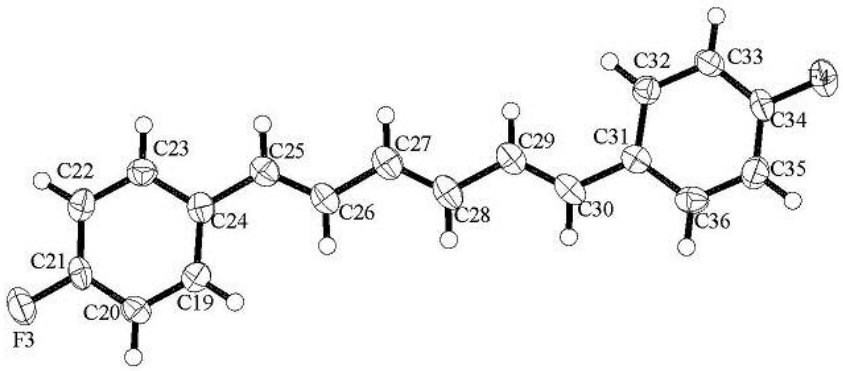
(a)



(b) molecule 1)



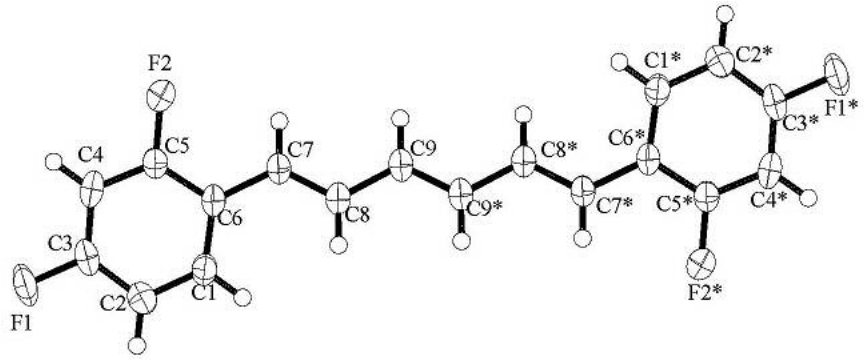
molecule 2)



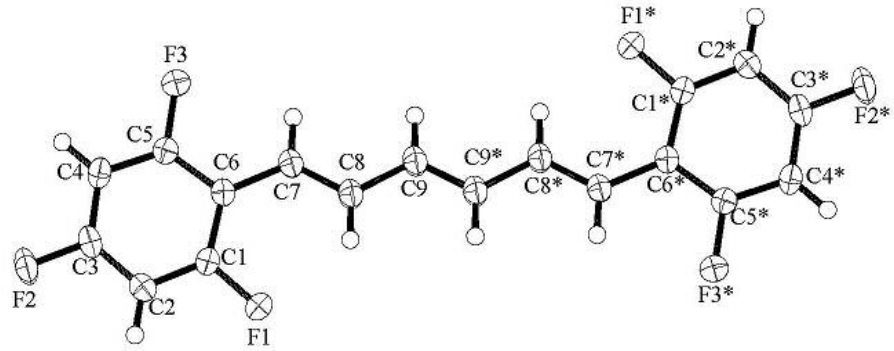
1) and 2): two crystallographically independent molecules

Figure S3. (continued)

(c)



(d)



(e)

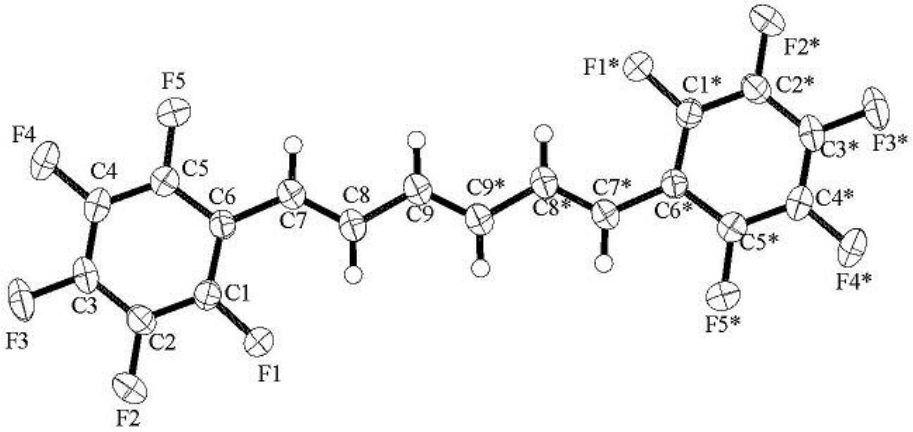
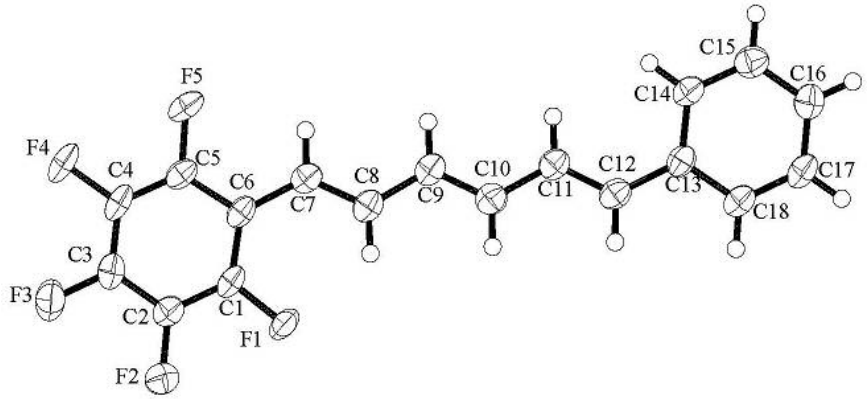


Figure S3. (continued)

(f)



(g)

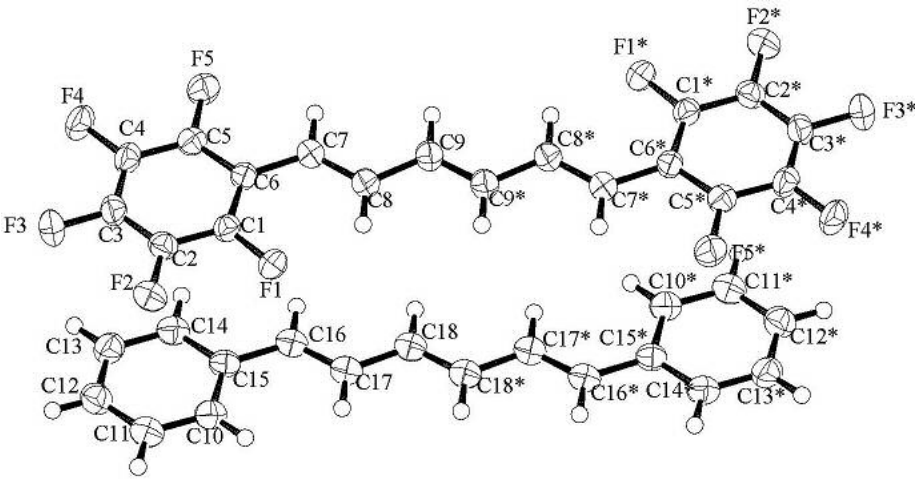


Table S1: Calculated Energy Levels of HOMO-1, HOMO, LUMO and LUMO+1
HF/6-31G*

		1		**2**		**3**		**4**		**5**		**6**	
HOMO-1	(AU)	-0.31152	BG	-0.31588	BG	-0.32291	BG	-0.33188	BG	-0.35258	BG	-0.33127	A"
HOMO	(AU)	-0.25708	AU	-0.26181	AU	-0.26514	AU	-0.27016	AU	-0.29099	AU	-0.27254	A"
LUMO	(AU)	0.0691	BG	0.06594	BG	0.06459	BG	0.05984	BG	0.03699	BG	0.05174	A"
LUMO+1	(AU)	0.1259	AU	0.12285	AU	0.12108	AU	0.11431	AU	0.09177	AU	0.10921	A"
HOMO-LUMO	(AU)	0.32618		0.32775		0.32973		0.33		0.32798		0.32428	
gap	(cm^{-1})	71588.1272		71932.702		72367.261		72426.519		71983.181		71171.126	
	(nm)	139.69		139.02		138.18		138.07		138.92		140.51	
HOMO-LUMO+1	(AU)	0.38298		0.38466		0.38622		0.38447		0.38276		0.38175	
gap	(cm^{-1})	84054.2674		84422.984		84765.364		84381.284		84005.983		83784.314	
	(nm)	118.97		118.45		117.97		118.51		119.04		119.35	
HOMO-1-LUMO	(AU)	0.38		0.38		0.39		0.39		0.39		0.38	
gap	(cm^{-1})	83536.3081		83799.677		85046.291		85972.473		85500.603		84060.852	
	(nm)	119.71		119.33		117.58		116.32		116.96		118.96	

HF/6-31G* level optimized geometry was used

Table S1: (continued)
B3LYP/6-311G**

		1		**2**		**3**		**4**		**5**		**6**	
HOMO-1	(AU)	-0.24509	BG	-0.24499	BG	-0.24946	BG	-0.25585	BG	-0.2692	BG	-0.25737	A"
HOMO	(AU)	-0.19971	AU	-0.20201	AU	-0.20486	AU	-0.20918	AU	-0.22406	AU	-0.21144	A"
LUMO	(AU)	-0.07022	BG	-0.07266	BG	-0.07392	BG	-0.07884	BG	-0.09472	BG	-0.0831	A"
LUMO+1	(AU)	-0.02436	AU	-0.02822	AU	-0.02754	AU	-0.03315	AU	-0.04848	AU	-0.03618	A"
HOMO-LUMO	(AU)	0.12949		0.12935		0.13094		0.13034		0.12934		0.12834	
gap	(cm^{-1})	28419.7271		28389.001		28737.965		28606.28		28386.806		28167.332	
	(nm)	351.87		352.25		347.97		349.57		352.28		355.02	
HOMO-LUMO+1	(AU)	0.17535		0.17379		0.17732		0.17603		0.17558		0.17526	
gap	(cm^{-1})	38484.8185		38142.439		38917.183		38634.061		38535.298		38465.066	
	(nm)	259.84		262.18		256.96		258.84		259.50		259.98	
HOMO-1-LUMO	(AU)	0.17		0.17		0.18		0.18		0.17		0.17	
gap	(cm^{-1})	38379.4708		37822.006		38526.519		38849.146		38293.876		38247.786	
	(nm)	260.56		264.40		259.56		257.41		261.14		261.45	

HF/6-31G* level optimized geometry was used

Table S2: Calculated Excitation Energy to Singlet States

CIS/6-311G**

		1			**2**			**3**			**4**			**5**			**6**		
		(nm)		f	(nm)		f	(nm)		f	(nm)		f	(nm)		f	(nm)		f
Excited state	1	282.02	BU	2.4396	279.44	BU	2.4184	274.06	BU	2.6235	273.79	BU	2.6042	276.21	BU	2.5886	280.84	A'	2.5000
	2	220.49	AG	0	219.57	AG	0	210.25	AG	0	209.41	AG	0	209.45	AG	0	215.91	A'	0.0374
	3	211.36	AG	0	212.59	BU	0.0814	209.04	BU	0.0221	204.42	BU	0.0149	202.88	BU	0.0147	211.52	A'	0.0029
TD-B3LYP/6-311G**																			
Excited state	1	360.38	BU	1.9206	360.62	BU	1.9128	355.23	BU	2.0086	356.91	BU	1.983	359.28	BU	1.9829	363.4	A'	1.8874
	2	296.15	AG	0	298.71	AG	0	292.52	AG	0	293.35	AG	0	295.58	AG	0	295.19	A'	0.0738
	3	277.82	AG	0	286.68	BU	0.0639	284.66	AG	0	279.28	AG	0	293.06	BU	0.0179	285.77	A'	0.0062

All ground-state molecular geometries were optimized at the HF/6-31G* level, assuming planar C_{2h} symmetry for **1-5** and C_s symmetry for **6**.
f: oscillator strength

Table S3: Mean Deviation from the Least-Squares Plane and Ar-CH= Torsion Angle

compound	mean deviation from the least-squares plane[a] (Å)	Ar-CH= torsion angle (degree)
1	0.007[b]	C2-C3-C4-C9 = -2.1[b]
2	0.143 (molecule 1)[c]	C1-C6-C7-C8 = -0.1(5)
		C11-C12-C13-C14 = 1.6(5)
	0.111 (molecule 2)[c]	C19-C24-C25-C26 = 6.3(6)
		C29-C30-C31-C32 = -6.1(6)
3	0.038	C1-C6-C7-C8 = 12.1(8)
4	0.029	C1-C6-C7-C8 = 11.9(2)
5	0.008	C1-C6-C7-C8 = -2.6(3)
6	0.025	C1-C6-C7-C8 = -5.8(5)
		C11-C12-C13-C14 = 4.4(4)
1/5	0.015 (molecule **1**)	C10-C15-C16-C17 = 3.3(3)
	0.023 (molecule **5**)	C1-C6-C7-C8 = 9.8(3)

[a]Defined by the DPH moiety of each molecule, [b]from the reported structure (ref 52, CSD#ZZZQNK02) and [c]for the two crystallographically independent molecules, 1) and 2).