Supplementary material

Table S1 Optimized geometry of fluorene with various methods (Hartree-Fock HF or DFT) and basis sets (BPW91 or B3LYP).

	HF/ 6-31+G(d)	HF/ 6-311+G(d,p)	HF/ cc-pVDZ	HF/ cc-pVTZ	HF/ Aug-cc-pVDZ	B3LYP/ 6-31G(d)	B3LYP/ cc-pVDZ	BPW91/ cc-pvDZ	Exp. Ref. 30	Exp. Ref. 31
C^{9}-C^{13}	1.514	1.513	1.513	1.510	1.514	1.516	1.515	1.516	1.505	1.505
C^{11}-C^{12}	1.474	1.474	1.475	1.472	1.476	1.470	1.471	1.472	1.471	1.491
C^{12}-C^{13}	1.396	1.394	1.397	1.391	1.396	1.411	1.413	1.421	1.398	1.399
C^{5}-C^{12}	1.386	1.385	1.388	1.382	1.389	1.397	1.399	1.407	1.387	1.391
C^{8}-C^{13}	1.381	1.381	1.383	1.377	1.384	1.391	1.393	1.399	1.386	1.397
C^{7}-C^{8}	1.391	1.388	1.390	1.384	1.391	1.400	1.401	1.407	1.385	1.388
C^{6}-C^{7}	1.389	1.388	1.391	1.385	1.392	1.400	1.401	1.408	1.385	1.383
C^{5}-C^{6}	1.388	1.386	1.388	1.382	1.389	1.397	1.398	1.404	1.390	1.391
$C^{10}C^{9}C^{13}$	102.35	102.35	102.43	102.33	102.39	102.80	102.80	103.00	102.66	102.66

Table S2- Optimized geometry of bifluorene with the DFT method and various basis sets. The carbon numbering is shown in fig. 1. Bond lengths in Å, angles in degrees.

	B3LYP/ 6-31G(d)	B3LYP/ cc-pVDZ	BPW91/ cc-pvDZ	Exp. Ref. 32[a]
C^{9}-C^{13}	1.516	1.515	1.516	1.510
C^{9}-C^{10}	1.517	1.515	1.517	1.539
C^{11}-C^{12}	1.468	1.471	1.472	1.471
C^{12}-C^{13}	1.412	1.414	1.421	1.407
C^{10}-C^{11}	1.411	1.413	1.420	1.409
C^{1}-C^{10}	1.387	1.390	1.396	1.362
C^{1}-C^{2}	1.410	1.401	1.418	1.404
C^{2}-C^{3}	1.409	1.411	1.419	1.409
C^{3}-C^{4}	1.394	1.396	1.401	1.365
C^{4}-C^{11}	1.397	1.399	1.406	1.381
C^{8}-C^{13}	1.390	1.393	1.399	1.393
C^{7}-C^{8}	1.400	1.402	1.408	1.386
C^{6}-C^{7}	1.400	1.402	1.408	1.370
C^{5}-C^{6}	1.397	1.398	1.404	1.388
C^{5}-C^{12}	1.397	1.400	1.407	1.391
C^{2}-$C^{2'}$	1.484	1.486	1.486	1.489
$C^{10}C^{9}C^{13}$	102.74	102.90	103.00	100.90
$C^{1'}C^{2'}C^{2}C^{1}$	143.3	142.4	142.4	145.3[b]

a) The experimental geometry corresponds to 2,2'-(9,9-npropyl) bifluorene.
b) For crystallized 2,2'- (7,7'-Br)- (9,9-hexyl) bifluorene[33].

Table S3- Energies E (in eV), symmetry and oscillator strengths f of the lowest excited states of bifluorene in gas phase depending on geometry, basis set and functional. Transition moments μ_{0i} between the ground state and excited states i (in Debye). BPW91/cc-pVDZ//B3LYP/cc-pVDZ means that the geometry has been optimized with B3LYP/cc-pVDZ and the excitation energies have been calculated with BPW91/cc-pVDZ.

BPW91/cc-pVDZ // BPW91/cc-pVDZ			BPW91/cc-pVDZ // B3LYP/cc-pVDZ			B3LYP/cc-pVDZ // B3LYP/cc-pVDZ			B3LYP/6-31G(d) // B3LYP/cc-pVDZ		
E	f	μ_{0i}	E	f	μ_{0i}	E	f	μ_{0i}	E	f	μ_{0i}
3.28B	1.03	9.10	3.34B	1.05	9.09	3.75B	1.35	9.77	3.79B	1.35	9.69
3.54A			3.59A			4.27A			4.35A		
3.74B			3.80A			4.37B			4.44B		
3.79A			3.83B			4.41A			4.44A		
3.97B			4.03A			4.63A			4.67A		
3.98A			4.04B			4.64B			4.68B		
4.18A			4.24A			4.69A			4.72A		
4.19B			4.25B			4.98B			5.05B		
4.31B	0.05	1.80	4.37A			5.01A			5.07A		
4.33A			4.37B	0.11	2.62	5.16A			5.22A		
4.37A			4.40A			5.16B	0.14	2.42	5.22B	0.13	2.52
4.44B	0.25	3.84	4.51B	0.18	3.23	5.26B	0.16	2.86	5.31B	0.17	2.92

The comparison of the two first columns gives the effect of the geometry that appears to be small (from 0.04 to 0.14 eV) particularly for the low energies. The comparison between columns 3 and 4 gives the effect of the basis set at constant geometry and constant functional. The difference does not exceed 0.08 eV. The most important effect comes from the functional: at constant geometry and basis set (columns 2 and 3), the difference between B3LYP and BPW91 varies from 0.43 to 0.79 eV.