Electronic Supplementary Information for

Photo-Responsive Metallomesogen for Optically and Electrically Tunable Polarized Light Modulator

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1. Materials

All chemicals were purchased form commercials sources and used without further purification. Solvents were dried and distilled by using standard methods when necessary.

2. Synthesis

4-(4-pentylphenylazo)phenol (1). A solution of 4-pentylaniline (50.0 mmol) and HCl (15 mL) in water (100 mL) was cooled at 0 °C and Na_2CO_3 (50.0 mmol) was added in small portions, keeping the temperature near 0 °C. After stirring for 1 h, the solution of the diazonium salt was slowly added to a chilled solution of phenol (50.0 mmol), NaOH (63.0 mmol) and water (25 mL). Here, the temperature was maintained below 5 °C. The product was precipitated by the addition of small portion of NaCl. By recrystallization of the product in ethanol, the purified reddish crystal was collected (yield: 71%). ^{1}H NMR (400 MHz, DMSO-*d*): δ = 10.2 (s, 1H), 7.76 (d, 2H), 7.72 (d, 2H), 7.35 (d, 2H), 6.92 (d, 2H), 2.64 (t, 2H), 1.60 (m, 2H), 1.29 (m, 4H), 0.85 ppm (t, 3H).

4-(6-bromohexyloxy)phenyl(4-pentylphenyl)diazene (2). A mixture of compound **1** (20.0 mmol), 1,6-dibromohexane (100.0 mmol), K_2CO_3 (36.0 mmol) and butanone (150 mL) was stirred and heated to reflux for 24 h. After the reaction, the solvent was removed in vacuum and the remaining residue was dissolved in chloroform and extracted with distilled water several times. Yellow crystals were obtained by recrystallization of the crude oil in methanol and acetone (yield: 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, 2H), 7.80 (d, 2H), 7.30 (d, 2H), 7.00 (d, 2H), 4.04 (t, 2H), 3.43 (t, 2H), 2.67 (t, 2H), 1.91 (m, 2H), 1.82 (m, 2H), 1.65 (m, 2H), 1.55 (m, 4H), 1.34 (m, 4H), 0.89 ppm (t, 3H).

3,5-bis[6-(4-(4-pentylphenylazo)phenoxy)hexyloxy]benzoic acid ethyl ester (3). A mixture of compound **2** (10.0 mmol), dihydroxybenzoate (3.0 mmol), K_2CO_3 (15.2 mmol), and butanone (50 mL) was heated to reflux for 48 h. After the reaction, solvent was removed in vacuum and the remaining residue was re-dissolved in chloroform and washed with distilled water three times. It was purified by column chromatography with silica gel by using ethyl acetate:chloroform = 1:20 and subsequent recrystallization with methanol. The resulting product was a yellowish solid (yield: 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, 4H), 7.78 (d, 4H), 7.72 (d, 4H), 7.16 (d, 2H), 6.98 (s, 4H), 6.64 (s, 1H), 4.04 (t, 4H), 3.99 (t, 4H), 3.89 (s, 3H), 2.66 (t, 4H), 1.84 (m, 8H), 1.65 (m, 4H), 1.55 (m, 8H), 1.34 (m, 8H), 0.89 ppm (t, 6H).

3,5-bis[6-(4-(4-pentylphenylazo)phenoxy)hexyloxy]benzoic acid (DA). Aqueous KOH (10 M, 10 mL) was added to a stirred solution of compound **3** (0.57 mmol) in ethanol (50 mL). The mixture was heated at reflux for 3 h, and then neutralized with an HCl to obtain a precipitate. The precipitate was filtered off and washed with water. The crude product was purified by reprecipitation from chloroform and ethanol, and dried under vacuum to afford **DA** as a yellow solid (yield: 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, 4H), 7.78 (d, 4H), 7.72 (d, 4H), 7.16 (d, 2H), 6.98 (s, 4H), 6.64 (s, 1H), 4.04 (t, 4H), 3.99 (t, 4H), 2.66 (t, 4H), 1.84 (m, 8H), 1.65 (m, 4H), 1.55 (m, 8H), 1.34 (m, 8H), 0.89 ppm (t, 6H).

iDLA. A mixture of compound **DA** (0.23 mmol), aminopyridine (0.93 mmol), EDC (1.17 mmol), and HOAt (0.93 mmol) was added in the 30 mL of chloroform and stirred for 24 h. After the reaction, solvent was removed in vacuum and the remaining residue was re-dissolved in chloroform and washed with distilled water three times. It was purified by column chromatography with silica gel by using tetrahydrofuran:methylene chloride = 1:9 and subsequent recrystallization with methanol. The resulting product was a yellowish solid (yield: 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 1H), 8.49 (s, 1H), 8.34 (d, 1H), 8.18 (d, 1H), 7.89 (d, 4H), 7.78 (d, 4H), 7.29 (d, 1H), 7.28 (d, 4H), 6.98 (s, 6H), 6.64 (s, 1H), 4.04 (t, 4H), 3.99 (t, 4H), 2.66 (t, 4H), 1.84 (m, 8H), 1.65 (m, 4H), 1.55 (m, 8H), 1.34 (m, 8H), 0.89 ppm (t, 6H).

Pd(iDLA)$_2$. The $PdCl_2$ (o.o5 mmol) and **iDLA** (0.11 mmol) in toluene (10 mL) were heated at reflux for 12 h. After reaction, the solvents were removed by vacuum. The residue was purified by using column chromatography on silica gel by using tetrahydrofuran:chloroform = 1:4 to afford a yellow powder (yield: 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.48 (s, 2H), 8.74 (s, 2H), 8.62 (d, 2H), 8.37 (d, 2H), 7.89 (d, 8H), 7.78 (d, 8H), 7.28 (d, 8H), 7.11 (d, 2H), 6.98 (s, 12H), 6.64 (s, 2H), 4.04 (t, 8H), 3.99 (t, 8H), 2.66 (t, 8H), 1.84 (m, 16H), 1.65 (m, 8H), 1.55 (m, 16H), 1.34 (m, 16H), 0.89 ppm (t, 12H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 166.7, 161.2, 160.5, 151.0, 147.1, 146.3, 136.9, 135.1, 129.8, 126.2, 124.7, 124.5, 114.6, 105.3, 104.2, 68.7, 68.4, 35.8, 31.7, 31.4, 30.9, 29.1, 25.8, 22.5, 21.5, 14.0 ppm. MS (MALDI-ToF) for m/z calcd. 2036.92; $[M+Na]^+$ found: 2059.91. Elemental analysis calcd. (%) for $C_{116}H_{140}Cl_2N_{12}O_{10}Pd$: C 68.30 H 6.92 N 8.24 O 7.84; found: C 66.82 H 6.59 N 8.04.

3. Characterizations

Proton (^{1}H) and carbon (^{13}C) resonances were recorded on a NMR spectrometer (JNMEX400) in deuterated solution of $CDCl_3$ and DMSO-*d*. Matrix assisted laser desorption ionization time-of-flight mass spectroscopy (Voyager-DE Workstation) and elemental analysis (Vario EL) were conducted to identify the chemical structure. UV-Vis absorption spectra were obtained with a spectrophotometer (SCINCO S-3100). The thermal behavior was monitored by using a DSC (PerkinElmer PYRIS Diamond). WAXD experiments were conducted in the reflection mode of 12 kW rotating-anode X-ray generator coupled with a diffractometer (Rigaku). SAXS measurements are used by a CuKα X-ray microsource (Rigaku). The changes of optical textures were observed with a POM (Nikon ECLIPSE E600POL). The minimal energy geometry of palladium-based metallomesogen was calculated utilizing the simulation software (Accelrys Cerius^2 Version 4.6).

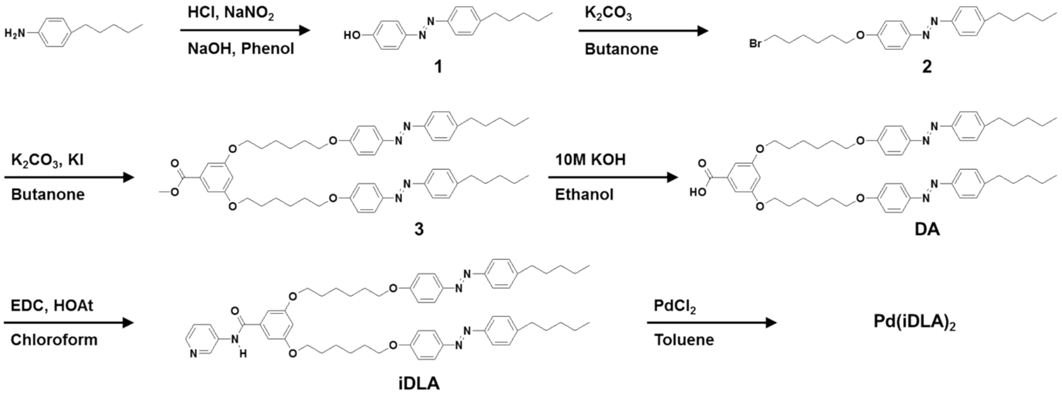

Fig. S1 Synthetic routes of Pd(iDLA)$_2$.

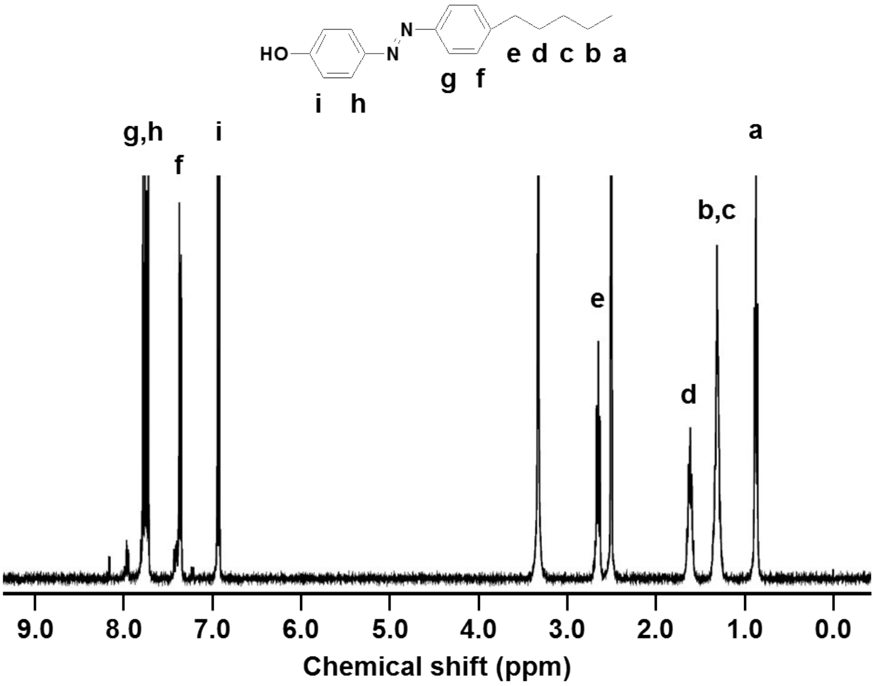

Fig. S2 ^{1}H NMR spectrum of compound **1**.

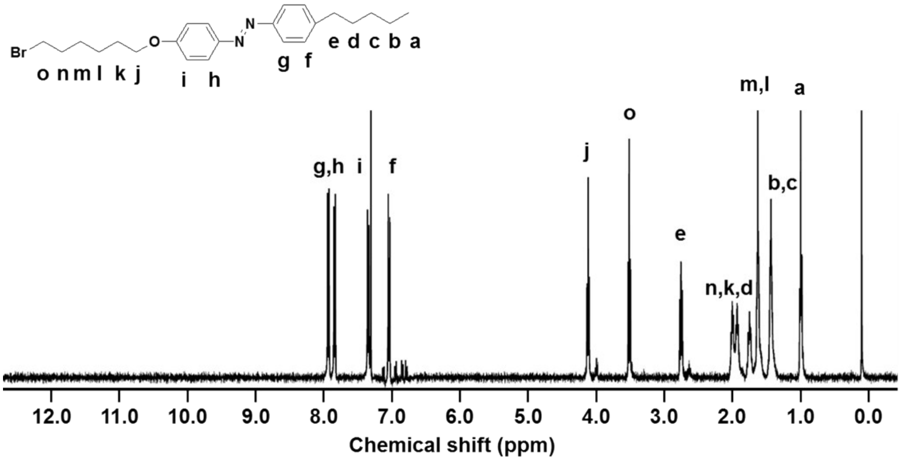

Fig. S3 ^{1}H NMR spectrum of compound **2**.

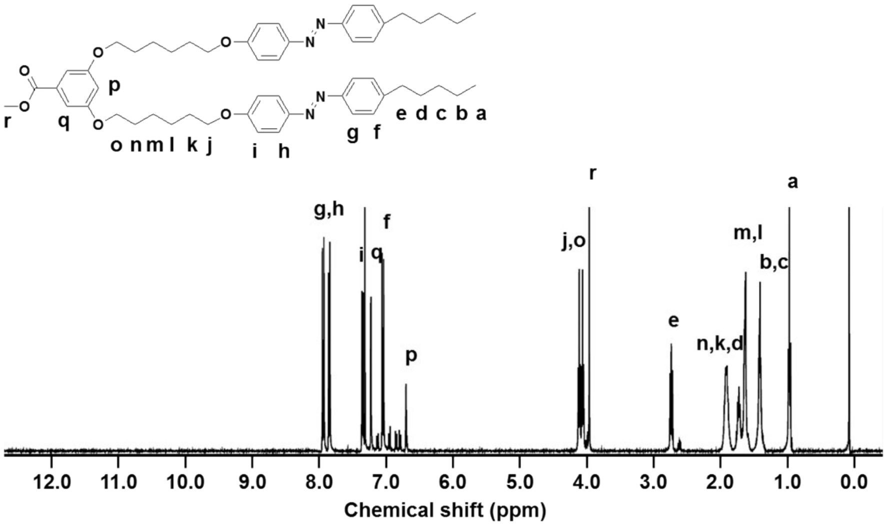

Fig. S4 ^{1}H NMR spectrum of compound **3**.

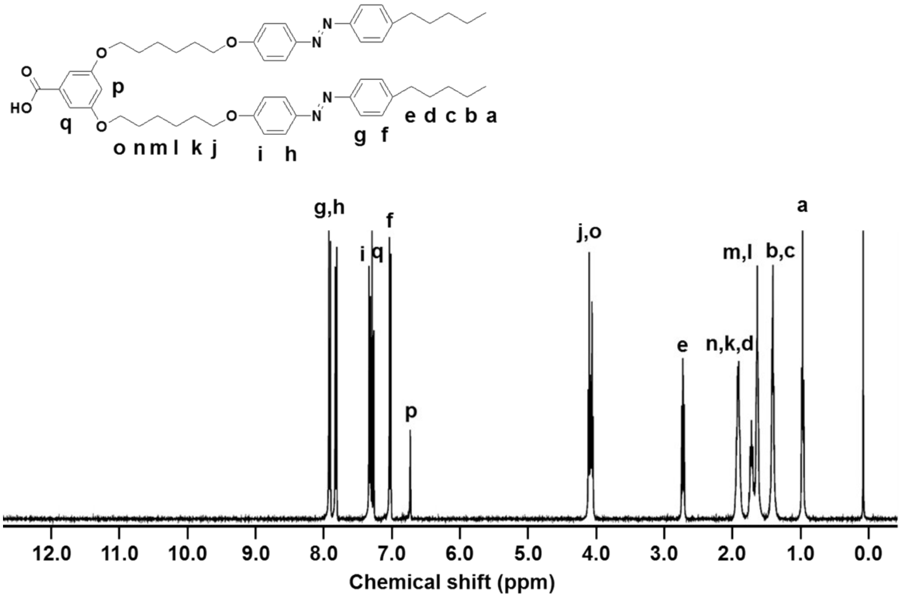

Fig. S5 ^{1}H NMR spectrum of compound **DA**.

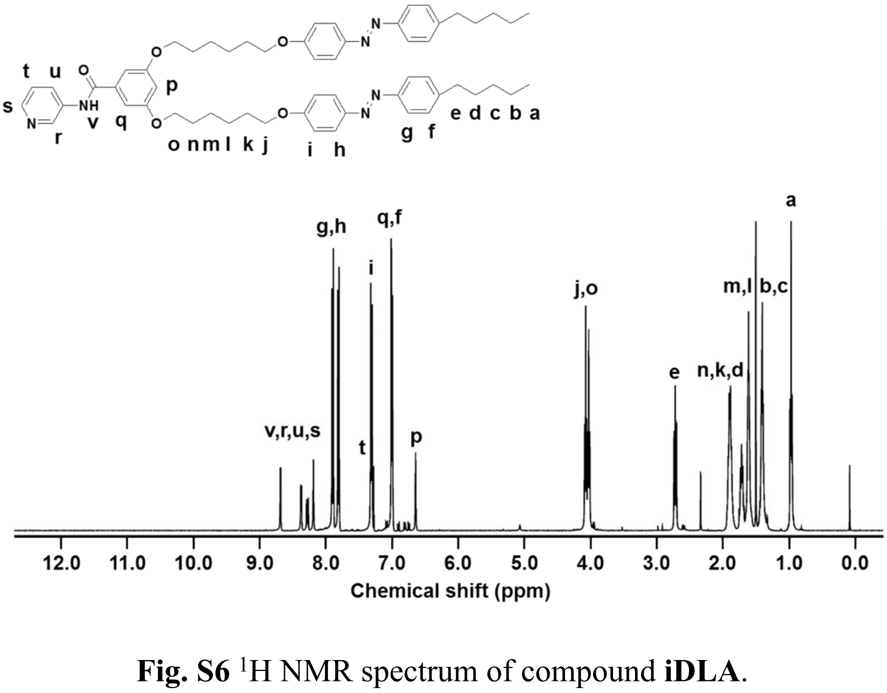

Fig. S6 ^{1}H NMR spectrum of compound **iDLA**.

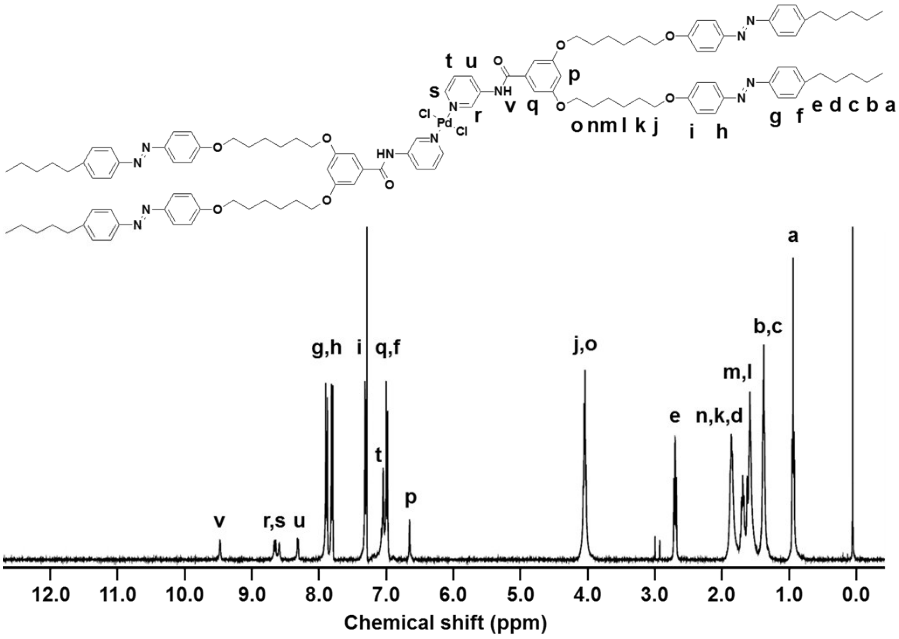

Fig. S7 ^{1}H NMR spectrum of Pd(iDLA)$_2$.

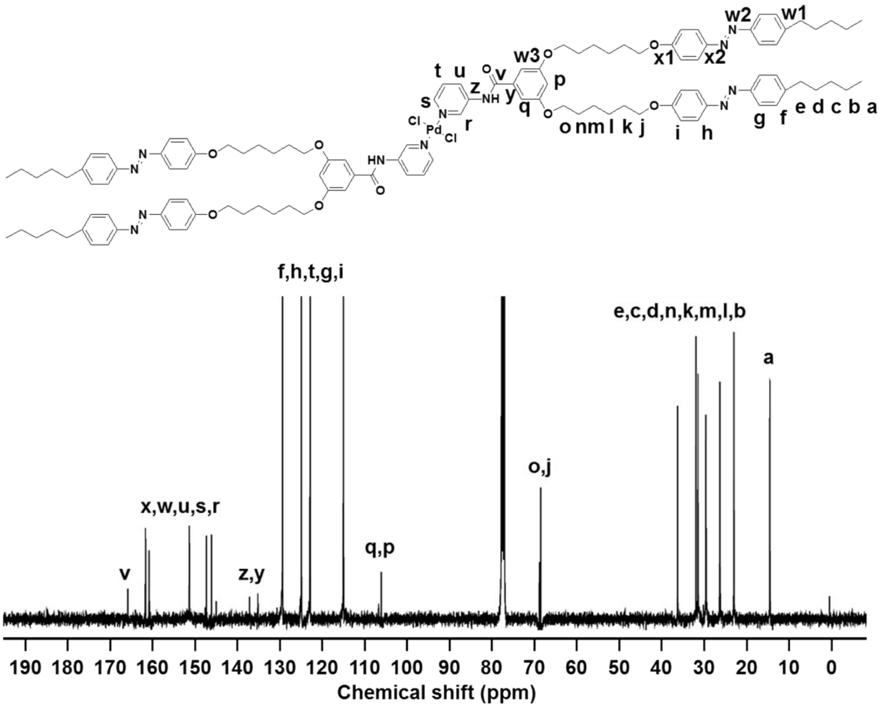

Fig. S8 ^{13}C NMR spectrum of Pd(iDLA)$_2$.

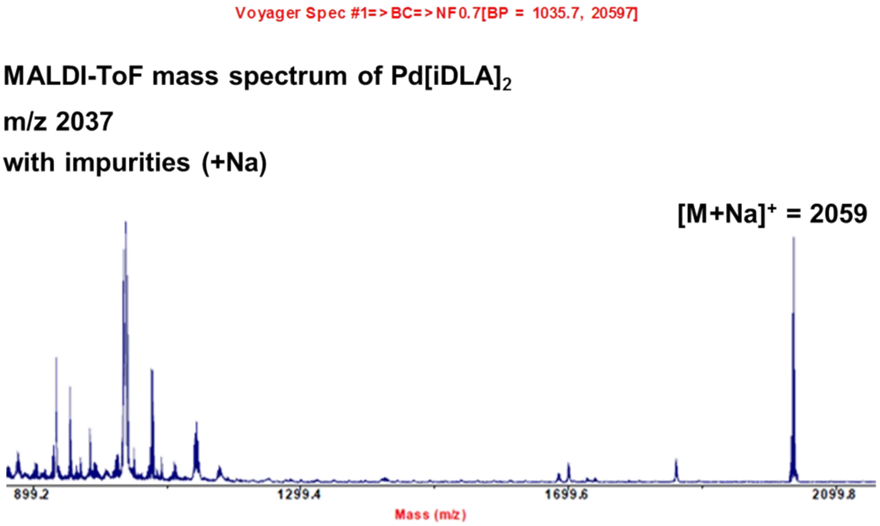

Fig. S9 MALDI-ToF mass spectrum of Pd(iDLA)$_2$.

	Experimental content (%)	Calculated content (%)
C	66.82 66.58 65.53	68.30
H	6.443 6.599 6.480	6.92
N	8.049 7.968 7.816	8.24

Fig. S10. Elemental analysis of Pd(iDLA)$_2$.

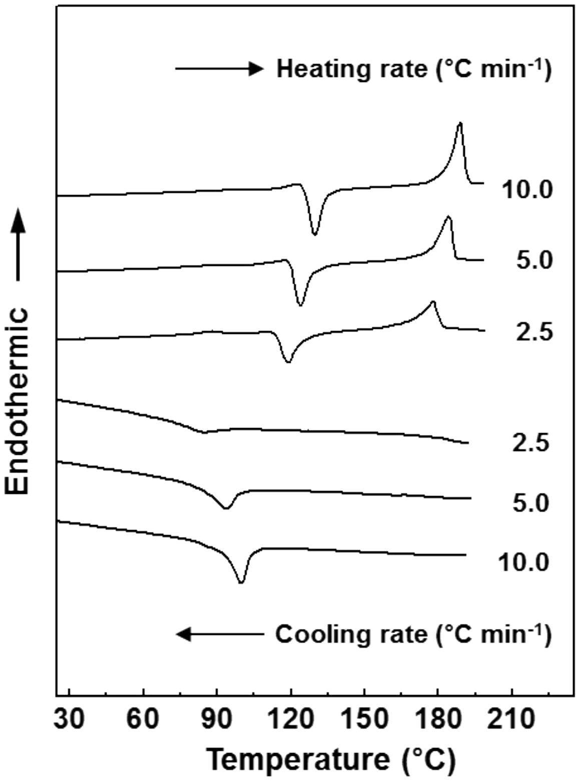

Fig. S11 DSC thermograms of Pd(iDLA)$_2$ during heating and subsequent cooling processes.

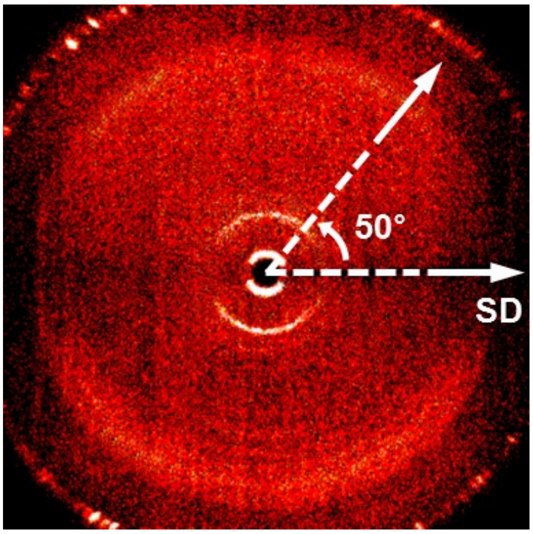

Fig. S12 2D WAXD image of a macroscopically oriented Pd(iDLA)$_2$ film.

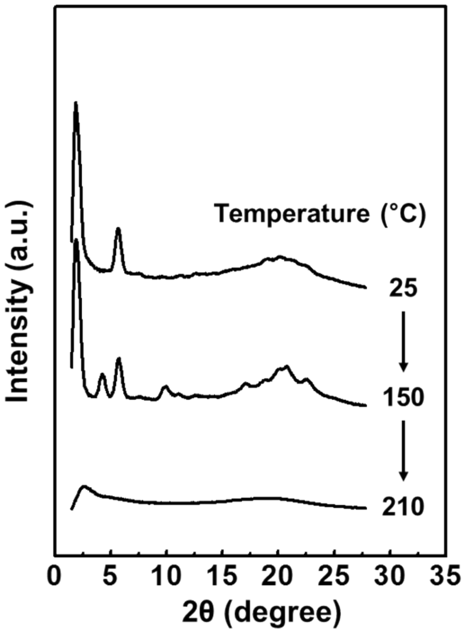

Fig. S13 1D WAXD pattern of the Pd(iDLA)$_2$ at different temperature during heating process.

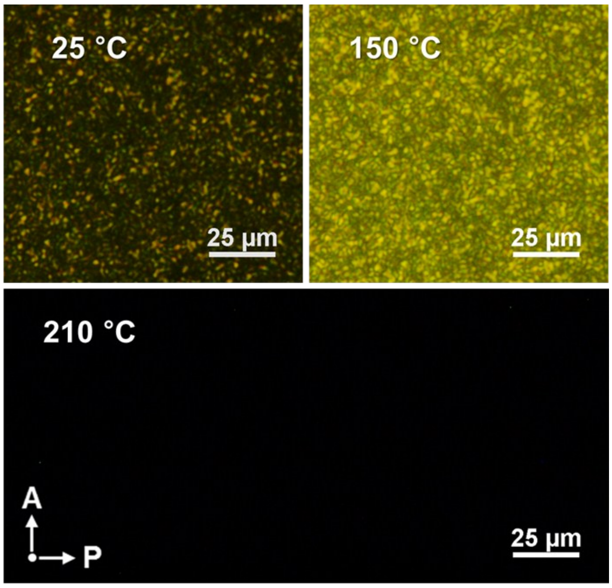

Fig. S14 POM microphotographs of Pd(iDLA)$_2$ at smectic crystal, highly ordered crystal and isotropic liquid phase.

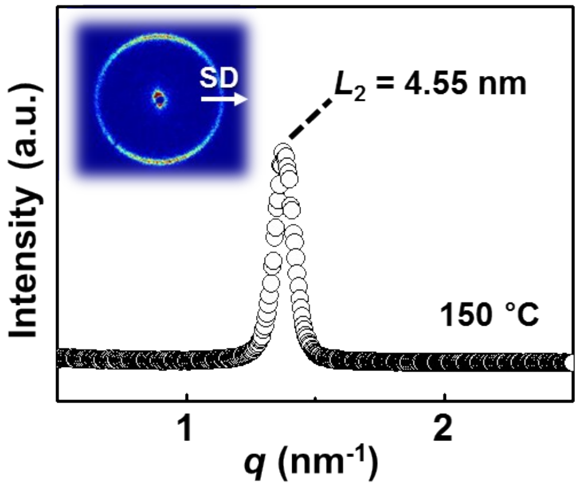

Fig. S15 SAXS patterns of Pd(iDLA)$_2$ at 150 °C.

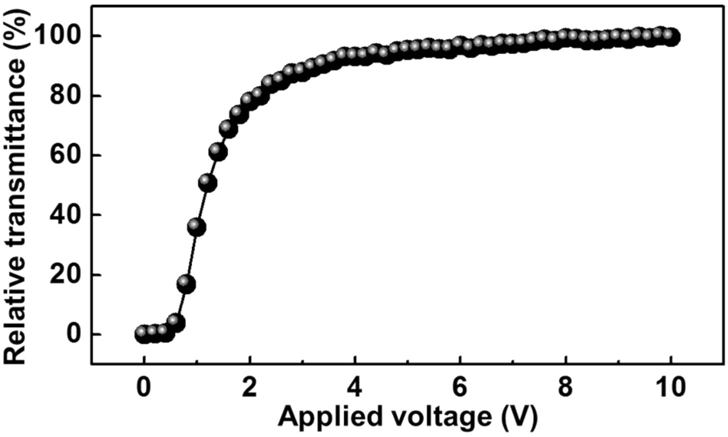

Fig. S16 Electro-optical switching of the Pd(iDLA)$_2$-filled ECB cell upon increasing and decreasing the applied voltage.

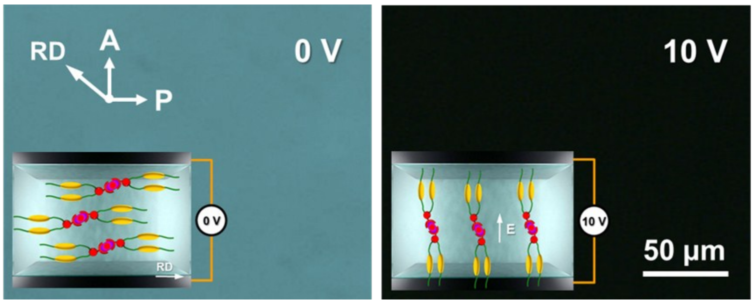

Fig. S17 POM images and their schematic illustration of the ECB cell with the 1.0 wt% Pd(iDLA)$_2$ at 0 V and 10 V, respectively.

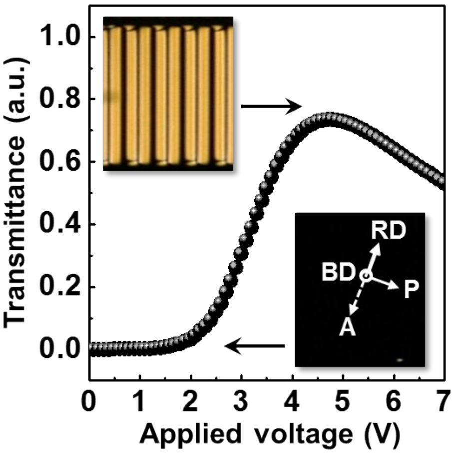

Fig. S18 Optical switching response for the Pd(iDLA)$_2$-doped IPS cell under an in-plane electric field from 0.0 V to 7.0 V.

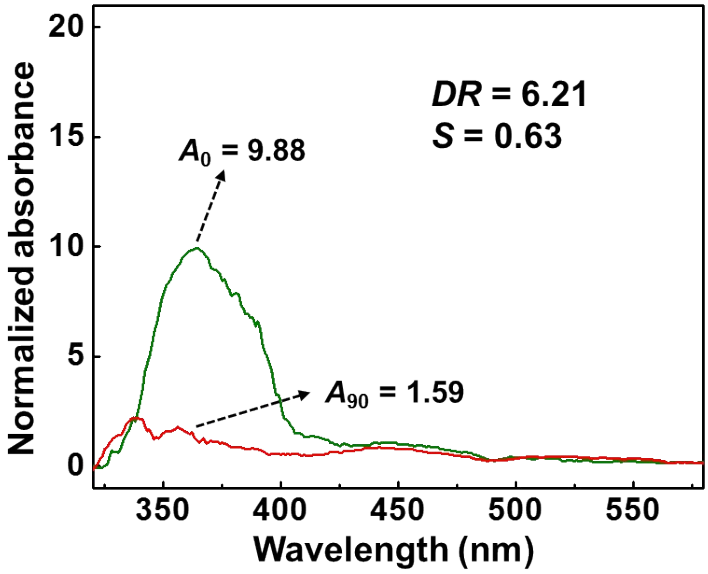

Fig. S19 Dichroic ratio and order parameter of iDLA.

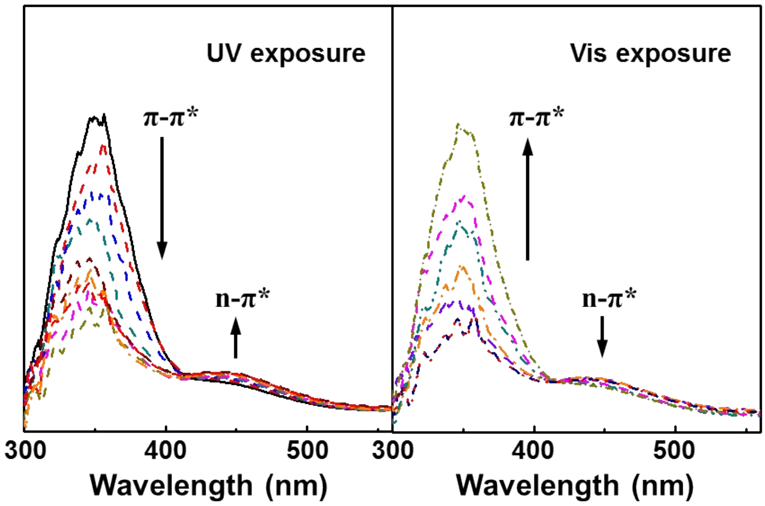

Fig. S20 UV-Vis absorption spectral changes of Pd(iDLA)$_2$ in chloroform solution upon UV and Vis light irradiations.

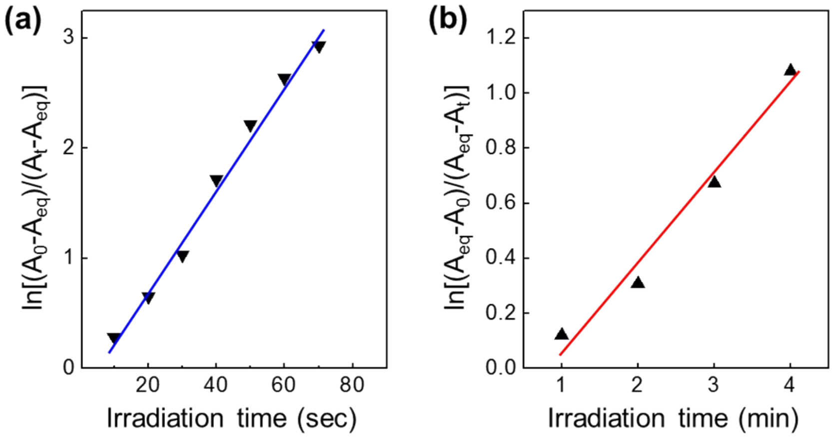

Fig. S21 Photo-isomerization rate constants of Pd(iDLA)$_2$ in chloroform solution upon irradiation of 365 nm light for *trans*-to-*cis* isomerization (a) and 450 nm light for *cis*-to-*trans* back isomerization (b).

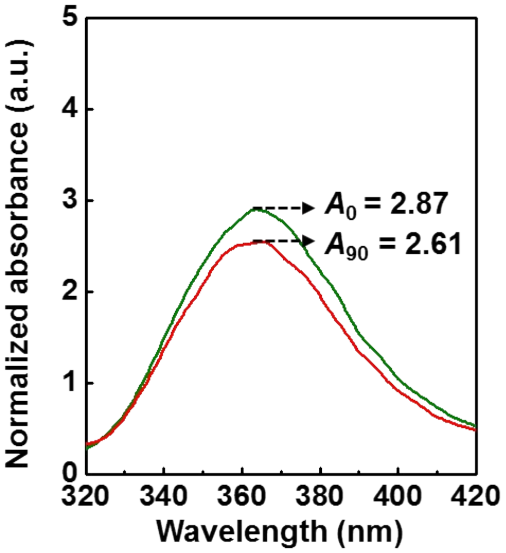

Fig. S22 Polarized absorption spectra of the aligned Pd(iDLA)$_2$ in a LC medium at different degrees of polarization after UV irradiation.