

Supplementary Information

Electronic structures of crystalline phases in poly(vinylidene fluoride) films probed by far- and deep-ultraviolet spectroscopy and quantum chemical calculations

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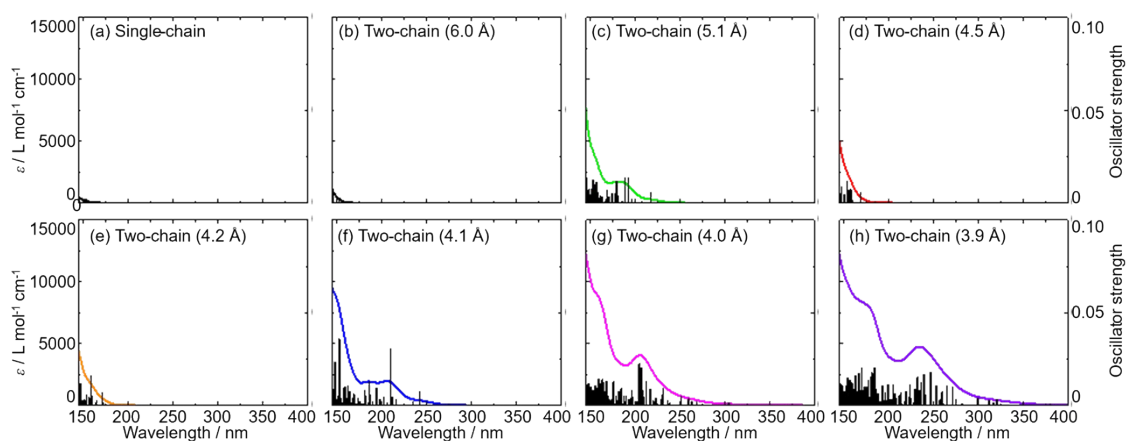


Fig. S1 TD-DFT-calculated oscillator strengths and molar extinction coefficients (ϵ) of (a) single-chain β phase and (b–h) two-chain β phase with the interchain distance varying from 6.0 to 3.9 Å.

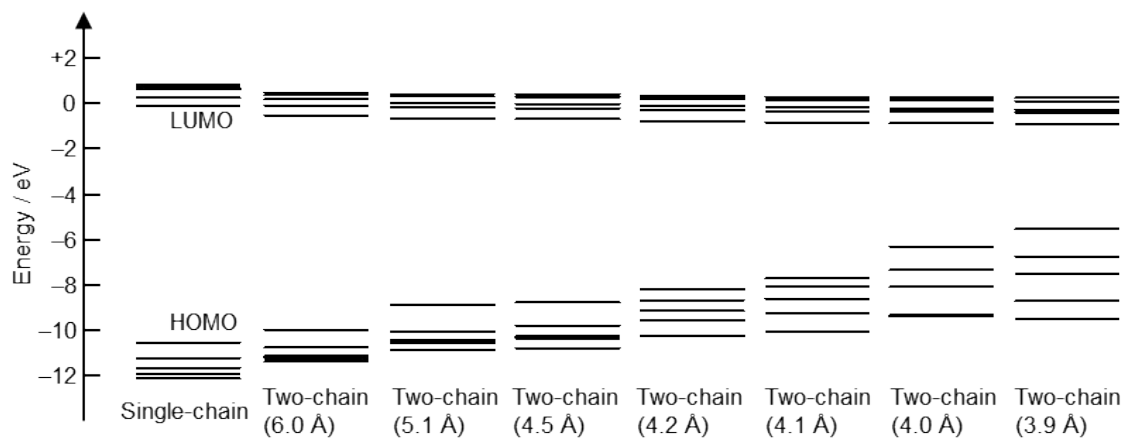


Fig. S2 Energy level diagrams from HOMO-4 to LUMO+4 of single-chain β phase and two-chain β phase with the interchain distance varying from 6.0 to 3.9 Å.

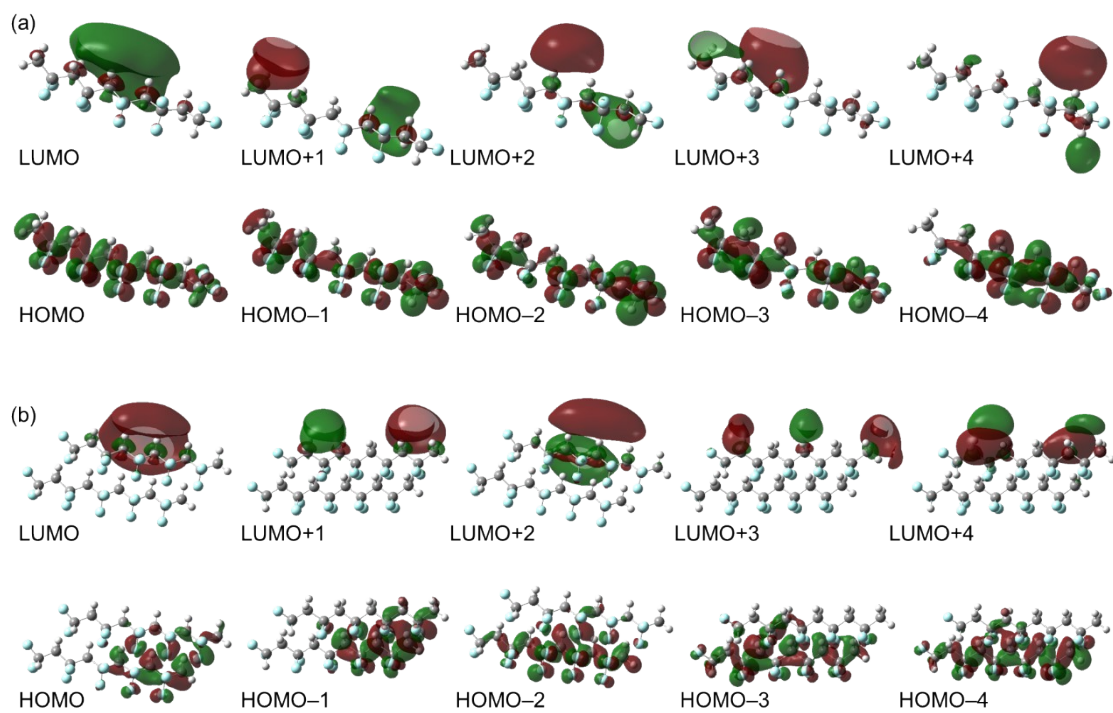


Fig. S3 Calculated molecular orbitals from HOMO-4 to LUMO+4 for (a) single-chain β phase and (b) two-chain β phase with an interchain distance of 4.0 Å.

Table S1 Main transition energies, oscillator strengths, and major electronic configurations (initial/final orbitals and their expansion coefficients) of (a) single-chain β phase and (b–h) two-chain β phase with the interchain distance varying from 6.0 to 3.9 Å.

(a) Single-chain β phase

Wavelength/nm	Energy/eV	Oscillator strength	Initial orbital	Final orbital	Coefficient
153.3	8.09	0.0021	HOMO	LUMO	0.643

(b) Two-chain β phase with an interchain distance of 6.0 Å

Wavelength/nm	Energy/eV	Oscillator strength	Initial orbital	Final orbital	Coefficient
152.5	8.13	0.0011	HOMO	LUMO	0.575
150.3	8.25	0.0027	HOMO–2	LUMO	0.625

(c) Two-chain β phase with an interchain distance of 5.1 Å

Wavelength/nm	Energy/eV	Oscillator strength	Initial orbital	Final orbital	Coefficient
168.0	7.38	0.0057	HOMO	LUMO+1	0.570
158.3	7.83	0.0065	HOMO–2	LUMO	0.320
156.9	7.90	0.0074	HOMO–1	LUMO	0.273
155.1	7.99	0.0070	HOMO	LUMO+4	0.454
153.2	8.09	0.0113	HOMO	LUMO+2	0.405

(d) Two-chain β phase with an interchain distance of 4.5 Å

Wavelength/nm	Energy/eV	Oscillator strength	Initial orbital	Final orbital	Coefficient
171.1	7.24	0.0065	HOMO	LUMO+2	0.416
160.3	7.73	0.0051	HOMO–2	LUMO	0.379
159.2	7.79	0.0158	HOMO	LUMO+5	0.352
156.5	7.92	0.0045	HOMO	LUMO+4	0.460
154.2	8.04	0.0053	HOMO–3	LUMO+1	0.287

(e) Two-chain β phase with an interchain distance of 4.2 Å

Wavelength/n m	Energy/e V	Oscillator strength	Initial orbital	Final orbital	Coefficien t
192.4	6.44	0.0137	HOMO	LUMO+2	0.537
188.8	6.57	0.0137	HOMO-2	LUMO	0.458
179.1	6.92	0.0118	HOMO-3	LUMO	0.460
156.6	7.92	0.0111	HOMO-1	LUMO+9	0.231
153.7	8.06	0.0102	HOMO-3	LUMO+2	0.212

(f) Two-chain β phase with an interchain distance of 4.1 Å

Wavelength/n m	Energy/e V	Oscillator strength	Initial orbital	Final orbital	Coefficien t
209.8	5.91	0.0302	HOMO	LUMO+2	0.377
186.6	6.64	0.0126	HOMO-2	LUMO+2	0.371
162.6	7.63	0.0102	HOMO-1	LUMO+11	0.269
153.1	8.10	0.0357	HOMO-3	LUMO+4	0.202
152.8	8.11	0.0114	HOMO-1	LUMO+14	0.175

(g) Two-chain β phase with an interchain distance of 4.0 Å

Wavelength/n m	Energy/e V	Oscillator strength	Initial orbital	Final orbital	Coefficien t
206.6	6.00	0.0204	HOMO	LUMO+17	0.251
204.4	6.07	0.0223	HOMO-2	LUMO+2	0.407
163.2	7.60	0.0140	HOMO	LUMO+47	0.177
161.9	7.66	0.0133	HOMO-5	LUMO	0.331
158.8	7.81	0.0139	HOMO	LUMO+17	0.216

(h) Two-chain β phase with an interchain distance of 3.9 Å

Wavelength/n m	Energy/e V	Oscillator strength	Initial orbital	Final orbital	Coefficien t
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246.4	5.03	0.0176	HOMO	LUMO+14	0.275
239.7	5.17	0.0165	HOMO	LUMO+31	0.212
183.7	6.75	0.0204	HOMO-4	LUMO	0.272
181.3	6.84	0.0174	HOMO-2	LUMO+7	0.211
169.7	7.31	0.0201	HOMO-1	LUMO+10	0.288

Table S2 Calculated orbital energies (eV) of HOMO-4 to LUMO+4 in single-chain β phase and two-chain β phase with the interchain distance varying from 6.0 to 3.9 Å.

	Single	6.0 Å	5.1 Å	4.5 Å	4.2 Å	4.1 Å	4.0 Å	3.9 Å
LUMO+4	0.70	0.15	0.11	0.17	0.20	0.28	0.29	0.35
LUMO+3	0.56	0.01	-0.03	0.03	0.07	0.15	0.18	0.23
LUMO+2	0.48	-0.35	-0.39	-0.30	-0.25	-0.14	-0.13	0.07
LUMO+1	0.12	-0.49	-0.53	-0.47	-0.43	-0.33	-0.29	-0.21
LUMO	-0.23	-1.00	-1.04	-0.96	-0.92	-0.81	-0.79	-0.65
HOMO	-10.65	-6.42	-5.65	-7.84	-8.30	-8.90	-8.99	-10.09
HOMO-1	-11.33	-7.46	-6.85	-8.17	-8.78	-9.90	-10.17	-10.86
HOMO-2	-11.77	-8.20	-7.61	-8.71	-9.27	-10.36	-10.56	-11.25
HOMO-3	-12.04	-9.45	-8.83	-9.36	-9.65	-10.47	-10.67	-11.32
HOMO-4	-12.25	-9.51	-9.61	-10.15	-10.35	-10.90	-10.96	-11.49