Supplementary Information

Effect of the conformer distribution on the properties of amorphous organic semiconductor films for organic light-emitting diodes

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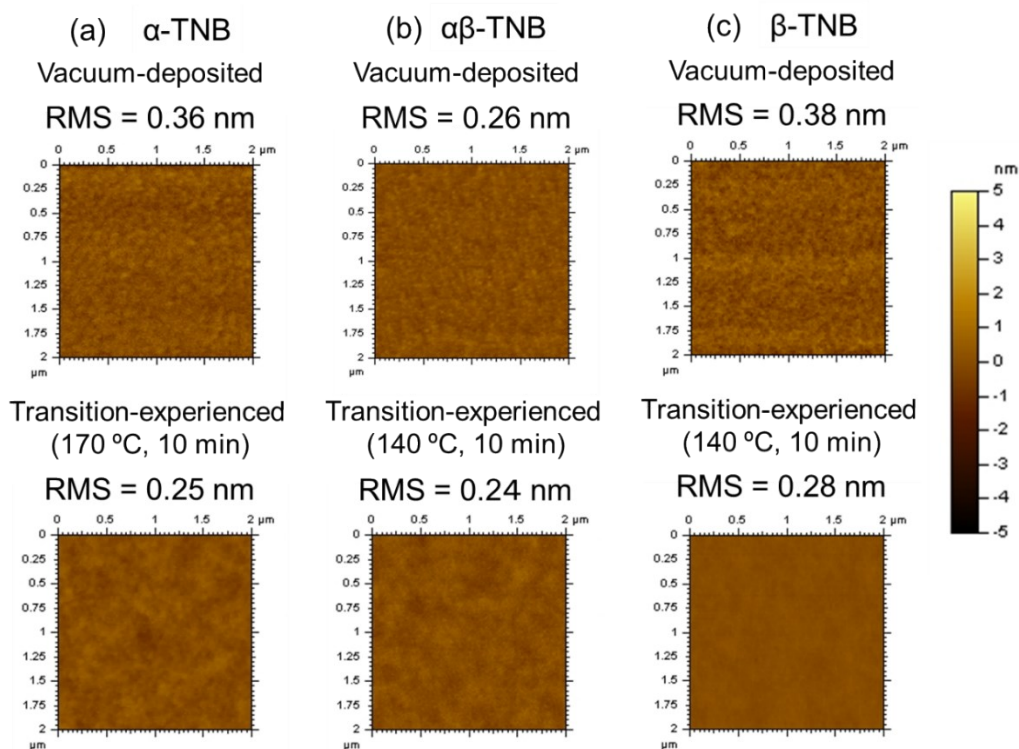
E-mail: d_yokoyama@yz.yamagata-u.ac.jp
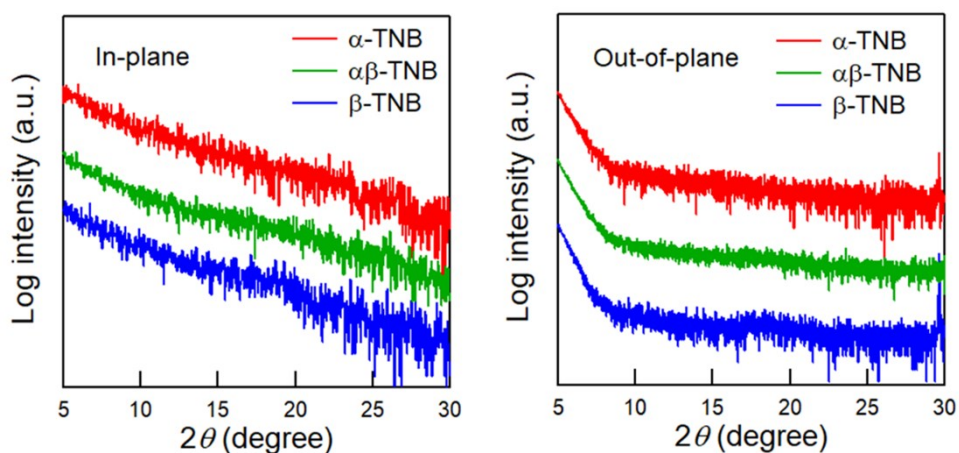Fax: +81-238-26-3890; Tel.: +81-238-26-3890

Contents

A. AFM images of the films

Fig. S1 AFM images of the surfaces of the vacuum-deposited and transition-experienced films of (a) α-TNB, (b) αβ-TNB, and (c) β-TNB. The thicknesses of the films were ~100 nm.

B. XRD patterns of the films

Fig. S2 In-plane and out-of-plane XRD patterns of vacuum-deposited α-, αβ-, and β-TNB films on a Si substrate. The thicknesses of the films were ~100 nm.

C. Reorganization energies for hole transport

Table S1 Reorganization energies in hole transfer between two molecules of α-, αβ, and β-TNB obtained by DFT B3LYP/6-31G(d). The α-, αβ-, and β-TNB molecules have 24, 72, and 24 conformers, respectively (see Section 2.4 in the main text for details), and the reorganization energies highly depend on the conformers. To compare the three isomers, the simple average and the average weighted with the conformer distribution are also given at the bottom of the table.

Conformation number	α-TNB (eV)	αβ-TNB (eV)	β-TNB (eV)
1	0.295	0.264	0.227
2	0.299	0.258	0.210
3	0.309	0.266	0.213
4	0.304	0.264	0.211
5	0.325	0.258	0.192
6	0.304	0.256	0.217
7	0.289	0.229	0.207
8	0.298	0.259	0.208
9	0.296	0.259	0.218
10	0.304	0.266	0.218
11	0.274	0.255	0.188
12	0.282	0.259	0.195
13	0.286	0.264	0.196
14	0.245	0.242	0.170
15	0.253	0.245	0.190
16	0.240	0.260	0.219
17	0.249	0.233	0.214
18	0.240	0.264	0.193
19	0.240	0.233	0.198
20	0.240	0.272	0.215
21	0.248	0.229	0.179
22	0.208	0.250	0.161
23	0.208	0.223	0.191
24	0.197	0.264	0.210
25		0.264	
26		0.226	
27		0.233	
28		0.245	
29		0.248	
30		0.201	
31		0.274	

(Continued on next page)

| Conformation number	α-TNB (eV)	αβ-TNB (eV)	β-TNB (eV)
32		0.202	
33		0.231	
34		0.240	
35		0.287	
36		0.221	
37		0.264	
38		0.245	
39		0.229	
40		0.245	
41		0.237	
42		0.246	
43		0.231	
44		0.251	
45		0.246	
46		0.221	
47		0.250	
48		0.249	
49		0.200	
50		0.235	
51		0.227	
52		0.241	
53		0.250	
54		0.233	
55		0.249	
56		0.202	
57		0.244	
58		0.240	
59		0.244	
60		0.219	
61		0.212	
62		0.221	
63		0.243	
64		0.220	
65		0.207	
66		0.212	
67		0.234	
68		0.124	
69		0.208	
70		0.219	
71		0.184	
72		0.222	
Simple average	0.268	0.238	0.202
Average weighted with the conformer distribution	0.301	0.244	0.206

D. Molecular orientation
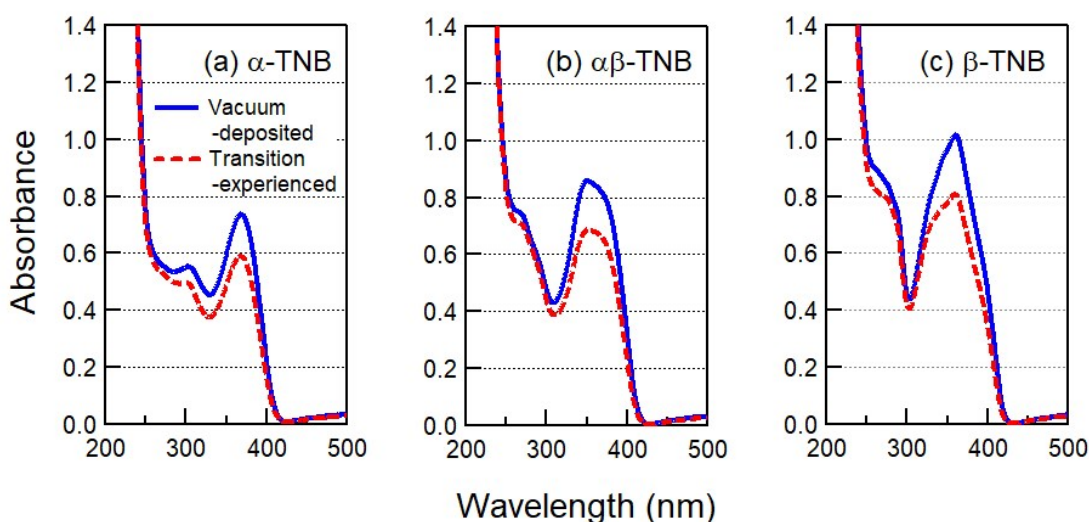

Fig. S3 Absorption spectra of the vacuum-deposited and transition-experienced films of (a) α-TNB, (b) αβ-TNB, and (c) β-TNB. The solid lines show the spectra of the vacuum-deposited films before annealing, and the dashed lines show those of the transition-experienced films after annealing. From the differences between the absorbance values at the long-wavelength peaks of the vacuum-deposited and transition-experienced films, the orientation order parameters of the long molecular axes (S) of α-, αβ-, and β-TNB (see Fig. S6) were estimated to be −0.23, −0.24, and −0.23, respectively.
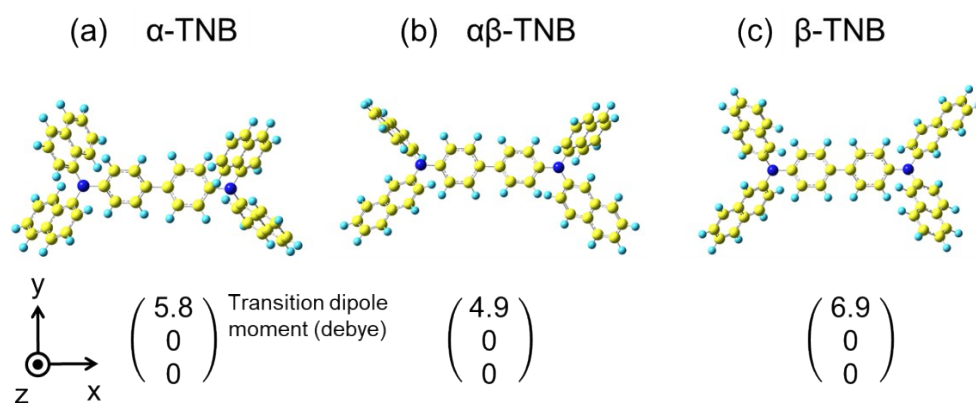
Fig. S4 Transition dipole moments of the α-, αβ-, and β-TNB molecules with the conformer structures optimized by DFT B3LYP/6-31G(d) calculations. The transition dipole moments along the long molecular axis were obtained by TD-DFT B3LYP/6-311+G(d,p) calculations and correspond to the long-wavelength absorption bands used for estimation of S.
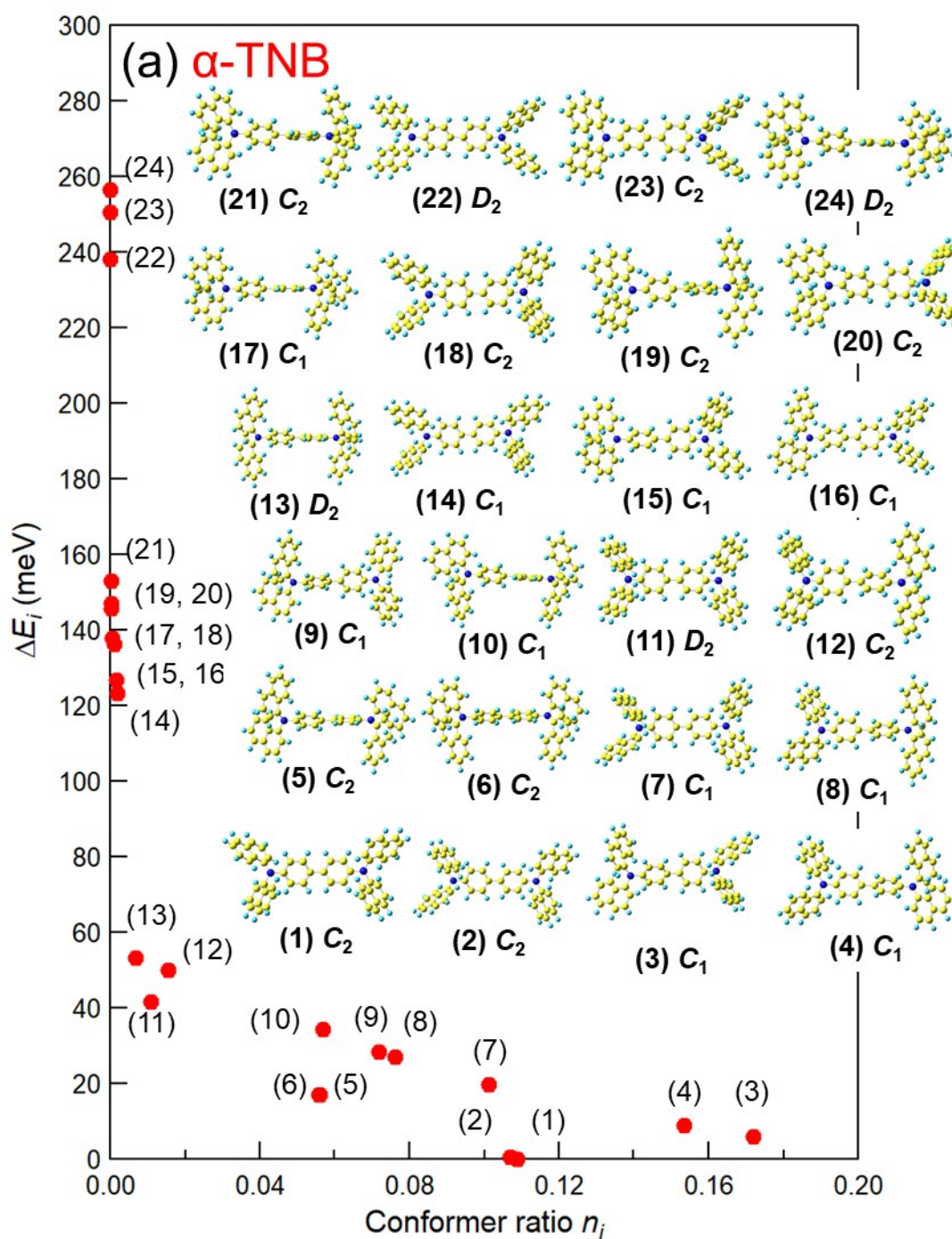
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E. XRR analysis

(a)

(b)
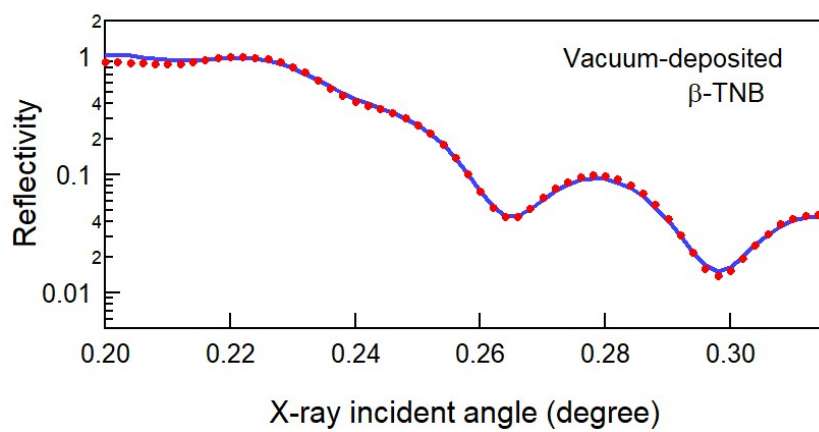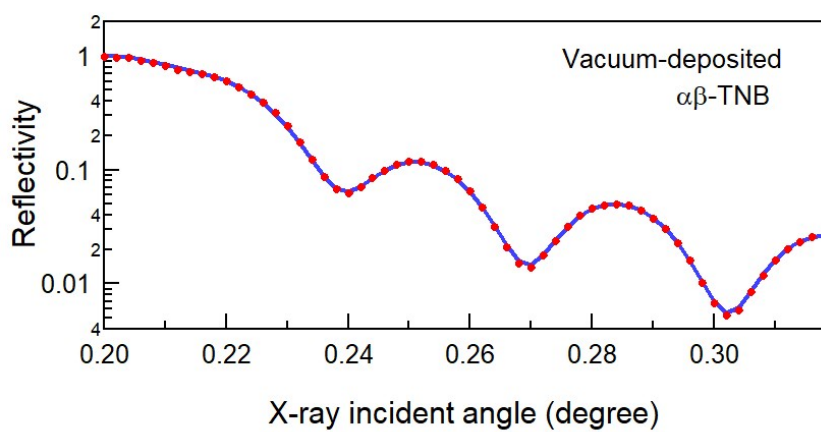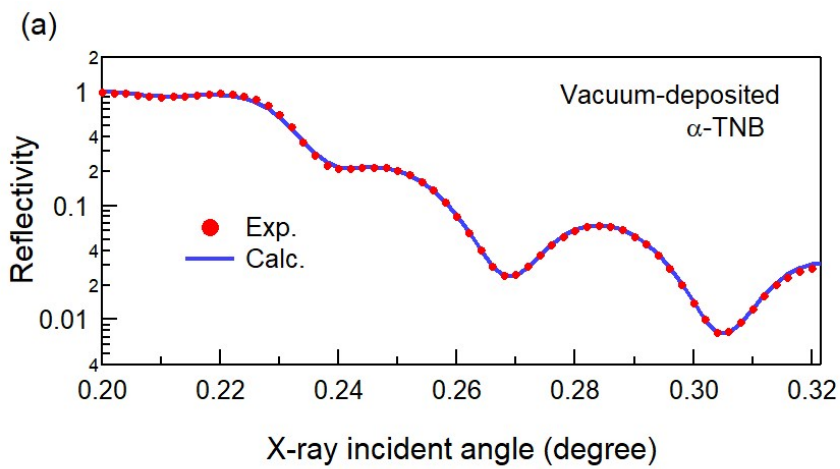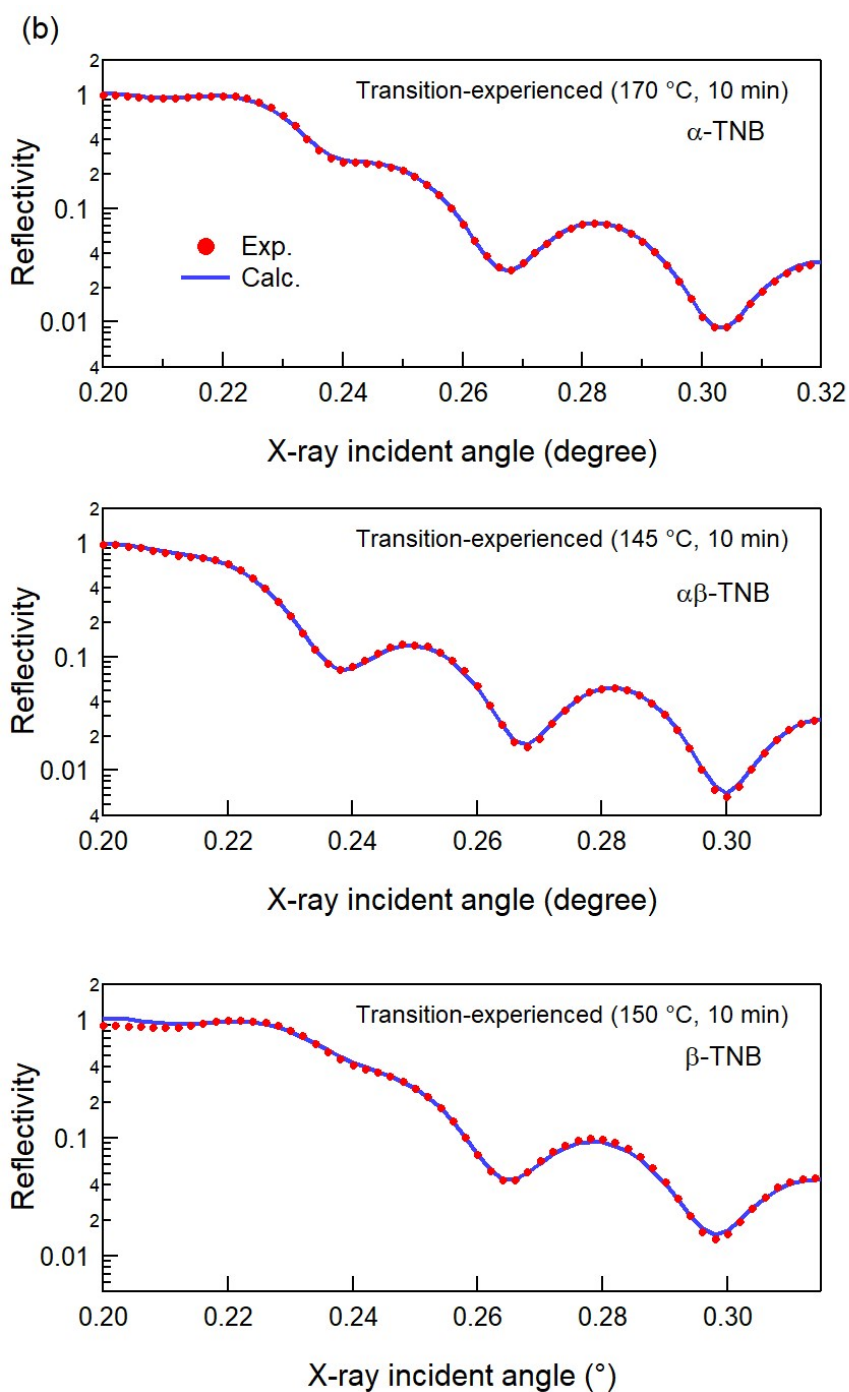
Fig. S5 XRR patterns of (a) vacuum-deposited and (b) transition-experienced films of α-, αβ-, and β-TNB with a thickness of ~100 nm on a Si substrate. From fitting analysis using the theoretical XRR patterns, the film densities of the α-, αβ-, and β-TNB vacuum-deposited films were determined to be 1.16, 1.17, and 1.17 ± 0.02 g cm^{-1}, respectively, and those of the transition-experienced films were determined to be 1.15, 1.16, and 1.16 ± 0.02 g cm^{-1}, respectively.

F. Conformer distributions

(b) αβ-TNB

(22) C_1 **(23)** C_1 **(24)** C_1

(19) C_1 **(20)** C_1 **(21)** C_1

(16) C_1 **(17)** C_1 **(18)** C_1

(13) C_1 **(14)** C_2 **(15)** C_2

(10) C_1 **(11)** C_1 **(12)** C_1

(7) C_1 **(8)** C_2 **(9)** C_2

(4) C_1 **(5)** C_1 **(6)** C_1

(1) C_2 **(2)** C_2 **(3)** C_1

(18-24)

(17)
(16)
(14,15)   (13)
(12)   (10,11)
(8,9)   (7)   (6)
            (4,5)
      (3)
(2) (1)

ΔE_i (meV)

Conformer ratio n_i

9

(c) β-TNB

ΔE_i (meV) vs Conformer ratio n_i

(24) (23) (22) (21) (19,20) (18) (17) (16) (15) (14) (13) (12) (11) (10) (9) (8) (7) (6) (5) (4) (3) (2) (1)

(23) C_2 (24) D_2
(20) C_2 (21) C_2 (22) D_2
(17) D_2 (18) C_2 (19) C_2
(14) D_2 (15) C_1 (16) C_1
(11) C_1 (12) C_1 (13) C_2
(8) C_2 (9) C_1 (10) C_1
(7) C_2 (5) C_1 (6) C_1
(3) C_1 (4) C_1
(1) C_2 (2) C_2

(d) CBP

(3) D_2

(2) C_2

(1) D_2

(3)

(2)

(1)

Conformer ratio n_i

ΔE_i (meV)

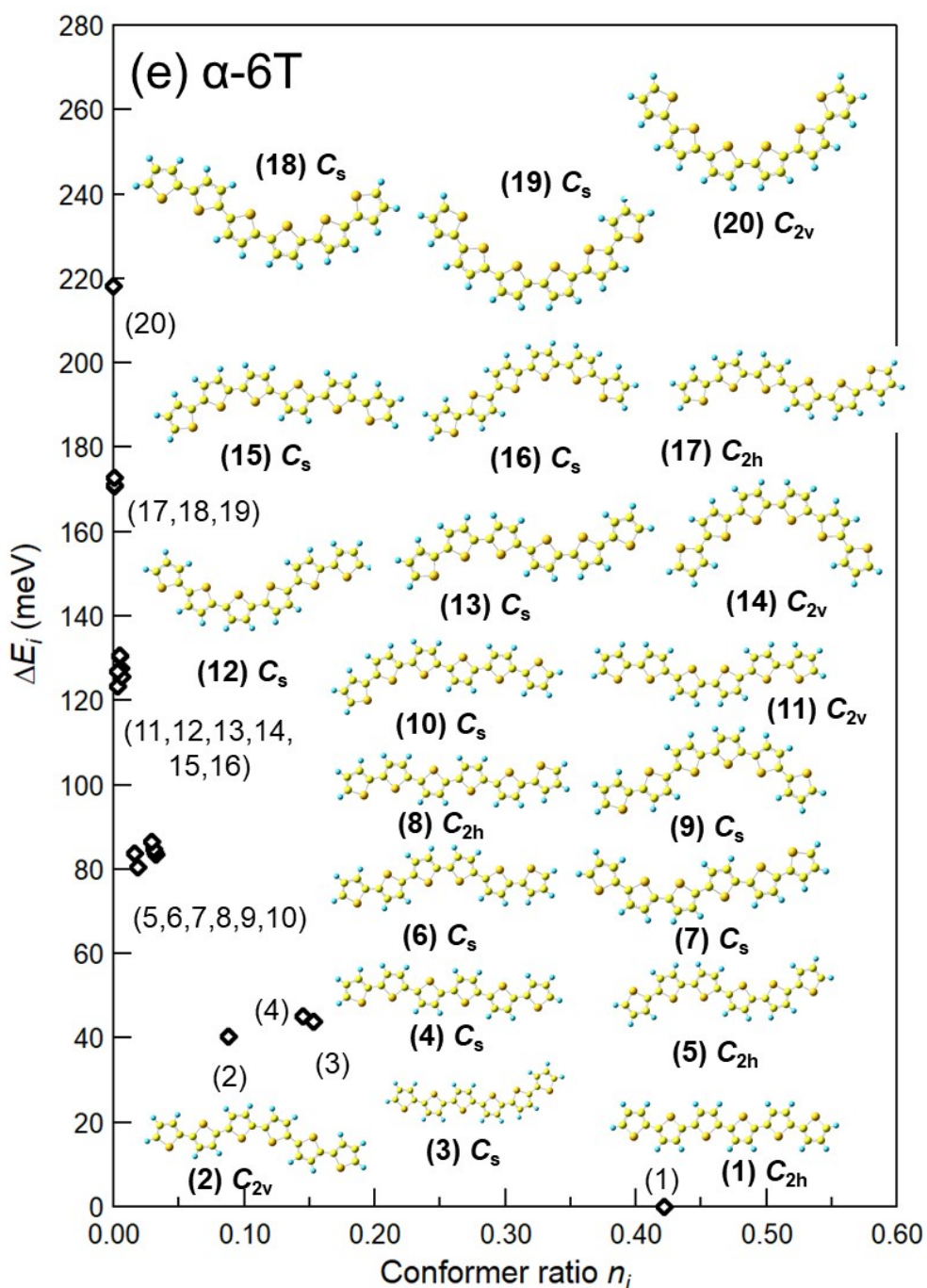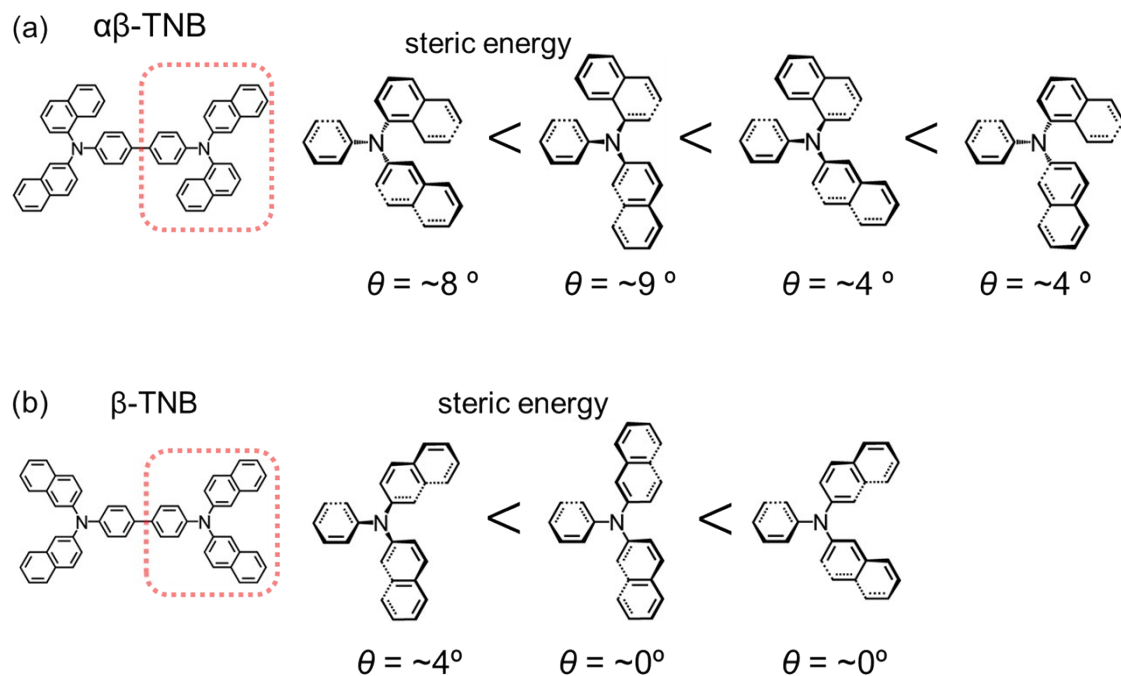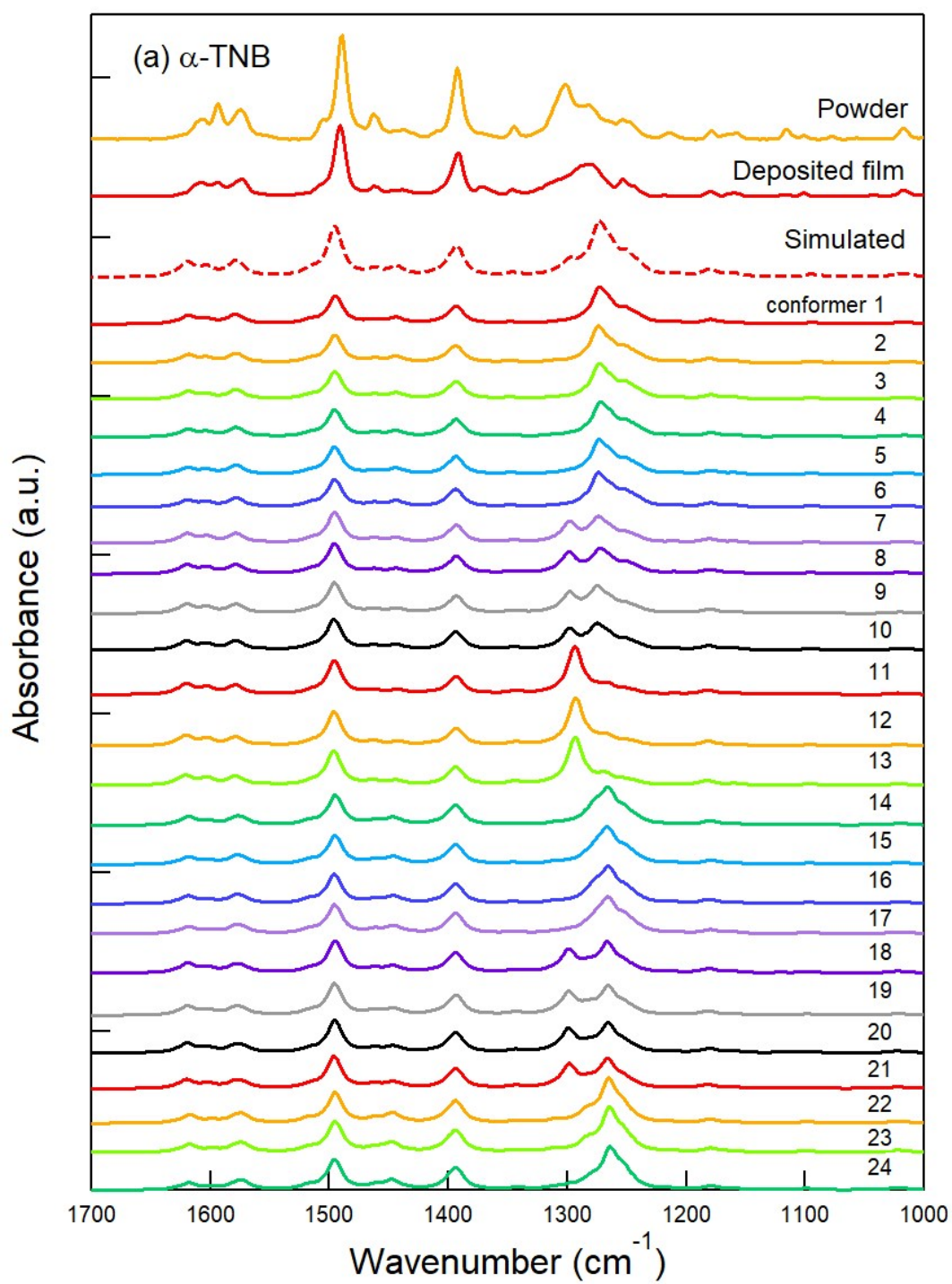**Fig. S6** Conformer distributions and conformational structures of (a) α-TNB, (b) αβ-TNB, (c) β-TNB, (d) CBP, and (e) α-6T with the conformer number and symmetry group of each conformer. The conformers were comprehensively extracted by MM calculations with the MMFF94s force field. The conformational structures and their steric energies were obtained by DFT B3LYP/6-31G(d) calculations.
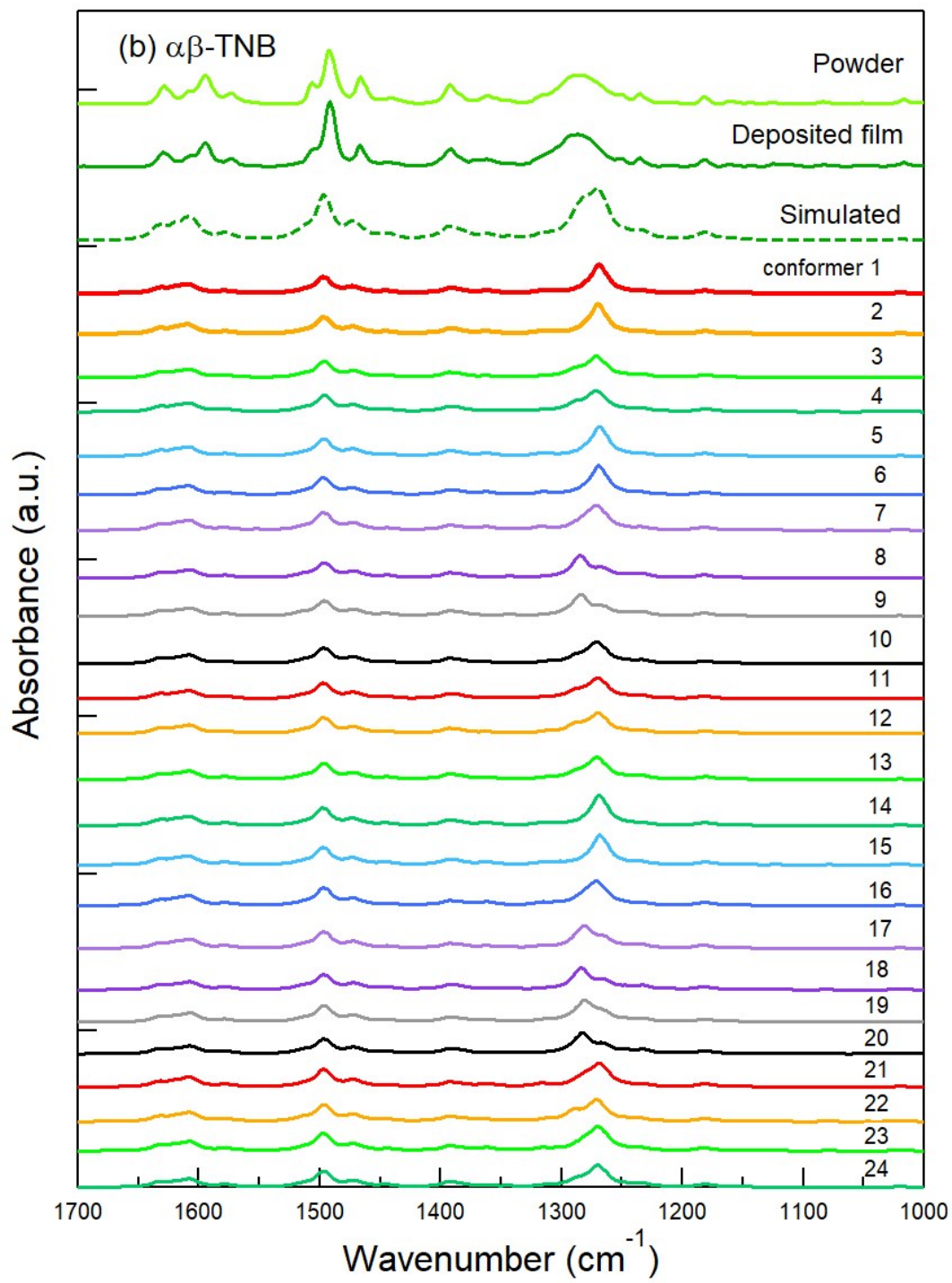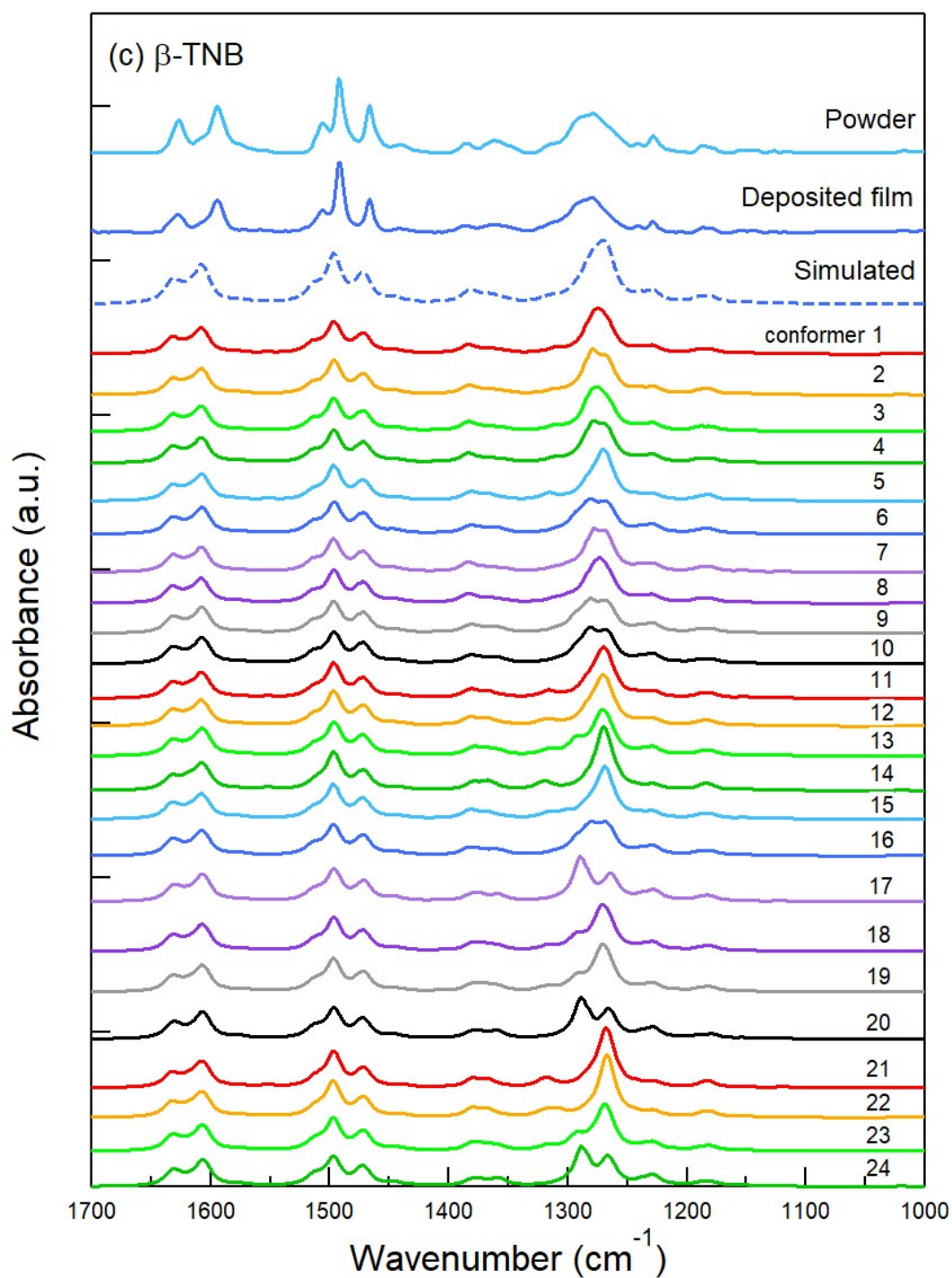
G. Distortion angles of the triarylamines θ

(a)   αβ-TNB

steric energy

$\theta = \sim 8°$ $<$ $\theta = \sim 9°$ $<$ $\theta = \sim 4°$ $<$ $\theta = \sim 4°$

(b)   β-TNB

steric energy

$\theta = \sim 4°$ $<$ $\theta = \sim 0°$ $<$ $\theta = \sim 0°$

Fig. S7 Relationship between the steric energy and the distortion angle of the conformers of the half structures of (a) αβ-TNB and (b) β-TNB obtained by MM and DFT B3LYP/6-31G(d) calculations.

H. IR absorption spectra

(a) α-TNB

Powder
Deposited film
Simulated
conformer 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

Absorbance (a.u.)

Wavenumber (cm⁻¹)

(b) αβ-TNB

Powder

Deposited film

Simulated

conformer 1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

Absorbance (a.u.)

Wavenumber (cm^{-1})

Fig. S8 Experimental IR absorption spectra of the powders (measured by the KBr method) and vacuum-deposited films, calculated spectrum of each conformer, and simulated spectra of (a) α-TNB, (b) αβ-TNB, and (c) β-TNB. The spectra of the conformers were obtained by DFT B3LYP/6-31G(d) calculations assuming a bandwidth of 8 cm^{-1} for all vibrational modes and a scaling factor of 0.97.
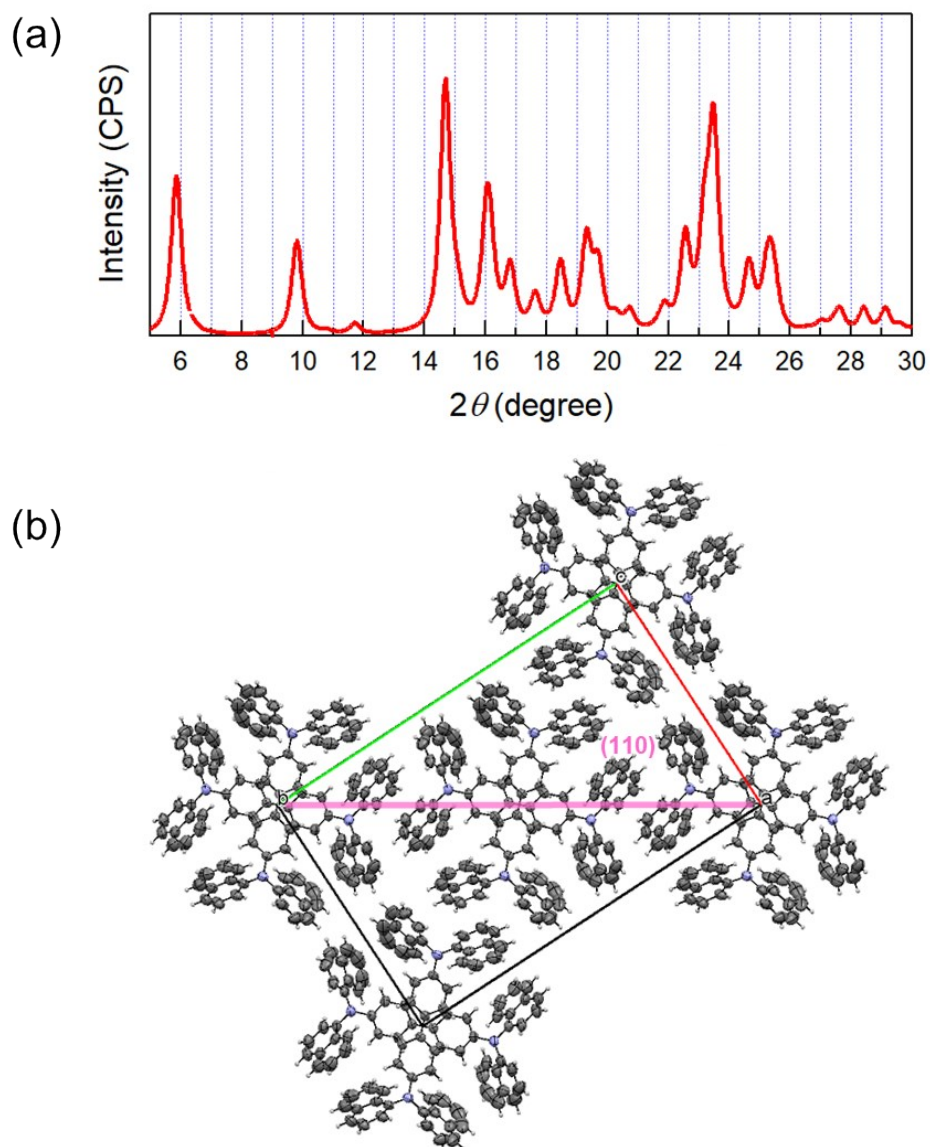
I. XRD patterns of the powders
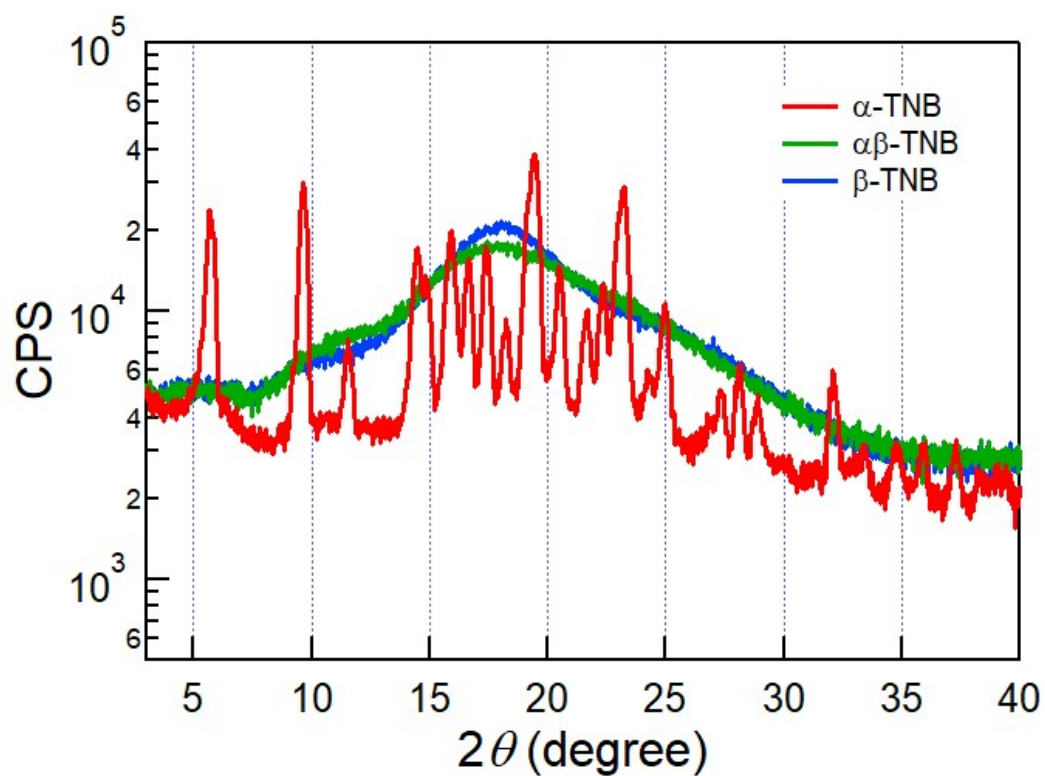
Fig. S9 XRD patterns of the sublimed powders of α-, αβ-, and β-TNB. Only the pattern of the α-TNB powder has sharp peaks, indicating crystallinity.

J. Single-crystal X-ray structure determination

Table S2 Crystal data and structure refinement of α-TNB

Empirical formula	$C_{52} H_{36} N_2$
Formula weight	688.83
Temperature	200 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Iba2*
Unit cell dimensions	*a* = 18.0128(10) Å *α* = 90°
	b = 27.5447(16) Å *β* = 90°
	c = 7.2185(3) Å *γ* = 90°
Volume	3581.5(3) Å³
Z	4
Density (calculated)	1.277 g/cm³
Absorption coefficient	0.074 mm⁻¹
F(000)	1448
Crystal size	0.15 x 0.07 x 0.05 mm³
Theta range for data collection	2.702 to 26.496°
Index ranges	–22<=h<=22, –34<=k<=34, –9<=l<=9
Reflections collected	22438
Independent reflections	3694 [*R*(int) = 0.0570]
Completeness to theta = 25.242°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.55297
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3694 / 1 / 244
Goodness-of-fit on F^2	1.039
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0637, wR_2 = 0.1495
R indices (all data)	R_1 = 0.0906, wR_2 = 0.1668
Largest diff. peak and hole	0.207 and –0.142 e.Å⁻³

Fig. S10 (a) XRD pattern of the single crystal of α-TNB. (b) Single-crystal structure of α-TNB. This structure is composed of only one conformer.
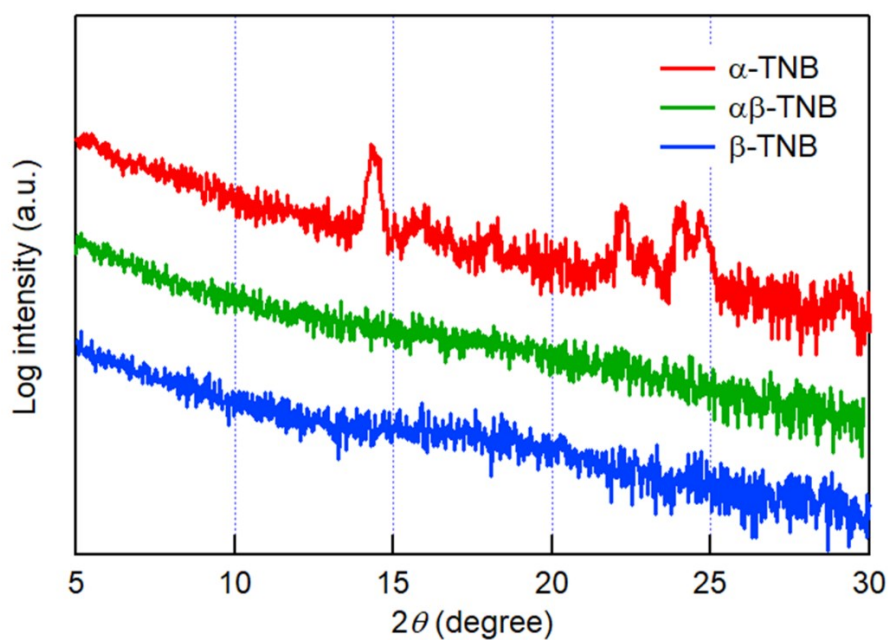
K. XRD patterns of the transition-experienced films

Fig. S11 In-plane XRD patterns of the α-, αβ-, and β-TNB films heated to ~200 °C and then cooled to room temperature.