Supplementary Information

Photophysical Analysis of Dual Fluorescence and Phosphorescence Emissions Observed for Semi-Aliphatic Polyimides at Lower Temperatures

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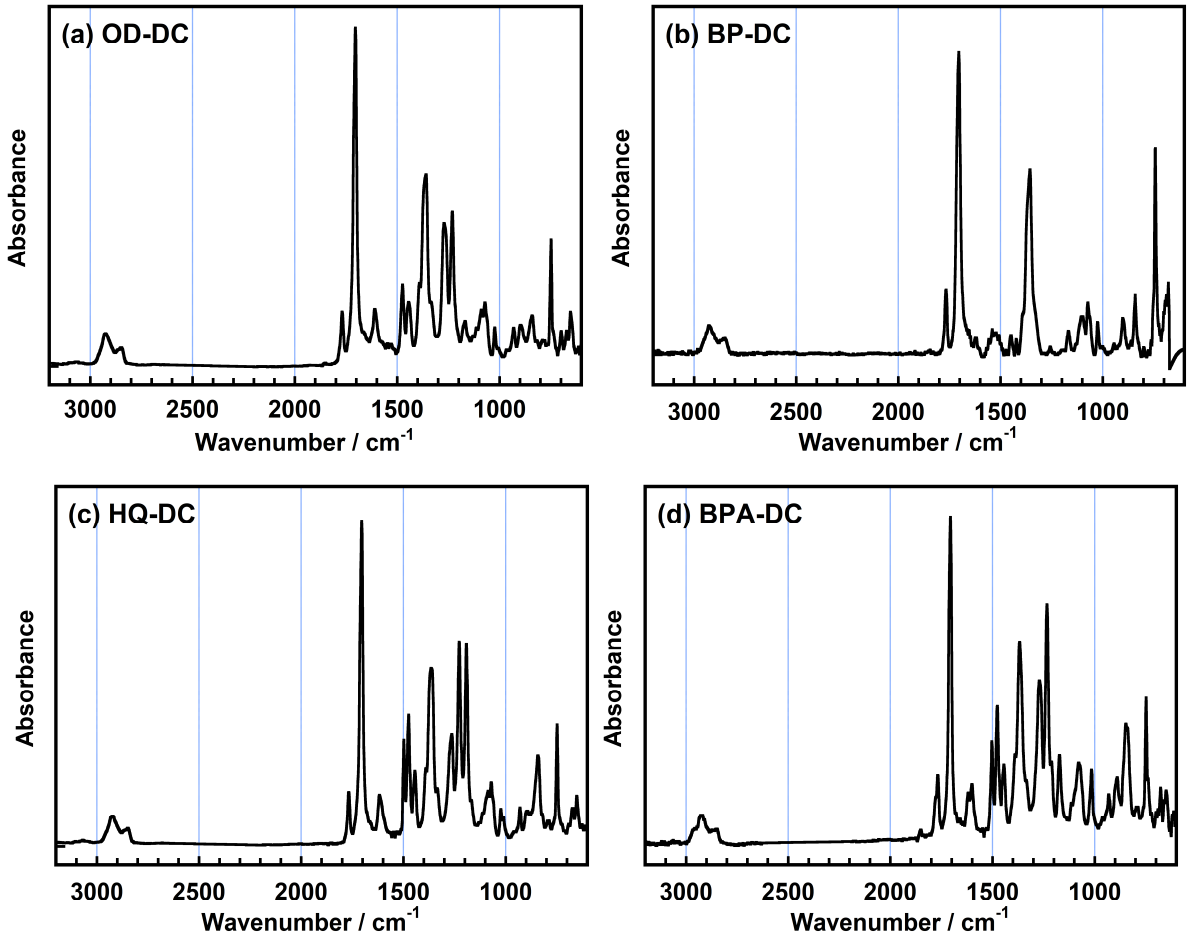

Figure S1. ATR-FT-IR spectra of polyimide films (PIs) depicted in **Chart 1**, (a) OD-DC, (b) BP-DC, (c) HQ-DC, and (d) BPA-DC.

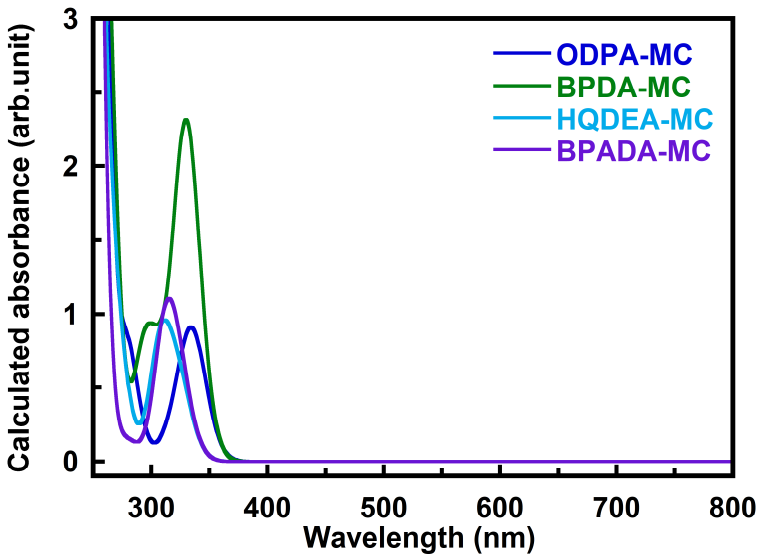

Figure S2. Calculated absorption spectra of the model compounds depicted in **Chart 2**.

Table S1. In-plane (n_{TE}), out-of-plane (n_{TM}), average refractive indices (n_{av}), and in-plane/out-of-plane birefringence of the polyimides (PIs) measured at 1310 nm, molecular weights (M_w), Van-der-Waals volume (V_{vdw}) (Å^3), molecular polarizability (Å^3) of model compounds (MCs), and molecular packing coefficients (K_p) of the PIs.

Polyimide	Refractive index			Birefringence	Calculated data for MCs			Packing Coeffs.
	n_{TE}	n_{TM}	n_{av}	Δn	M_w	V_{vdw}	Polari-zability	K_p
OD-DC	1.5753	1.5695	**1.5734**	**0.0058**	486.55	438.27	55.64	**0.6200**
BP-DC	1.6003	1.5896	**1.5967**	**0.0107**	470.55	429.68	55.56	**0.6288**
HQ-DC	1.5788	1.5771	**1.5782**	**0.0017**	578.64	518.56	67.30	**0.6106**
BPA-DC	1.5797	1.5773	**1.5789**	**0.0024**	696.81	641.04	83.48	**0.6092**

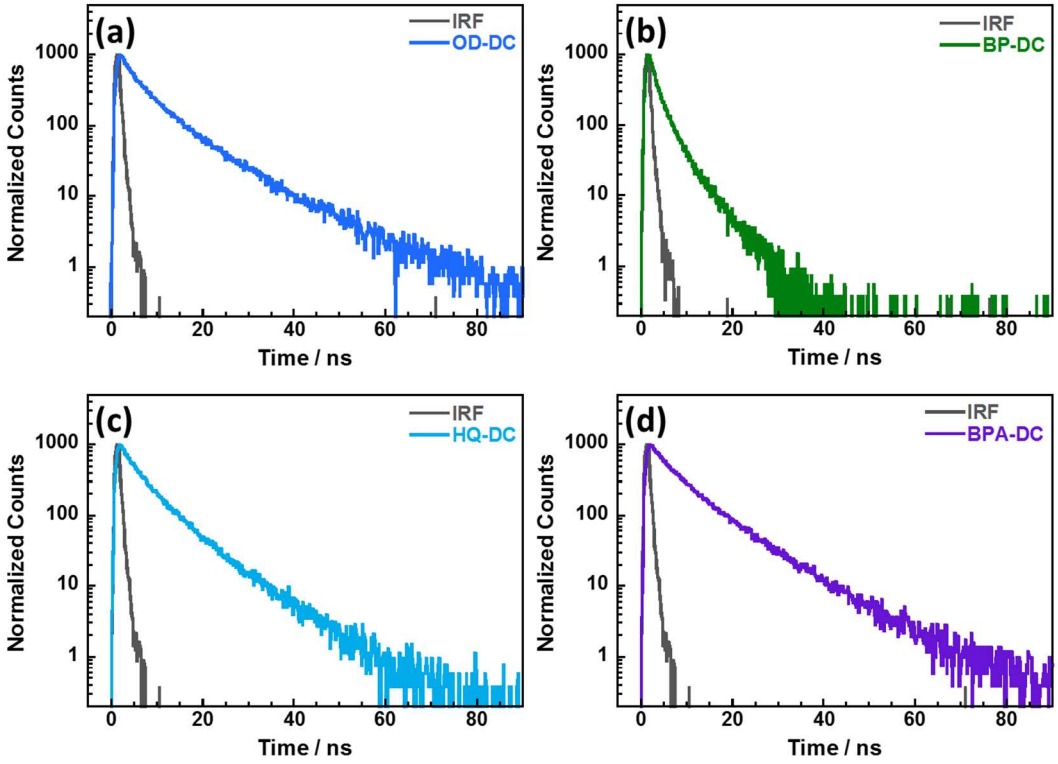

Figure S3. Fluorescence decay curves of (a) OD-DC, (b) BP-DC, (c) HQ-DC, (d) BPA-DC.

Table S2. Transition wavelengths, oscillator strengths (*f*), contribution of molecular orbitals, and assignment of one electron transitions of imide model compounds (MCs) calculated by the TD-DFT theory.

Imide compound	State	Transition wavelength/nm	Oscillator strength, *f*	Orbitals			Assignment
	S_1	**339.6**	**0.0808**	**HOMO**	→	**LUMO**	**LE($\pi-\pi^*$)**
OD-MC	S_2	324.7	0.0008	HOMO−3	→	LUMO	LE($n-\pi^*$)
	S_3	323.3	0.0021	HOMO−2	→	LUMO	LE($n-\pi^*$)
	S_1	**335.5**	**0.2195**	**HOMO**	→	**LUMO**	**LE($\pi-\pi^*$)**
BP-MC	S_2	330.0	0.0002	HOMO−2	→	LUMO	LE($n-\pi^*$)
	S_3	329.2	0.0104	HOMO−3	→	LUMO	CT($\pi-\pi^*$)
	S_1	**348.1**	**0.0775**	**HOMO**	→	**LUMO**	**LE($\pi-\pi^*$)**
HQ-MC	S_2	336.6	0.0446	HOMO	→	LUMO+1	LE($\pi-\pi^*$)
	S_3	331.1	0.0004	HOMO−5	→	LUMO	LE($n-\pi^*$)
	S_1	**340.4**	**0.0542**	**HOMO**	→	**LUMO**	**LE($\pi-\pi^*$)**
BPA-MC	S_2	335.5	0.0338	HOMO−1	→	LUMO+1	LE($\pi-\pi^*$)
	S_3	328.4	0.0002	HOMO−6	→	LUMO	LE($n-\pi^*$)

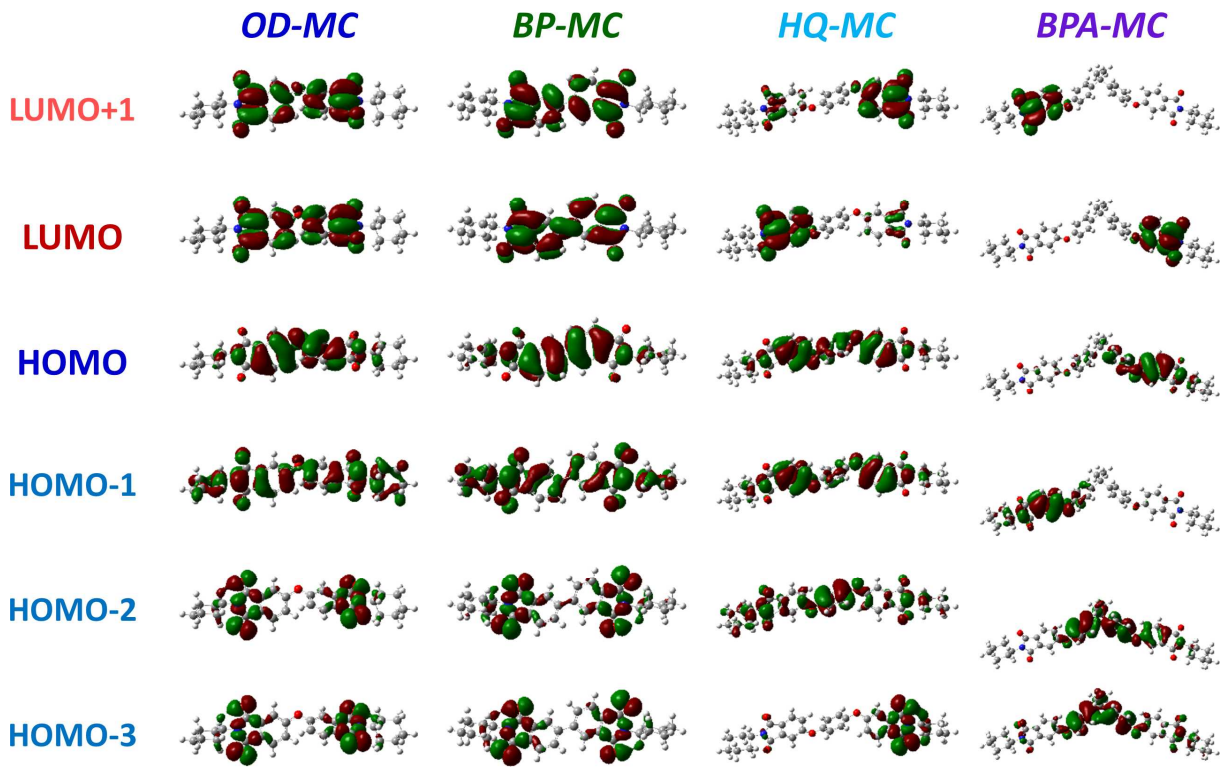

Figure S4. Spatial distributions of the molecular orbitals of imide model compounds (MCs) calculated by the DFT theory.

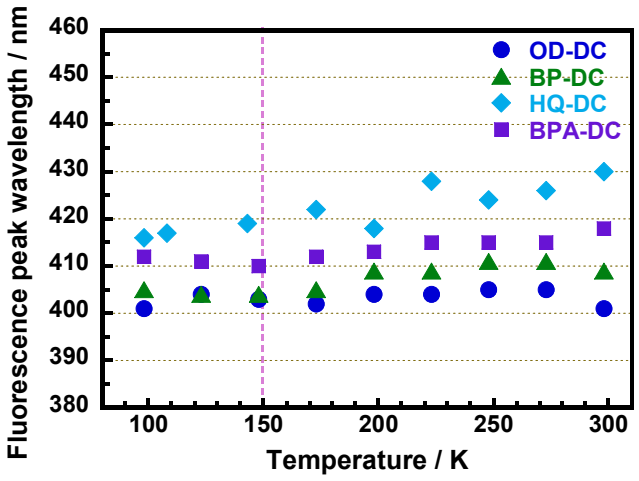

Figure S5. Temperature dependence of the fluorescence wavelength of the PI films.

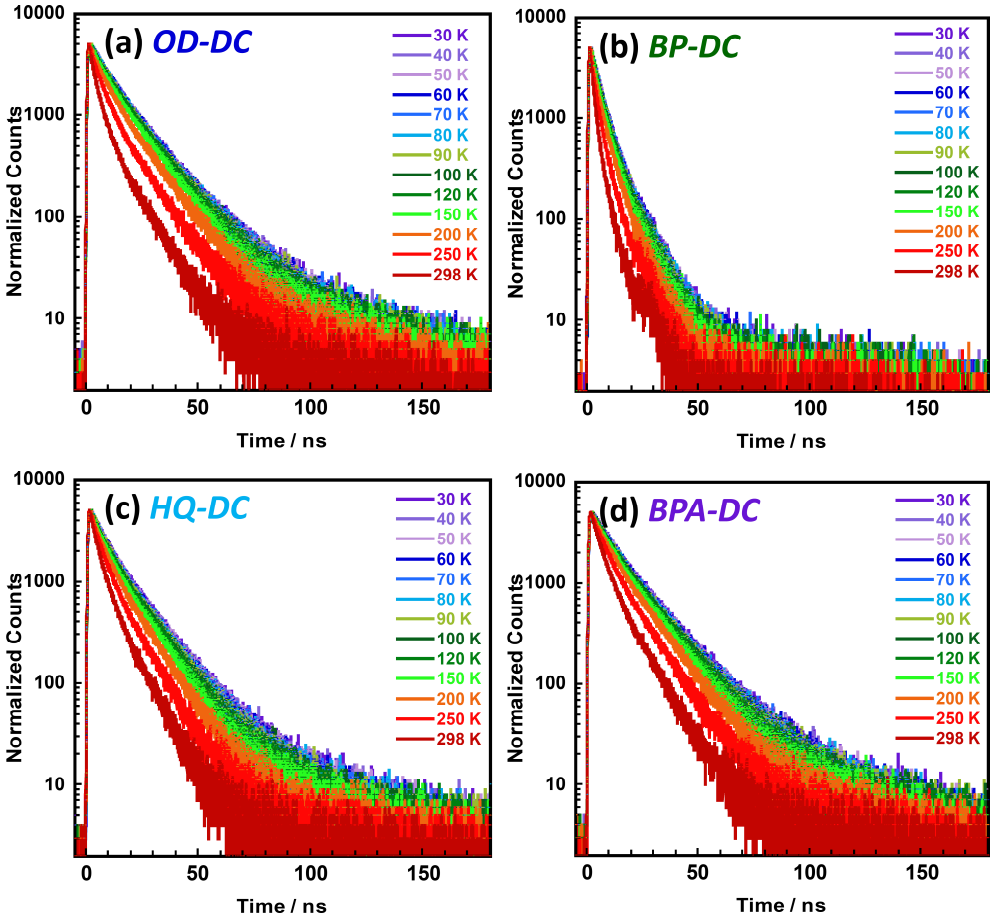

Figure S6. FL decay curves of (a) OD-DC, (b) BP-DC, (c) HQ-DC, and (d) BPA-DC at variable temperatures.

Table S3. Fitting parameters and phosphorescence (PH) lifetimes of the PH decay curve of OD-DC at each temperature. τ_p is the average PH lifetime.

Temp. / K	χ	τ_p / ms	τ_1 / ms	τ_2 / ms	A_1	A_2
180	1.0	97.3	22.2	130	72	28
170	1.2	136	30.1	199	80	20
160	1.2	180	36.9	247	76	24
150	1.2	233	51.8	300	68	32
140	1.1	309	85.6	397	65	35
130	1.3	**369**	96.3	457	61	39
120	1.1	425	113	509	55	45
110	1.2	485	143	571	50	50
100	1.1	538	184	632	48	52
90	1.1	577	190	658	42	58
80	1.2	619	230	702	39	61

Table S4. Fitting parameters and phosphorescence (PH) lifetimes of the PH decay curve of BP-DC at each temperature. τ_p is the average PH lifetime.

Temp. / K	χ	τ_p / ms	τ_1 / ms	τ_2 / ms	A_1	A_2
140	1.1	83.0	15.0	88.4	32	68
130	0.8	**167**	21.8	188	55	45
120	0.8	268	45.7	334	69	31
110	1.0	303	67.9	346	48	52
100	0.9	366	91.1	422	49	51
90	0.9	435	34.2	458	44	56
80	1.0	515	92.6	557	37	63

Table S5. Fitting parameters and phosphorescence (PH) lifetimes of the PH decay curve of HQ-DC at each temperature. τ_p is the average PH lifetime.

Temp. / K	χ	<τ> / ms	τ_1 / ms	τ_2 / ms	A_1	A_2
150	1.0	176	32.4	243	78	22
140	1.1	211	35.6	267	71	29
130	1.0	**296**	62.2	392	72	28
120	1.1	342	75.6	427	64	36
110	1.1	415	107	501	57	43
100	1.0	475	139	571	54	46
90	1.1	527	158	621	50	50
80	1.2	577	157	661	46	54

Table S6. Fitting parameters and phosphorescence (PH) lifetimes of the PH decay curve of BPA-DC at each temperature. τ_p is the average PH lifetime.

Temp. / K	χ	<τ> / ms	τ_1 / ms	τ_2 / ms	A_1	A_2
180	1.1	71.2	18.8	100	74	25
170	1.0	123	32.2	177	77	23
160	1.3	179	40.8	235	70	30
150	1.2	255	65.3	336	68	32
140	1.1	325	86.5	410	63	387
130	1.2	**397**	116	481	55	45
120	1.1	466	139	555	52	48
110	1.1	520	153	606	48	52
100	1.1	569	180	658	45	55
90	1.1	614	219	708	44	56
80	1.1	657	241	745	40	60

Table S7. Fitting parameters and fluorescence (FL) lifetimes of the FL decay curve of OD-DC at each temperature. τ_F is the average FL lifetime.

Temp. / K	χ	τ_F / ns	τ_1 / ns	τ_2 / ns	A_1	A_2
373	3.6	1.34	0.82	4.8	87	13
350	3.5	2.07	1.2	6.1	82	18
298	1.18	4.4	2.63	10.6	77	23
250	1.16	7.1	4.04	13.2	67	33
200	1.12	9.7	5.95	15.6	61	39
150	1.10	11.4	7.43	17.1	59	41
120	1.09	12.2	8.29	17.9	60	40
100	1.11	12.4	8.55	18.3	60	40
90	1.07	12.6	8.70	18.3	60	40
80	1.08	12.7	8.95	18.7	62	38
70	1.10	12.8	9.00	18.8	62	38
60	1.06	12.9	9.09	18.8	61	39
50	1.06	12.9	9.22	19.0	62	38
40	1.16	12.6	9.17	18.0	61	39
30	1.09	13.0	9.27	19.6	62	38

Table S8. Fitting parameters and fluorescence (FL) lifetimes of the FL decay curve of BP-DC at each temperature. τ_F is the average FL lifetime.

Temp. / K	χ	τ_F / ns	τ_1 / ns	τ_2 / ns	A_1	A_2
373	2.4	0.50	0.37	2.08	93	7
350	2.6	0.64	0.47	2.53	92	8
298	0.77	1.5	1.00	4.19	83	17
250	0.88	2.5	1.53	5.35	75	25
200	0..89	3.5	2.17	6.39	68	32
150	0.91	4.2	2.69	7.15	67	33
120	0.96	4.5	2.93	7.43	66	34
100	0.95	4.6	3.03	7.66	66	34
90	0.91	4.7	3.17	7.80	67	33
80	0.93	4.7	3.14	7.80	67	33
70	0.94	4.8	3.28	8.00	69	31
60	0.94	4.7	3.17	7.88	67	33
50	0.92	4.8	3.23	7.94	67	33
40	0.92	4.8	3.32	8.03	67	33
30	0.93	4.9	3.39	8.15	69	31

Table S9. Fitting parameters and fluorescence (FL) lifetimes of the FL decay curve of HQ-DC at each temperature. τ_F is the average FL lifetime.

Temp. / K	χ	τ_F / ns	τ_1 / ns	τ_2 / ns	A_1	A_2
373	1.1	2.39	1.68	5.28	80	20
350	1.2	3.06	2.08	6.17	76	23
298	1.01	4.8	2.91	8.93	68	32
250	1.16	6.6	3.91	13.2	63	37
200	1.12	8.3	4.99	15.6	60	40
150	1.10	9.6	5.94	17.1	57	43
120	1.09	10.2	6.46	17.9	58	42
100	1.11	10.6	6.80	18.3	58	42
90	1.07	10.7	6.77	18.3	56	44
80	1.08	10.6	6.28	18.7	56	44
70	1.10	11.0	6.97	18.8	56	44
60	1.06	11.1	7.25	18.8	58	42
50	1.06	11.2	7.15	19.0	56	44
40	1.16	11.4	7.46	18.0	57	43
30	1.08	11.5	7.52	16.9	58	42

Table S10. Fitting parameters and fluorescence (FL) lifetimes of the FL decay curve of BPA-DC at each temperature. τ_F is the average FL lifetime.

Temp. / K	χ	τ_F / ns	τ_1 / ns	τ_2 / ns	A_1	A_2
373	1.0	2.81	1.89	5.9	77	23
350	1.1	3.88	2.71	7.7	77	23
298	1.00	6.3	4.03	10.9	66	34
250	1.07	8.8	5.62	13.5	59	41
200	1.03	10.9	7.32	15.9	57	43
150	1.11	12.3	8.49	17.2	56	44
120	1.06	12.9	9.00	17.9	57	43
100	1.07	13.2	9.23	18.1	56	44
90	1.04	13.4	9.65	18.7	58	42
80	1.10	13.5	9.53	18.6	57	43
70	1.08	13.6	9.50	18.5	55	45
60	1.05	13.7	9.83	18.9	57	43
50	1.06	13.8	9.97	19.0	57	43
40	1.06	13.8	9.97	19.1	58	42
30	1.10	13.8	10.0	19.3	58	42