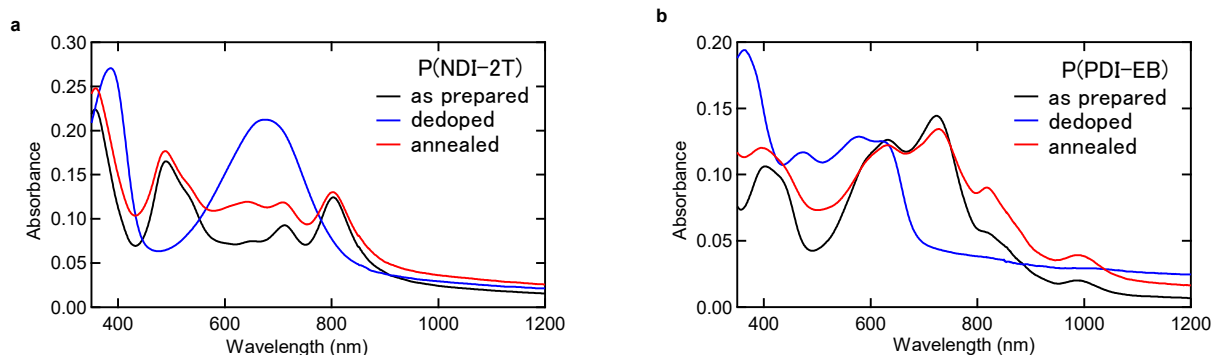**Supplementary Materials for**

Highly air-stable, n-doped conjugated polymers achieved by dimeric organometallic dopants

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Supplementary Figure S 1: UV-Vis absorption spectra of $(RuCp*Mes)_2$-doped, dedoped and annealed samples for (a)P(NDI2OD-T2) and (b) P(PDI-EB) polymer thin films. In the dedoping process, samples were stored under temperature of 40 °C and humidity of 80 % for 10 minutes. In the annealing process, dedoped samples were heated at 180 °C in Ar atmosphere for 20 minutes. The observed small discrepancy between absorption spectra of the as doped and annealed state is expected to be reduced by further tuning process conditions.
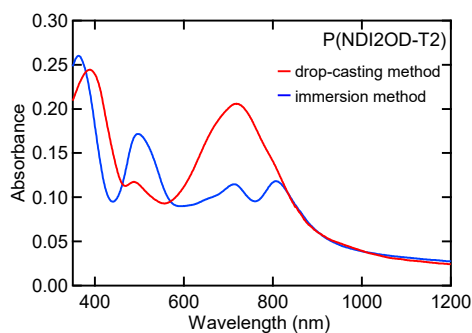
Supplementary Figure S 2: UV-Vis absorption spectrum of $(RuCp*Mes)_2$-doped P(NDI2OD-T2) thin film through the drop-casting method. The sample was encapsulated with CYTOP polymer film to prevent dedoping to the lower doped state that is observed in the immersion method. As a comparison, the spectrum of P(NDI2OD-T2) thin film doped through the immersion method is also presented which is measured without encapsulation.
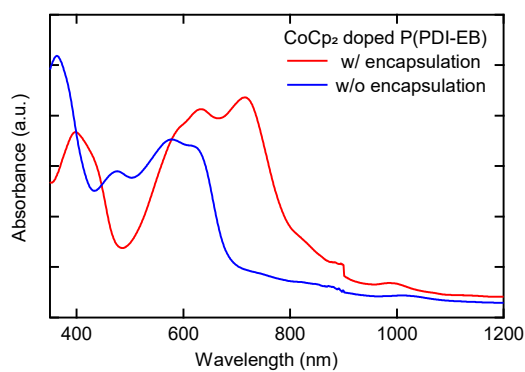
Supplementary Figure S 3: UV-Vis absorption spectra of P(PDI-EB) thin films doped with $CoCp_2$ through the drop-casting method measured in air with and without encapsulation. Encapsulation was conducted in an Ar atmosphere by covering the thin film with CTL809M and a top glass substrate so that to sandwich the thin film with two glass substrates.
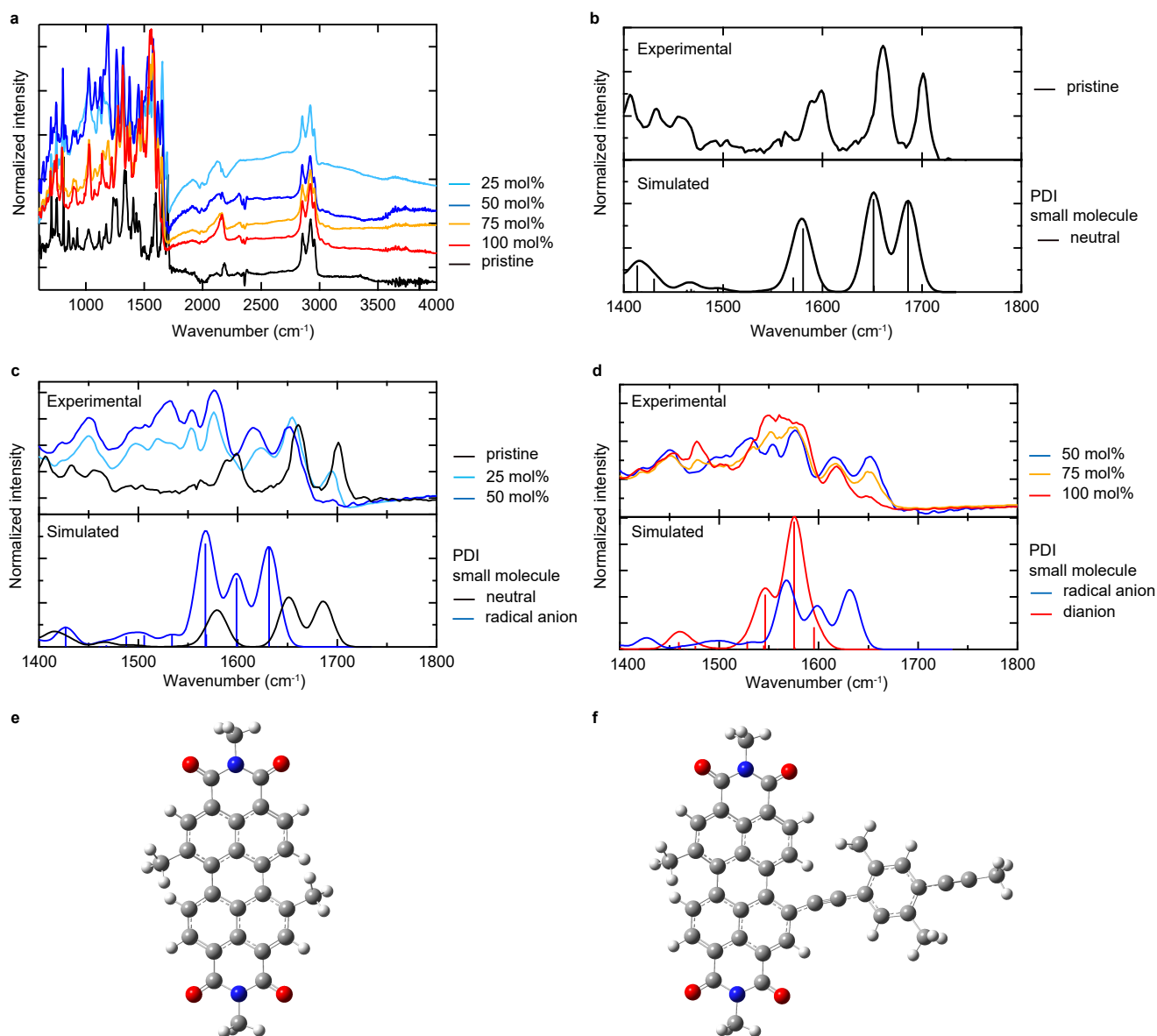
Supplementary Figure S 4: **FTIR spectra of P(PDI-EB) thin films fabricated from mixed solution with (RuCp∗Mes)₂.** (**a**) FTIR spectra in a wide range and (**b**–**d**) ranges around the vibrational modes of carbonyl group. Upper panels are experimental spectra. Lower panels are simulated spectra for a PDI small molecule. Solid lines in the simulated spectra are the sum of all simulated peaks with a constant Gaussian broadening of 10 cm^{-1}. (e) The optimized structure of small molecular PDI. (f) The optimized structure of the model small molecule representing a monomer of P(PDI-EB) which was employed in our calculations. The inclusion of diethynylbenzene was necessary to reproduce some features of the spectra observed experimentally. Note that alkyl groups were replaced with a methyl group in order to reduce calculation costs.

Supplementary Table 1: Assignment of vibrational modes in neutral state

frequency (cm^{-1})	main mode	assignment in the main text
1568	ring stretching	–
1573	ring stretching	v1
1578	ring stretching	v1
1587	ring stretching	–
1591	ring stretching	–
1650	C=O stretching (asymmetric in PDI)	v2
1652	C=O stretching (asymmetric in PDI)	v2
1685	C=O stretching (symmetric in PDI)	v3
1690	C=O stretching (symmetric in PDI)	v3

Supplementary Table 2: Assignment of vibrational modes in anion state

frequency (cm^{-1})	main mode	assignment in the main text
1533	ring stretching	–
1547	ring stretching	–
1560	ring stretching	v1
1567	ring stretching	v1
1586	ring stretching	–
1604	C=O stretching (asymmetric in PDI)	v2
1608	C=O stretching (asymmetric in PDI)	v2
1637	C=O stretching (symmetric in PDI)	v3
1646	C=O stretching (symmetric in PDI)	v3

Supplementary Table 3: Assignment of vibration modes in dianion state

frequency (cm^{-1})	main mode	assignment in the main text
1528	ring stretching	–
1540	ring stretching	–
1557	C=O stretching (asymmetric in PDI)	v2
1564	ring stretching	v1
1568	C=O stretching (asymmetric in PDI)	v2
1577	ring stretching	v1
1583	ring stretching	–
1604	C=O stretching (symmetric in PDI)	v3
1613	C=O stretching (symmetric in PDI)	v3