Supporting information for

Stable Spontaneous Orientation Polarization by Widening Optical Band Gap with 1,3,5,7-Tetrakis(1-phenyl-1H-benzo[d]imidazol-2-yl)adamantane

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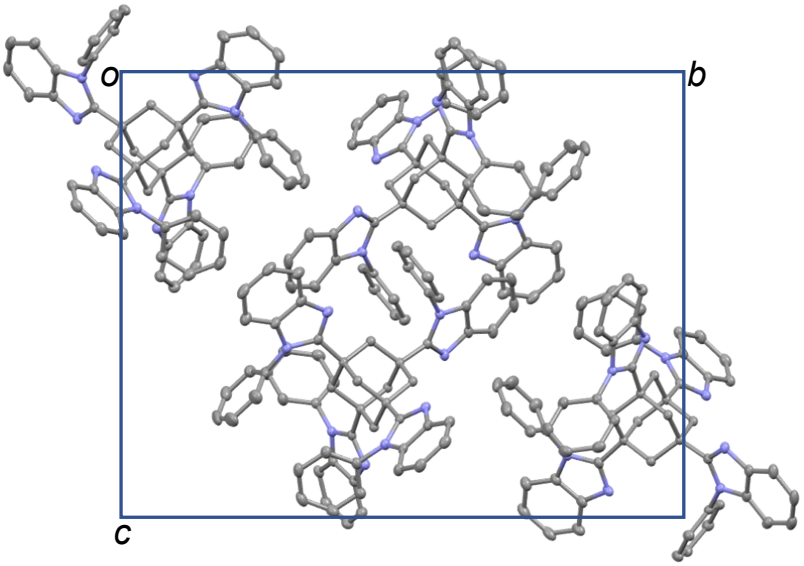

Figure S1. Crystal structure of TPBAD viewed along the *a*-axis. The ellipsoids are drawn at a 50% probability level.

Table S1. Crystallographic data for TPBAD.

Chemical formula	$C_{62}H_{48}N_8$
Molecular weight	905.12
Temperature (K)	90
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	11.2081(2)
b (Å)	22.9128(4)
c (Å)	18.1963(4)
α (°)	90
β (°)	95.696(2)
γ (°)	90
V (Å^3)	4649.9(16)
Z	4
F(000)	1904.0
Crystal size (mm)	0.042 × 0.107 × 0.131
Radiation	MoKα (0.71073 Å)
2θ (°)	1.778 to 31.406
Index ranges	$-15 \leq h \leq 15$, $-32 \leq k \leq 32$, $-26 \leq l \leq 26$
Reflections collected	113,677
Data/restraints/parameters	13,694/3/823
Goodness of fit on F^2	1.021
Final R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0506$, $wR_2 = 0.1204$
Final R indices [all data]	$R_1 = 0.0812$, $wR_2 = 0.1089$

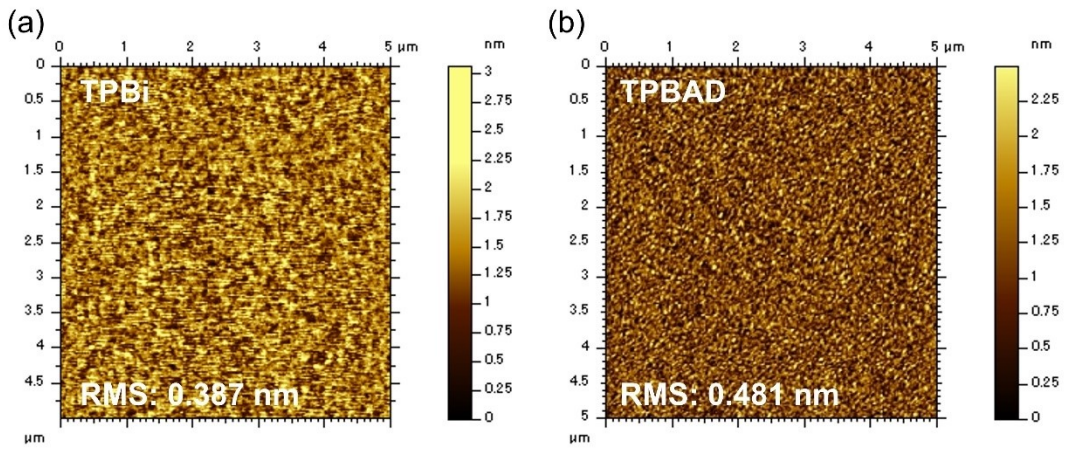

Figure S2. AFM height images of (a) TPBi and (b) TPBAD films. RMS: root mean square average of the height deviations.

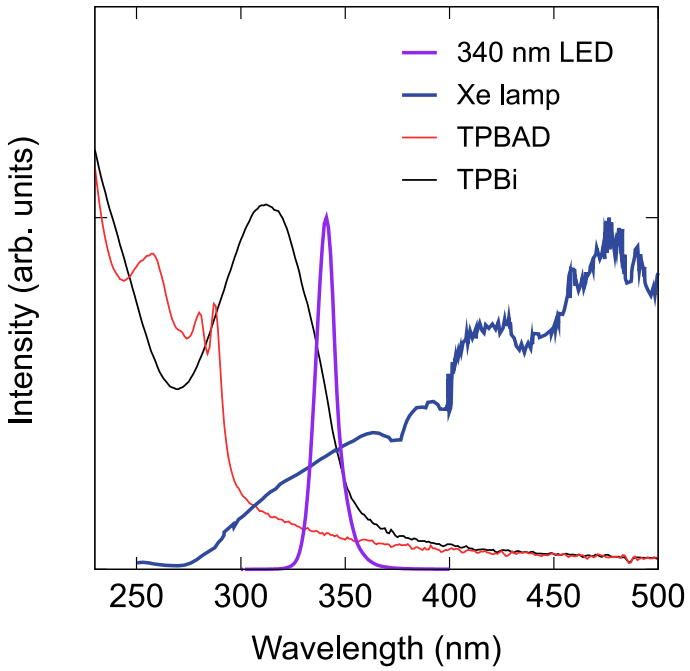

Figure S3. Emission spectra of IR-cut Xe lamp and 340 nm LED used for the aging test of SOP under light irradiation. Light absorptance spectra of TPBi and TPBAD are shown for comparison.

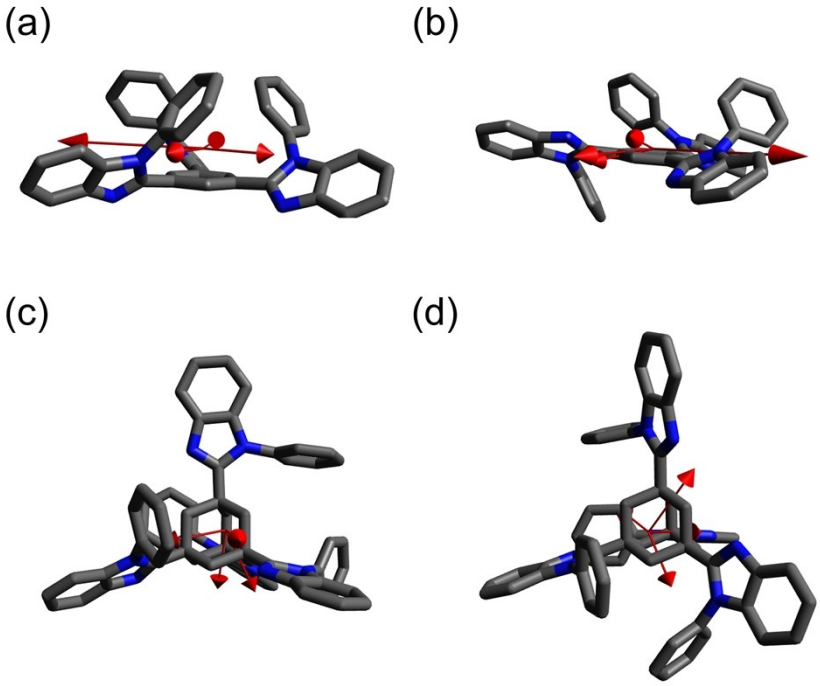

Figure S4. Side views of the optimized structures of the (a) C_3 and (b) C_1 conformers of TPBi, and the (c) A and (d) B conformers of TPBAD. Red arrows represent the first four strongest transition dipole moments. Hydrogen atoms are omitted for clarity.

Table S2. Calculation results of the first 50 transition dipole moments of TPBi-C_1.

State	Energy (eV)	X	Y	Z	Oscillator strength
1	3.7333	0.0108	0.0672	-0.101	0.0014
2	3.9562	0.1126	-1.6633	0.0381	0.2695
3	3.9715	2.5678	0.089	-0.0602	0.6427
4	4.0242	-0.3209	0.9484	0.0136	0.0988
5	4.1099	-0.402	-0.5254	-0.1501	0.0463
6	4.1315	-0.0702	0.1576	0.2502	0.0094
7	4.1427	-0.1846	-1.1466	-0.0933	0.1378
8	4.1662	0.4982	-0.9863	0.2657	0.1318
9	4.2001	0.7677	-0.08	-0.1617	0.064
10	4.2134	-0.6432	-0.4001	0.272	0.0669
11	4.2233	-0.1835	-0.3534	0.2318	0.022
12	4.2959	-0.0062	0.1906	-0.0482	0.0041
13	4.4108	0.2024	-0.0905	0.0449	0.0055
14	4.4584	0.183	0.3301	-0.1518	0.0181
15	4.5006	-0.3891	-0.3134	-0.0038	0.0275
16	4.5298	0.0851	0.4798	-0.1663	0.0294
17	4.5458	-0.1469	-0.3372	0.0376	0.0152
18	4.5755	0.2044	-0.3404	0.002	0.0177
19	4.6088	0.6186	-0.1581	0.0387	0.0462
20	4.633	-0.1189	-0.0997	-0.051	0.003
21	4.6482	-0.2314	0.3392	0.2122	0.0243
22	4.6673	-0.0922	0.2128	0.1023	0.0073
23	4.6769	0.12	0.7748	-0.0764	0.0711
24	4.6915	-0.0592	0.0803	-0.0037	0.0011
25	4.703	-0.1918	0.7784	-0.0683	0.0746
26	4.7159	0.535	0.4318	-0.3923	0.0724

27	4.7468	-0.1297	-0.0008	-0.0134	0.002
28	4.7596	-0.0812	-0.188	0.137	0.0071
29	4.7727	-0.0135	-0.3827	0.0662	0.0177
30	4.7764	0.0802	0.3958	-0.1629	0.0222
31	4.8154	0.6145	-0.3172	-0.0856	0.0573
32	4.82	-0.5004	-0.2592	0.0113	0.0375
33	4.8461	0.4615	-0.2722	-0.1968	0.0387
34	4.8618	-0.3917	-0.5398	0.2726	0.0618
35	4.8638	0.3268	0.1819	-0.0139	0.0167
36	4.8738	0.3817	-0.6041	-0.0615	0.0614
37	4.8756	-0.2517	0.242	0.0695	0.0151
38	4.8987	0.0014	-0.3446	0.1328	0.0164
39	4.9118	-0.0423	-0.2915	0.0657	0.011
40	4.9181	0.0037	0.1692	-0.0531	0.0038
41	4.9295	-0.0336	-0.2479	0.1313	0.0096
42	4.9393	-0.157	0.0059	0.0831	0.0038
43	4.9579	-0.0617	-0.389	0.1944	0.0234
44	4.9652	0.0316	0.0488	-0.0439	0.0006
45	4.9741	-0.0657	0.0389	0.1072	0.0021
46	4.9939	0.0769	0.2719	0.1728	0.0134
47	5.023	0.1385	0.1053	-0.0631	0.0042
48	5.0406	-0.0367	-0.0659	0.0416	0.0009
49	5.0635	-0.0152	-0.0537	0.0449	0.0006
50	5.0705	-0.0648	0.0397	0.0455	0.001

Table S3. Calculation results of the first 50 transition dipole moments of TPBi-C_3.

State	Energy (eV)	X	Y	Z	Oscillator strength
1	3.9433	-0.0013	0.0008	0.1142	0.0013
2	4.1224	-0.9684	1.7802	0.0001	0.4148
3	4.1225	-1.7801	-0.9683	-0.0001	0.4147
4	4.2088	0.0047	0.0015	0.1083	0.0012
5	4.226	0.1719	-1.0035	-0.0001	0.1073
6	4.2262	1.0031	0.1763	-0.0029	0.1074
7	4.2513	-0.0056	0.003	-0.6474	0.0437
8	4.2622	-0.714	-0.0971	0.001	0.0542
9	4.2623	0.1041	-0.7154	-0.0023	0.0546
10	4.2987	0.0036	0.0069	0.0122	0
11	4.3053	0.2956	0.0884	-0.0006	0.01
12	4.3056	-0.0879	0.294	0.001	0.0099
13	4.4396	0.0782	-0.0873	0.0001	0.0015
14	4.4398	0.0862	0.0797	0	0.0015
15	4.5396	0.0004	-0.0007	0.0971	0.001
16	4.5815	-0.1708	-0.123	-0.0002	0.005
17	4.5817	0.1262	-0.172	0.0008	0.0051
18	4.6055	-0.2192	-0.5847	-0.0395	0.0442
19	4.6056	0.5861	-0.2168	-0.0309	0.0442
20	4.6059	-0.0184	0.0589	-0.5088	0.0296
21	4.6294	0	-0.0006	-0.3045	0.0105
22	4.6636	0.7636	0.4521	-0.0005	0.09
23	4.6637	0.4524	-0.7633	-0.0006	0.09
24	4.6983	-0.0086	-0.0141	0.0636	0.0005
25	4.6987	0.0533	0.053	0.0126	0.0007
26	4.6988	-0.0533	0.0541	0.0022	0.0007

27	4.7135	0.0011	0.0019	-0.04	0.0002
28	4.7331	0.062	0.5438	0.0009	0.0347
29	4.7333	0.5418	-0.0614	-0.0047	0.0345
30	4.735	0.0456	-0.0148	0.05	0.0006
31	4.8045	-0.0008	-0.0011	-0.0538	0.0003
32	4.87	-0.1133	-0.0694	-0.0501	0.0024
33	4.8703	-0.2782	0.0403	0.0204	0.0095
34	4.8705	0.0117	0.2893	-0.0161	0.01
35	4.8874	-0.0013	-0.0014	0.1084	0.0014
36	4.8916	-0.1896	0.1171	-0.0007	0.006
37	4.8919	-0.1172	-0.1907	-0.0012	0.006
38	4.9071	0.1486	-0.3294	-0.0686	0.0163
39	4.9073	0.3711	0.1183	0.0369	0.0184
40	4.9075	0.0271	0.1883	-0.1416	0.0068
41	4.9524	0.2884	0.1907	-0.0002	0.0145
42	4.9526	0.1913	-0.293	-0.0002	0.0149
43	4.9771	0.0064	0.0008	-0.1465	0.0026
44	4.9856	0.4897	0.5391	0.001	0.0648
45	4.9857	0.5408	-0.4888	0.0011	0.0649
46	5.0121	0.0001	0.0035	0.036	0.0002
47	5.0156	0.4085	0.2397	-0.001	0.0276
48	5.0157	-0.2334	0.4146	-0.0002	0.0278
49	5.018	0.2761	0.172	0.0003	0.013
50	5.0181	-0.18	0.2671	0.0001	0.0128

Table S4. Calculation results of the first 50 transition dipole moments of TPBAD-A.

State	Energy (eV)	X	Y	Z	Oscillator strength
1	4.3828	0.0043	0.0073	-0.0473	0.0002
2	4.4356	-0.1283	0.0413	0.0482	0.0022
3	4.4878	0.1058	-0.0187	-0.0235	0.0013
4	4.5021	-0.022	0.0006	-0.0418	0.0002
5	4.5719	0.0314	0.0064	0.0298	0.0002
6	4.5776	-0.0148	0.0049	-0.0078	0
7	4.5895	0.1285	-0.0089	0.02	0.0019
8	4.6014	-0.0279	-0.0324	-0.0001	0.0002
9	4.6264	-0.0093	-0.0244	0.0324	0.0002
10	4.6493	-0.0301	0.0569	0.0205	0.0005
11	4.6514	-0.0098	-0.0066	0.008	0
12	4.6548	0.0007	-0.0259	0.0348	0.0002
13	4.6608	0.0511	0.0047	-0.0507	0.0006
14	4.6657	0.0168	0.0249	-0.0248	0.0002
15	4.6704	-0.0037	-0.045	0.0322	0.0004
16	4.6856	0.0224	-0.0088	0.0057	0.0001
17	4.6905	0.0277	-0.0486	-0.0085	0.0004
18	4.7027	0.1072	-0.0899	-0.0521	0.0026
19	4.7232	-0.0276	-0.0991	-0.0787	0.0019
20	4.7356	-0.0722	-0.0221	0.0134	0.0007
21	4.7581	0.1168	-0.1472	-0.1323	0.0062
22	4.7589	0.2264	-0.1636	-0.1744	0.0126
23	4.7676	0.205	-0.175	-0.2738	0.0172
24	4.7923	0.1167	0.4021	-0.3335	0.0336
25	4.8024	-0.023	0.2421	0.0881	0.0079
26	4.8134	-0.397	-0.1232	-0.0714	0.021

27	4.8217	-0.0137	-0.2748	0.175	0.0126
28	4.8439	-0.2307	-0.0316	-0.0203	0.0065
29	4.8563	0.3242	-0.2618	-0.8924	0.1154
30	4.8593	0.0802	-0.143	-0.2022	0.0081
31	4.8714	-0.0177	0.0536	0.1323	0.0025
32	4.8797	-0.0473	0.3126	-0.8721	0.1029
33	4.8893	-0.1834	0.237	-0.0131	0.0108
34	4.8943	-0.0106	0.1518	-0.2737	0.0118
35	4.9334	0.071	0.4704	0.0133	0.0274
36	4.9347	-0.1296	-0.9344	-0.1318	0.1097
37	4.937	-0.0779	0.0712	0.0117	0.0014
38	4.946	-0.0912	-0.3866	-0.1029	0.0204
39	4.9541	-0.9288	0.0172	-0.1415	0.1072
40	4.9677	-0.1721	0.0882	0.0603	0.005
41	4.9717	0.0326	0.0101	-0.0566	0.0005
42	4.9856	-0.0696	-0.1805	-0.0246	0.0046
43	4.9994	0.3157	0.2432	0.2104	0.0249
44	5.012	0.5043	-0.249	0.0038	0.0388
45	5.0247	-0.55	-0.1557	0.4467	0.0648
46	5.0296	0.1188	-0.0698	-0.1194	0.0041
47	5.0362	-0.1575	0.0648	0.0549	0.004
48	5.0407	-0.0737	-0.0581	0.0072	0.0011
49	5.0474	0.0176	0.0091	0.003	0
50	5.0494	0.0146	-0.0699	-0.1064	0.002

Table S5. Calculation results of the first 50 transition dipole moments of TPBAD-B.

State	Energy (eV)	X	Y	Z	Oscillator strength
1	4.3597	0.0065	-0.0883	0.0603	0.0012
2	4.3678	0.083	0.0364	-0.0898	0.0017
3	4.3833	0.0292	-0.1051	0.0958	0.0023
4	4.3898	0.0896	0.0641	-0.0168	0.0013
5	4.4749	0.0736	0.0004	0.0243	0.0007
6	4.4857	0.0125	0.0888	-0.0894	0.0018
7	4.5212	0.0441	-0.1187	0.1375	0.0039
8	4.528	0.0843	-0.0097	-0.0939	0.0018
9	4.543	-0.0949	-0.0886	0.0244	0.0019
10	4.5458	0.0138	0.1502	-0.0459	0.0028
11	4.5578	-0.0506	0.0405	-0.0716	0.001
12	4.5709	-0.2289	-0.085	0.0037	0.0067
13	4.6001	-0.0831	-0.0041	-0.0648	0.0013
14	4.602	-0.0773	-0.0529	0.0751	0.0016
15	4.6224	-0.1009	-0.0641	0.0217	0.0017
16	4.6371	0.024	-0.0053	-0.0745	0.0007
17	4.6551	-0.0705	0.0645	0.0057	0.001
18	4.66	-0.0049	0.0444	-0.0354	0.0004
19	4.683	0.1257	-0.0242	0.1081	0.0032
20	4.6845	0.0597	-0.0132	0.0781	0.0011
21	4.7016	0.0976	0.1743	0.0502	0.0049
22	4.7102	-0.0151	0.0482	0.0903	0.0012
23	4.7204	0.051	0.1174	0.0189	0.0019
24	4.7352	-0.1134	-0.0437	-0.0463	0.002
25	4.7427	0.0696	0.1906	-0.0542	0.0051
26	4.7525	-0.171	-0.355	-0.0082	0.0181

27	4.7558	0.0656	0.0985	-0.0371	0.0018
28	4.7619	-0.0645	0.1003	-0.0314	0.0018
29	4.7635	0.0433	-0.0123	-0.057	0.0006
30	4.7735	0.0674	-0.0485	0.0666	0.0013
31	4.7869	0.0203	-0.1328	0.0482	0.0024
32	4.7946	-0.1239	0.0167	0.007	0.0018
33	4.7982	0.0675	0.1246	-0.1789	0.0061
34	4.8065	0.1848	-0.384	0.2686	0.0299
35	4.8301	-0.1125	0.8486	-0.7338	0.1504
36	4.8319	-0.004	0.1619	-0.1359	0.0053
37	4.8382	-0.0844	0.3674	-0.2899	0.0268
38	4.8433	-0.2069	-0.0324	-0.1058	0.0065
39	4.8541	0.0638	0.0442	-0.0195	0.0008
40	4.8667	-0.0527	-0.0268	0.0746	0.0011
41	4.8749	-0.264	-0.0104	-0.0556	0.0087
42	4.8805	0.5299	-0.2457	-0.1318	0.0429
43	4.8885	0.794	-0.3317	-0.0954	0.0898
44	4.9012	-0.0979	-0.2321	-0.2429	0.0147
45	4.9191	-0.3941	-0.6226	-0.8515	0.1528
46	4.9282	0.0102	-0.0171	-0.0221	0.0001
47	4.9311	-0.5252	0.0438	0.2791	0.043
48	4.9431	0.077	0.0586	-0.0505	0.0014
49	4.9502	0.1236	0.151	0.2604	0.0128
50	4.9538	0.2533	0.4083	0.0972	0.0292

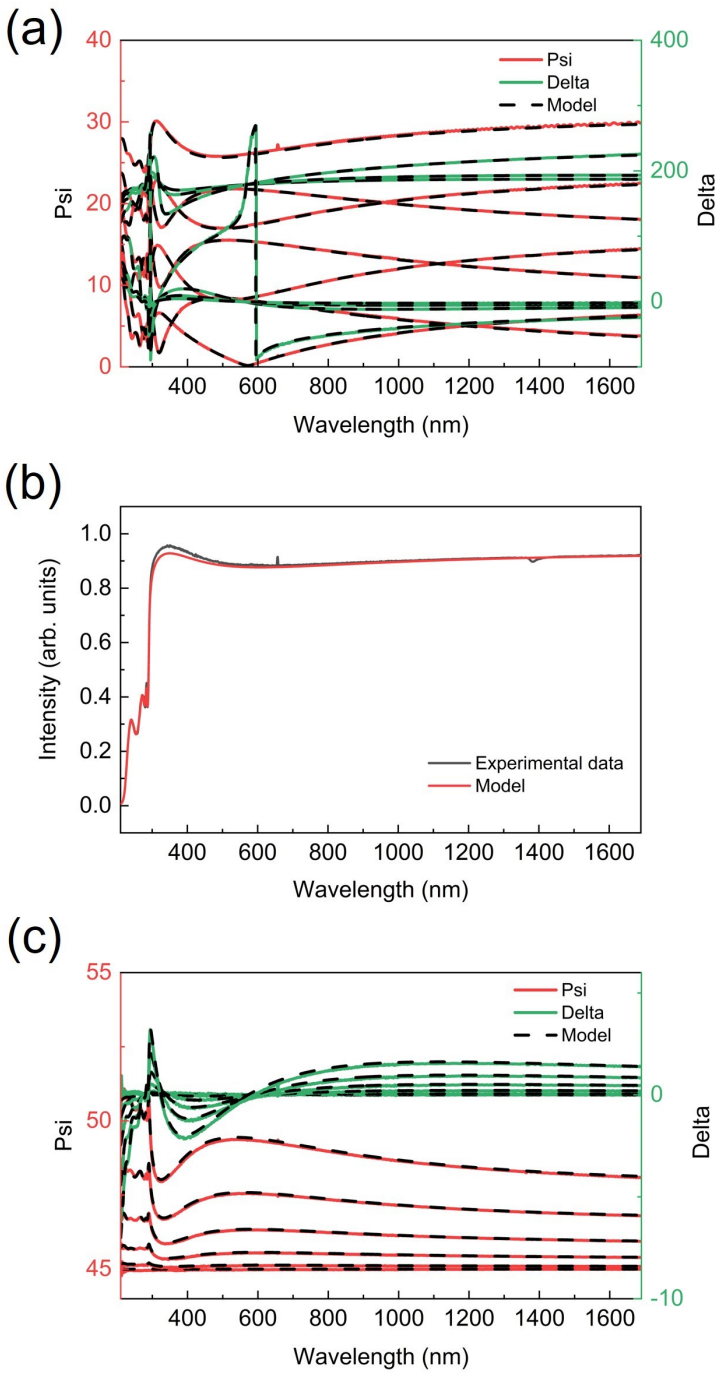

Figure S5. Spectra and fitting results of (a) angle-dependent reflective ellipsometry, (b) transmission absorption, and (c) angle-dependent transmission ellipsometry for a 100-nm-thick TPBAD film.

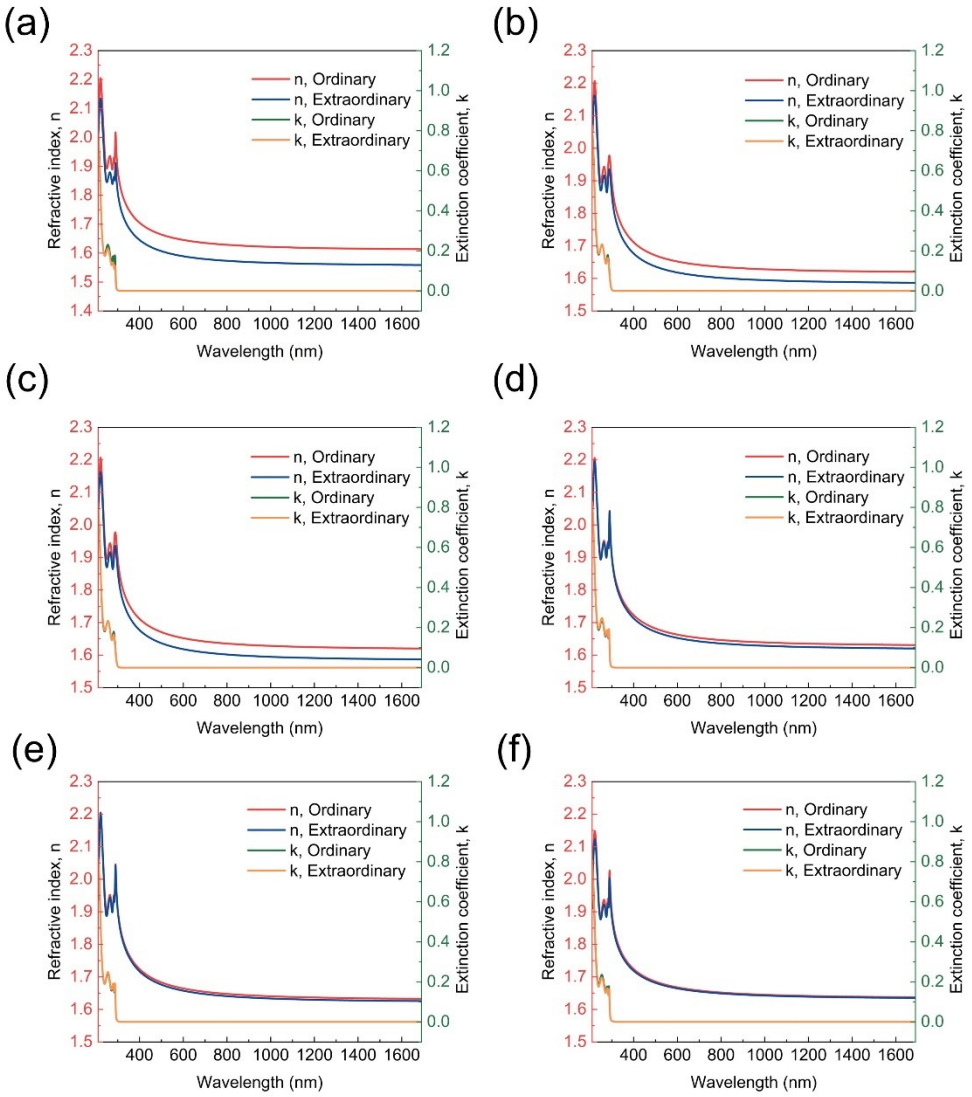

Figure S6. Spectra of the refractive indices and extinction coefficients in the directions normal and parallel to the film plane for TPBAD films with thicknesses of (a) 25, (b) 50, (c) 80, (d) 100, (e) 125, and (f) 150 nm.

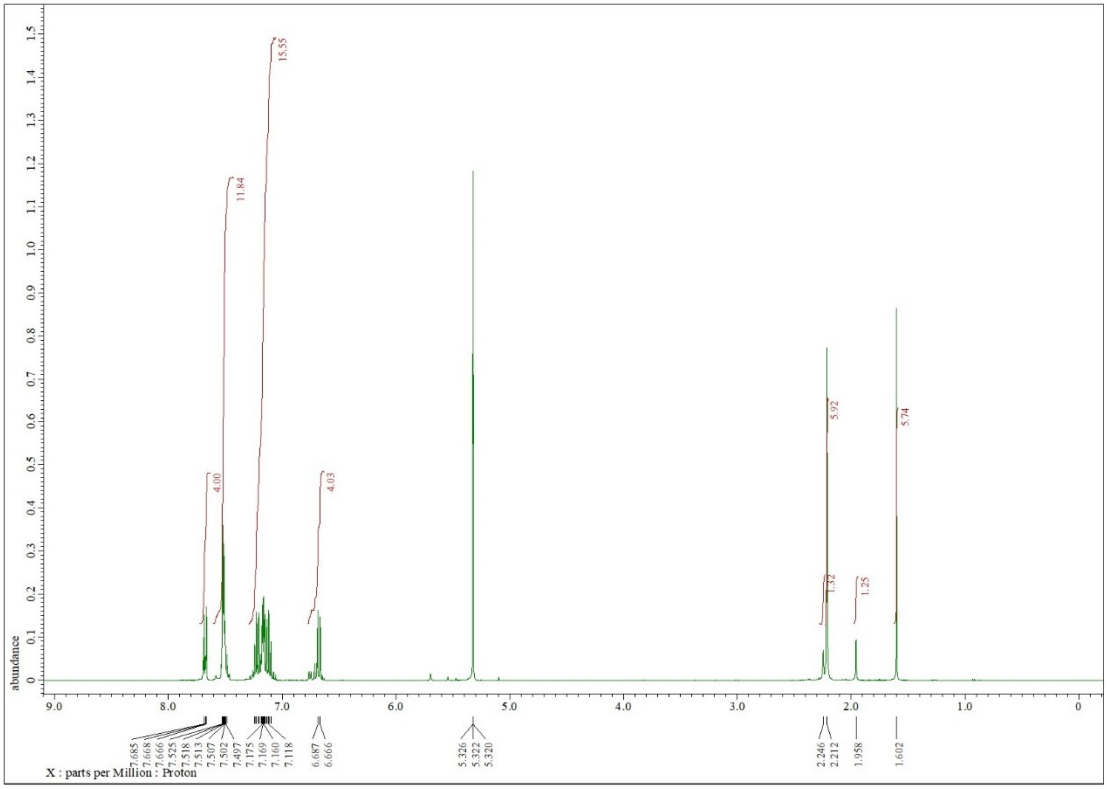

Figure S7. ^{1}H NMR spectrum of TPBAD.