

Photolithographic Hole-Transport Layer Derived from Electrochemical Deposition of Oligo(5-vinyl-2-nitrobenzyl triphenylamine-4-carboxylate)

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Electrochemically deposited layer (EDL) prepared from electropolymerization of oligo(5-vinyl-2-nitrobenzyl triphenylamine-4-carboxylate) on conductive indium tin oxide glass (ITO) showed photolithographic properties as well as good hole-injection and transport properties. Under the optimized conditions, the polymeric light-emitting device (PLED) of ITO/EDL/polyvinylcarbazole(PVK)-Ir(PPy)₃-[2-biphenyl-5-(4'-*tert*-butylphenyl)oxadiazole] (PBD)/Mg–Ag had a turn-on voltage of 13.5 V (100 cd/m²) with a maximum brightness of 9100 cd/m², and the current efficiency of 10.3 cd/A. When the EDL was exposed to UV light (365 nm) through a patterned photomask and developed in CH₂Cl₂, a positive image was obtained. After irradiation for 8 min through a band-pass filter (17 mW/cm²) by a Xeon lamp, the EDL became soluble and could be depleted completely in CH₂Cl₂. Patterned PLED device was also fabricated by this technique.

Introduction

Organic optoelectronic devices based on conjugated or nonconjugated polymers have become extremely important areas of study.^{1–3} Multilayer optoelectronic devices of functional polymers were usually fabricated through layer-by-layer spin-coating or dip-coating techniques.^{4,5} However, swelling or redissolution of the precoated layers from the substrate may occur during the sequential coating process, and thus lead to the destruction of the device structures. Therefore, various methods such as thermal and photochemical cross-linking methods^{6–10} have been developed to consolidate the precoated layers against solvent etching in the latter step. Another approach of electrochemical deposition method has been adopted to solve this problem.^{11–16}

Photolithography^{17–21} has been an important technique for fabrication of integrated circuits. To expand the scope of its applications, it is worthwhile to explore the integration of organic semiconducting polymers with lithographic properties.^{22–26} For example, oxetane group has been used as the crossing-linking sites in the photoimaging PLED system.²⁵ Because the properties of organic polymers,

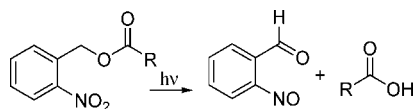
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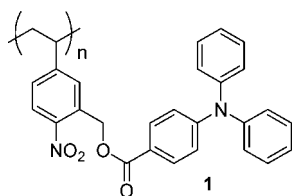
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Scheme 1. Photodissociation of *o*-Nitrobenzyl Ester

including band gap, absorption region, charge mobility, and conductivity, could be tuned through skeletal modification, a large variety of the electronic polymers could be developed. In this study, we report the development of the electrochemically active and photosensitive oligomer **1**, and its application to optoelectronics.



Ortho-Nitrobenzyl carboxylate is a photolabile moiety.^{27–33} When it is exposed to UV light, *o*-nitrobenzyl carboxylate would undergo dissociative intramolecular rearrangement³⁴ to give nitrosobenzaldehyde as well as a carboxylic acid (Scheme 1). This approach has been adopted for photogenerated acids²⁸ or bases^{29–31} in photolithographic applications.

In our design, triphenylamine containing photochemically active oligo(5-vinyl-2-nitrobenzyl carboxylate) (**1**) was prepared. Because the triphenylamine moiety would dimerize to form benzidine under electrochemical oxidation,³⁵ the oligomeric precursor **1** could therefore be electrochemically polymerized to form an insoluble polymeric network onto the electrode surface (Scheme 2). The *o*-nitrobenzyl carboxylate was then used as a photoscissors³⁶ to disintegrate the polymer network in the latter photolithographic step. After being exposed to UV-light, the cross-linked network was degraded and became soluble in organic solvents. A pattern could therefore be transferred from a photomask to the photolithographic layer and be developed in organic solvents. By using this technique, patterned PLED devices could be fabricated.

Results and Discussion

The preparation of **1** was started from nitration of 3-bromobenzaldehyde,³⁷ followed by Heck coupling with ethene to

yield 2-nitro-5-vinylbenzaldehyde³⁸ (Scheme 3). The aldehyde group on 2-nitro-5-vinylbenzaldehyde was reduced to alcohol by NaBH₄ to afford **2**.³⁹ Esterification of **2** with 4-(diphenylamino)benzoic acid in the presence of *N,N*-dimethylaminopyridine (DMAP) and 1-(3-dimethylamino-propyl)-3-ethylcarbodiimide hydrochloride (EDC) as the dehydration reagent yielded **3**.⁴⁰ By using nitroxide-mediated free radical polymerization (NMRP),^{41,42} the styryl monomer **3** was oligomerized ($M_n = 1750$, PDI = 2.06) to form **1**.

The photochemical activity of **1** was evaluated by using FT-IR spectroscopy. A layer of **1** was spin-coated onto a KBr plate, followed by exposure to UV light. Before irradiation, the FT-IR spectrum clearly showed vibrational absorption bands of the $-\text{NO}_2$ group at 1338 and 1513 cm^{-1} and the absorption bands of the $-\text{CO}_2-$ group at 1100 and 1710 cm^{-1} .⁴³ When exposed to UV light (365 nm), the absorption bands of the $-\text{NO}_2$ and $-\text{CO}_2-$ groups gradually faded away. On the other hand, new IR absorption bands at 1507 and 1698 cm^{-1} , along with a broad absorption band ranged from 3400–2500 cm^{-1} , gradually showed up, indicating the formation of the nitroso and carboxylic groups. These observations were consistent with the literature proposed reaction mechanisms of intramolecular dissociative photorearrangement³⁴ to form nitrosobenzaldehyde and carboxylic acid (Scheme 4).

Electrochemically deposited layer (EDL) **4** was prepared from electrochemical oxidation of **1** under cyclic voltammetry (CV) conditions (Figure 1) on a Pt electrode. In this experiment, an oligomer solution of **1** (5 mg) in the supporting electrolyte of TBAP/CH₂Cl₂ (0.1 M/10 mL) was employed. In the first CV cycle, only a single anodic wave peaking at 1.26 V was observed. This wave formed due to electrochemical oxidation of the triphenylamino moieties. When the CV cycle was repeatedly swept, a new wave grew at 1.13 V. This observation suggested that dimerization of the triphenylamino units occurred during electrochemical oxidation to form benzidine moiety (Scheme 5).

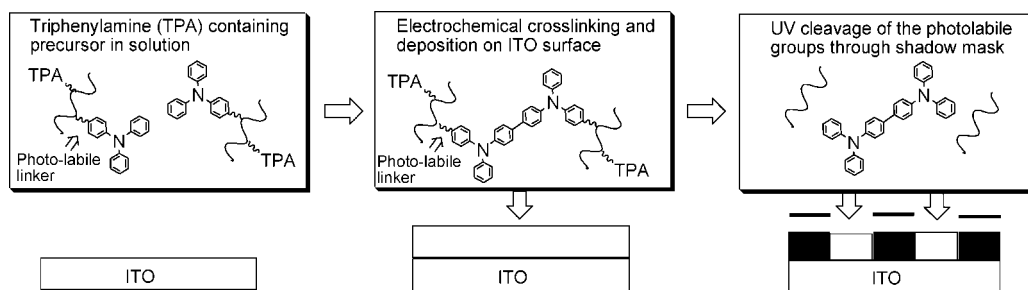
Because of the growth of **4** on the electrode surface, repetitive scans led to constant growth of the anodic and cathodic currents (Figure 1a, inset). The electrode with the newly formed thin films were taken out of the solution, rinsed with CH₂Cl₂, and reinserted into a fresh supporting electrolyte for CV characterization (Figure 1b). The peak CV current obtained, which reflected the amounts of **4** deposited on the surface, was found to be proportional to the number of CV sweeps. In addition, the thickness, which was monitored by an alpha-step instrument, was also proportional to the number of CV cycles.

Similar situations were observed when the deposition was taken place on an ITO glass-electrode surface. The HOMO

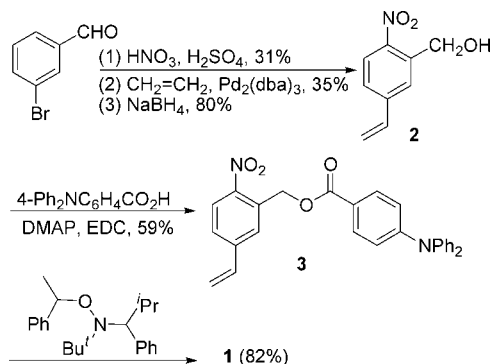
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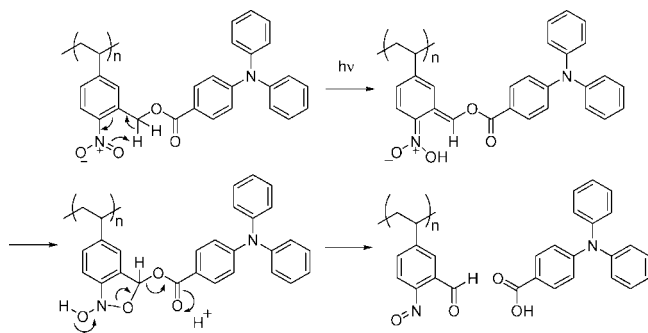
Scheme 2. Dimerization Reaction of Triphenylamine Enabled 1 to Cross-Link and Deposit onto Electrode; Photoimaging Process Led to a Patterned Host Transport Layer



Scheme 3. Preparation of Oligomer 1



Scheme 4. Photochemically-Induced Rearrangement of *o*-Nitrobenzyl Alcohol Derivatives into *o*-Nitrosobenzaldehyde



of the layer was estimated as 5.5 eV, according to the empirical equation of HOMO = ($E_{1/2} - E_{Fc} + 4.8$) against the $E_{1/2}$ of ferrocene.⁴⁴

The benzidine-containing layer of **4** could serve as a hole-transport layer. A PLED device of ITO/**4**/PVK-Ir(PPy)₃-PBD/Mg–Ag was fabricated in this study. The layer of **4** was first electrochemically deposited on the ITO substrate. The light emitting layer of PVK-Ir(PPy)₃-PBD was then spin-coated on top, followed by thermal vapor-deposition of the Mg/Ag cathode. Because the performance of the PLED devices was dependent on the thickness of the electrochemically deposited layers, which was governed by the number of CV sweeps, PLED devices derived from different number of CV sweeps were fabricated for comparison purposes. Measurements obtained using this set of devices enabled an evaluation of the thickness effect of **4** on device performance. Figure 2 shows the voltage–brightness plot of the PLED devices. When **4** was first introduced by one CV cycle, the

turn-on voltage was found to be 15.2 V (at 100 cd/m²). The turn-on voltage dropped to 13.5 V when three CV cycles were applied. However, when the film thickness of **4** increased further, the turn-on voltage bounced back to higher values of 14.2 (five cycles) and 14.3 V (seven cycles), respectively. Under the ideal conditions, when the film was obtained by three CV cycles with the thickness of 50 nm obtained, the PLED turn-on voltage of 13.5 V (100 cd/m²) with the maximum brightness of 9100 cd/m², and the current efficiency of 10.3 cd/A were found (Table 1).

It is noteworthy to point out that the insoluble EDL **4** is also photolabile. When exposure to UV irradiation, photodegradation of the *o*-nitrobenzyl ester linking groups would occur, leading to cleavage of the cross-linked polymeric network. The solubility of the exposed areas would therefore be enhanced. The layer could be used for photoimaging purposes.

Because the layer has the absorption band peaking at 342 nm, we subjected the layer to UV irradiation at the wavelength of $\lambda_{max} = 365$ nm through a band-pass filter (17 mW/cm²) by a Xeon lamp for photocleavage (Scheme 6).

The EDL would be gradually degraded photochemically and became soluble in organic solvents such as CH₂Cl₂. After washing with CH₂Cl₂, the polymeric layer left on the ITO surface was characterized again by CV. The anodic current at the onset electrical potential of 0.9 V gradually decreased after irradiation and development (Figure 3). The current was almost completely suppressed after irradiation for 8 min, indicating that the deposited layer was totally photodepleted.

The positive SEM image, shown in Figure 4, was obtained when the layer was exposed to UV light through a patterned photomask and with CH₂Cl₂ as the developer. The darker zone corresponded to the area of the uncovered ITO surface, in which electrical conductivity is higher, whereas the brighter zone corresponded to the area covered by the polymeric layer.

PLED devices of ITO/**4**/PVK-Ir(PPy)₃-PBD/Mg–Ag could also be built on top of the patterned electrochemically deposited layer. Figure 5 showed images of a PLED device with the surface area of 2 mm × 2 mm under different applied electrical voltage. The film thickness of the electrochemically deposited hole-transport layer was 50 nm (three CV cycles). After 5 min of UV exposure and image development in CH₂Cl₂, the light emissive layer was spin-coated on top, followed by vacuum deposition of the Mg–Ag cathode with the surface area of 5 mm × 5 mm. Because of

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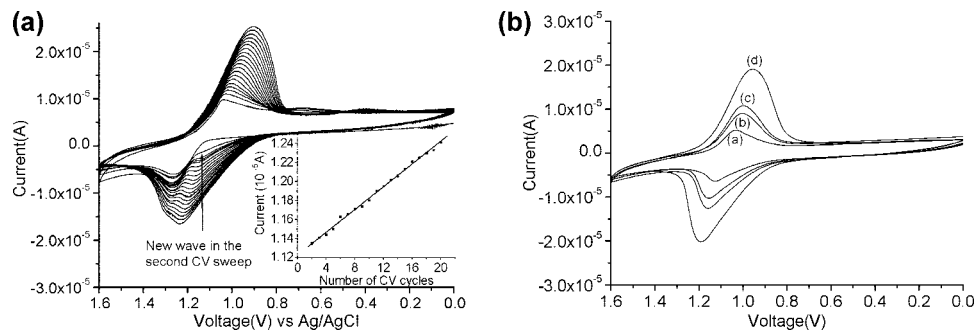
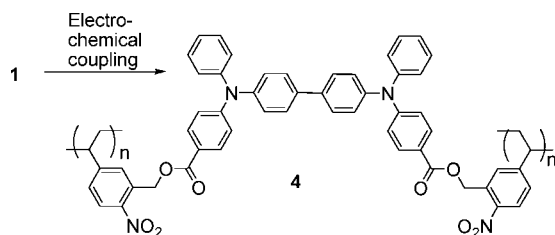
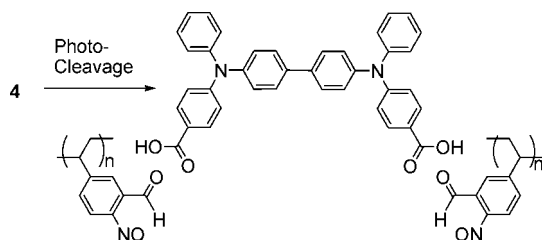


Figure 1. (a) CV plots of **1** in CH_2Cl_2 with Bu_4NClO_4 (0.1 M) as supporting electrolyte. Inset is the plot of number of CV cycles versus the anodic current at 1.13 V. (b) CV plots of **4** (in the absence of **1**) after electrochemical deposition by (a) 3, (b) 5, (c) 10, and (d) 20 cycles.

Scheme 5. Electrochemical Cross-Coupling of **1** Leads to the Formation of EDL **4**



Scheme 6. Photodegradation of **4**



the effective hole-injection and transport properties of the polymeric layer, the area where **4** was covered would have a lower turn-on voltage. Pictures in Figure 5 shows three images of the device operating at different applied electrical

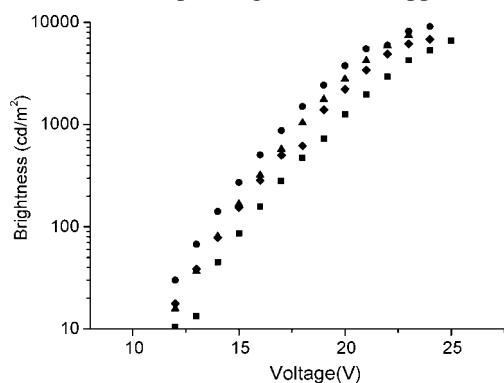


Figure 2. Voltage–brightness plots for the PLED devices with different number of CV sweep cycles: (■) 1, (●) 3, (▲) 5, and (◆) 7 cycles.

Table 1. Electroluminescence Performance Using 4 ITO/4/PVK-Ir(PPY)₃-PBD (50 nm)/Mg (2 nm)–Ag (100 nm)

sweep cycles	thickness of 4 (nm)	turn-on voltage (V)	maximum brightness (cd/m^2)	efficiency (cd/A)
1	26 ± 5	15.2 ± 0.2	6600	8.7 ± 0.8
3	57 ± 5	13.5 ± 0.2	9100	10.3 ± 0.7
5	91 ± 4	14.2 ± 0.2	7500	8.1 ± 0.7
7	123 ± 7	14.3 ± 0.1	6900	9.0 ± 0.7

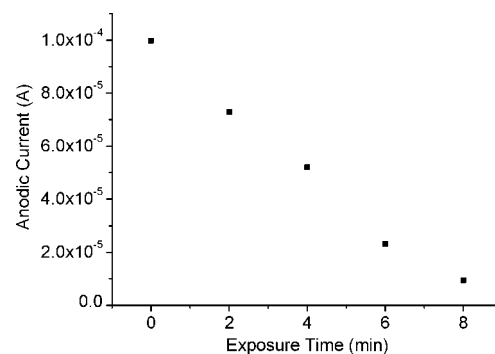


Figure 3. Plot of the CV anodic current at 0.9 V against the UV exposure time.

voltage of 10, 11, and 12, respectively. With assistance of the hole-injection and transport layer of **4**, the central squares ($2 \text{ mm} \times 2 \text{ mm}$) exhibited higher brightness than the peripheral area.

A contrast curve of the brightness versus the exposure time was established in Figure 6. Under the applied electrical voltage of 15 V, the standard device showed the brightness of $272 \text{ cd}/\text{m}^2$. After being exposed to UV-light for 2 min for development, the PLED brightness dropped dramatically to $53 \text{ cd}/\text{m}^2$, which was around 20% of the original output. As the exposure time increased, the brightness of the device continuously decreased.

In summary, this study demonstrated the development of electrochemically deposited hole-injection and transport layer that could be patterned by photolithographic techniques. By using a photomask technique, the pattern image could be transferred onto the electrochemically deposited layer. This technique may be beneficial for future PLED applications.

Experimental Section

Caution! Chemical hazards: Some chemicals being used in the following procedures are hazardous. 4-Dimethylaminopyridine, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide, and anisole are toxic and cause burns when in direct contact with skin. THF and sodium borohydride are highly flammable. Methanol is toxic and irritating to the eyes, respiratory system, and skin. Dichloromethane and chloroform are possible carcinogens.

General procedures: NMR spectra were recorded on a 400 or 500 MHz spectrometer. Elemental analyses were carried out for new compounds we prepared. The M_n and M_w of the polymers were determined using a GPC system with a column of AM GPC Gel ($10 \mu\text{m}$; American Polymer Standard Company) and THF as the

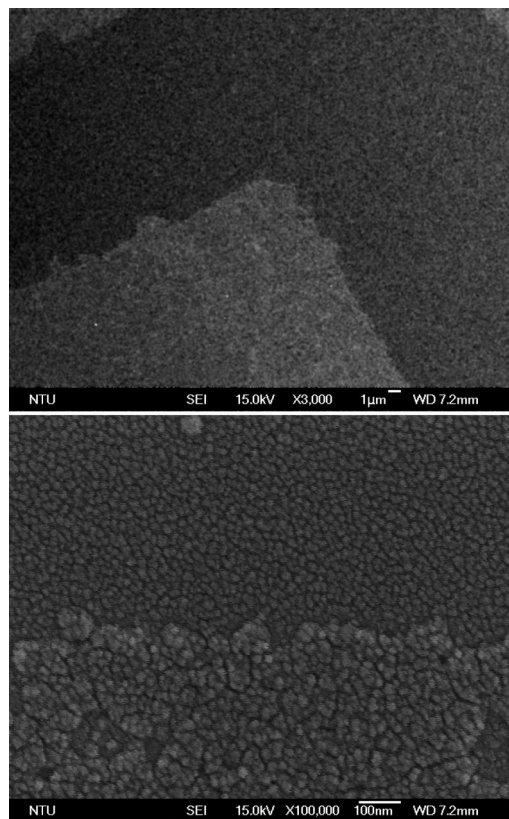


Figure 4. (Top) SEM image of patterned **4** on ITO glass after UV exposure through a photomask and developed in CH_2Cl_2 . (Bottom) Enlarged image.

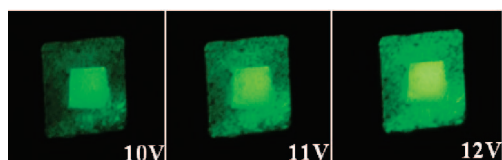


Figure 5. Images of the PLED device with the surface area of $2 \text{ mm} \times 2 \text{ mm}$ under applied electrical voltage.

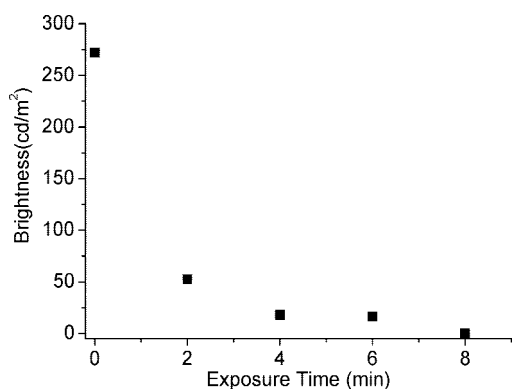


Figure 6. Contrast curve of the brightness of the PLED devices versus the exposure time.

eluent. The molecular weight was calibrated against polystyrene standards. TGA and DSC analyses were performed under nitrogen at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. Cyclic voltammetry (CV) was performed in CH_2Cl_2 , using tetrabutylammonium perchlorate (TPAB, 0.1 M) as the supporting electrolyte. The thickness of the thin film was measured using a Kosaka Laboratory Ltd. Surfcoorder ET3000 microfigure measuring instrument. The morphology of the polymeric film surface was observed by utilizing field emission

scanning electron microscope. Electroluminescence was recorded using a luminance meter (Minolta LS100). The J - V and L - V characteristics of the devices were measured using a source meter as the voltage and current source in conjunction with the luminance meter. All of the measurements and device fabrication processes were handled within a dust-controlled (HEPA protected) environment.

Device Fabrication. EL devices, with the studied hole-transport polymers being applied as the HTL, were fabricated in the configuration of ITO/electropolymerized HTL/light emissive layer (EML) (PVK-PBD-Ir(ppy)₃; 50 nm)/Mg(2 nm)/Ag(100 nm). 2-*tert*-Butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) was used as an electron-transport material in the EML. The ITO surface was cleaned by sonication and rinsed sequentially in deionized water, aqueous Triton-100 solution, deionized water, acetone, and methanol before use.

Electrochemical Deposition of HTL Films. Electropolymerization of **1** in CH_2Cl_2 (5 mg/10 mL) were carried out by cyclic voltammetry (0–1.6 V; 100 mV/s) with a three-electrode cell in CH_2Cl_2 containing TBAP (0.1 M) as the supporting electrolyte. A platinum wire was used as the auxiliary electrode, and a Ag/AgCl (saturated) functioned as the reference electrode. The polymeric film obtained on an ITO-coated glass electrode was rinsed with CH_2Cl_2 , and dried before use. The film thickness was monitored by using Surfcoorder ET3000 profilometer.

EML and Metal Cathode Formation. A solution of PVK, PBD, and Ir(ppy)₃ (PVK:Ir(ppy)₃:PBD = 100 mg:30 mg:40 mg) in CHCl_3 (8 mL) was prepared and allowed to stand on the bench for several hours to guarantee complete dissolution of the materials. The solutions were filtered by microfiltration to remove any dust or insoluble particles before spin-coating. A membrane filter having channel size of $0.45 \text{ }\mu\text{m}$ was used in the filtration. The polymeric solution was spin-coated onto the pretreated substrate, which contained a layer of electropolymerized HTL on the ITO anode, at 3000 rpm for 90 s and dried under vacuum for 5 min at $80 \text{ }^\circ\text{C}$. The metallic cathode composed of Mg and Ag, was deposited onto the ITO/HTL/polymer system at pressure below 1×10^{-6} torr. The deposition rates for the Mg and Ag cathodes were 1 and $4 \text{ \AA}/\text{s}$, respectively, together with thickness up to 2 and 100 nm, respectively.

Compound 2. To a solution of 5-vinyl-2-nitrobenzaldehyde (0.3 g, 1.68 mmol) in a THF- H_2O (9 mL: 0.3 mL) was added NaBH_4 (0.03 g, 0.84 mmol) and reacted for 10 min at room temperature. The product was extracted with CH_2Cl_2 ($2 \times 20 \text{ mL}$). The combined extracts were washed with water, dried (MgSO_4), concentrated under reduced pressure, and purified by liquid chromatography (CH_2Cl_2 :hexane, 1:1 rf 0.5) on silica gel to give **2** (0.24 g, 80%): mp = $85\text{--}87 \text{ }^\circ\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 2.63 (t, $J = 6.4 \text{ Hz}$, 1 H), 4.97 (d, $J = 6.4 \text{ Hz}$, 2 H), 5.49 (d, $J = 11.2 \text{ Hz}$, 1 H), 5.93 (d, $J = 17.6 \text{ Hz}$, 1 H), 6.75 (dd, $J = 11.2, 17.6 \text{ Hz}$, 1 H), 7.45 (dd, $J = 1.6, 8 \text{ Hz}$, 1 H), 7.71 (d, $J = 1.6 \text{ Hz}$, 1 H), 8.07 (d, $J = 8 \text{ Hz}$, 1 H), $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 62.72, 118.70, 125.59, 127.43, 134.73, 137.19, 143.23. HRMS Calcd for $\text{C}_9\text{H}_9\text{NO}_3$: 179.0582. Found: 179.0574. Anal. Calcd for $\text{C}_9\text{H}_9\text{NO}_3$: C, 60.33, H, 5.06, N, 7.82, O, 26.79. Found: C, 60.62, H, 5.50, N, 8.05, O, 25.83.

Compound 3. To a solution of 4-(diphenylamino)benzoic acid (4.75 g, 16.4 mmol) in CH_2Cl_2 (25 mL) was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (3.93 g, 20.5 mmol). The mixture was stirred for 10 min. Compound **2** (2.45 g, 13.7 mmol) and *N,N*-dimethylaminopyridine (DMAP) (1.67 g, 13.7 mmol) were added and reacted for 3 h at room temperature. The crude product was extracted with CH_2Cl_2 , dried over MgSO_4 , concentrated under reduced pressure, and purified by liquid chromatography (ethyl acetate: hexane, 1:5, rf: 0.5) on silica

gel to give **3** (3.6 g, 59%): mp = 60–63 °C. ¹H NMR (400 MHz, CDCl₃) δ 5.47 (d, *J* = 10.8 Hz, 1H), 5.72 (d, *J* = 5.2 Hz, 2 H), 5.88 (d, *J* = 17.6 Hz, 1 H), 6.73 (dd, *J* = 10.8, 17.6 Hz, 1 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 7.10–7.16 (m, 6 H), 7.29–7.33 (m, 4 H), 7.48 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.61 (s, 1 H), 7.89 (d, *J* = 8.4 Hz, 2 H), 8.09 (d, *J* = 8.4 Hz, 1 H), ¹³C NMR (100 MHz, CDCl₃) δ 63.12, 118.41, 119.36, 120.74, 124.26, 125.29, 125.59, 126.35, 129.19, 130.64, 132.89, 134.43, 142.44, 145.91, 151.82, 164.96. HRMS Calcd for C₂₈H₂₂N₂O₄: 450.1580. Found: 450.1582. Anal. Calcd for C₂₈H₂₂N₂O₄: C, 74.65, H, 4.92, N, 6.22, O, 14.21. Found: C, 73.23, H, 5.01, N, 6.06, O, 15.70.

Oligomer 1. Compound **3** (1 g, 2.22 mmol) and 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TIPNO) (72.0 mg, 0.2 mmol) in dry anisole (0.74 mL) were reacted at refluxed temperature (120 °C) under argon for 6 h. The crude product was dissolved in CH₂Cl₂ (20 mL) and repeatedly precipitated from methanol (150 mL) for several times. The precipitate was collected to get

compound **1**. (0.82 g): ¹H NMR (400 MHz, CDCl₃) δ 1.30 (br, 3H), 5.46 (br, 2H), 6.75–8.15 (m, 17H) ¹³C NMR (100 MHz, CDCl₃) δ 62.65, 118.81, 124.92, 126.21, 129.65, 130.83, 132.92, 146.06, 152.52, 165.42. Anal. Calcd for C₂₈H₂₂N₂O₄: C, 74.65, H, 4.92, N, 6.22, O, 14.21. Found: C, 74.41, H, 5.25, N, 5.99, O, 14.35. Thermal Anal. *T*_g, 114 °C; *T*_d, 250 °C.

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Supporting Information Available: ¹H and ¹³C NMR spectra, and their preparation procedures and figures, PLED brightness–voltage plots (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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