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Preparation and Luminescence Properties of Polymeric 2,5-Bis[2′-(8′′-alkoxyquinolin-2′′-yl)ethenyl]hydroquinone Derivatives

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A PPV-type polymer (1) incorporating 5,5′-diquinolinyl moieties is prepared by a Yamamoto homo-coupling reaction from the dibromide (2). Since all the hydroxyl groups were alkylated, this polymer showed high solubility in most organic solvents. It can be spin-coated readily to form a thin layer in the fabrication of light emitting diode (LED) devices. The adjacent quinoline rings are twisted to form a dihedral angle due to steric hindrance, so that π-conjugation is confined within each monomer unit. The emission spectra of (1) and (2) are nearly identical. The reduction potential of (1) was estimated to be –1.10 V (onset), with a band gap of 2.53 eV (490 nm). A single hetero-junction LED device fabricated by combining the films of poly(vinylkarbazol) (PVK) and (1) yielded promising results. The device ITO/PVK/(1)/Ca/Al exhibited a turn-on voltage at 6 V and reached a maximal brightness of 250 cd/m^2 at 15 V. An alternate potential usage of (1) as an electron-injecting material was also explored on a green-light device using coumarin-6 as an emitter.

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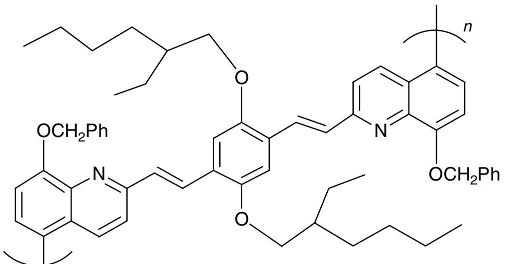
Introduction

Designing organic materials for the fabrication of light emitting diodes (LED) has been a area of intensive research interest.[1] Following the pioneer works of Tang,[2] a tremendous amount of effort has gone into the development of new materials and devices.[3] The fabrication of multilayer structures and the usage of dopants has been quite successful for producing LED devices of high quantum efficiency and good stability.[4] The discovery by Friend using single-layer poly(*p*-phenylenevinylene) (PPV) as an emitting material represented another major breakthrough,[5] for it became possible to produce large and flexible display devices at low cost by a spin-coating technique. Further improvements on device performance is still in demand through structural modifications on organic polymers.[6] In particular, polymers containing heterocycles such as pyrroles, pyridines, and thiophenes have been found to exhibit characteristic electrochemical effects. Due to their intrinsic electron-withdrawing property and good thermal stability, polymers containing a quinoline moiety have attracted extensive interest.[7] In this report we describe the preparation of a PPV-type polymer (1) (see Diagram 1) containing 8-alkoxyquinoline moieties along the main chain. Although tris(8-hydroxyquinolinato)aluminum (Alq$_3$) has been widely used as an effective electron-transporting material, polymeric materials incorporating alkoxyquinoline groups have not yet been fully investigated. The performance of (1) on the fabrication of organic light emitting diode (OLED) devices is examined, both as an emitting material and as an electron-transporter.



(1)

Diagram 1

Results and Discussion

Synthesis

Polymer (1) can be envisioned as a modified derivative of PPV in which some phenyl groups along the main chain are replaced by 8-alkoxyquinoline moieties. It was synthesized from the dibromide (2) through Yamamoto coupling,[8] whereas (2) was prepared by a double Wittig reaction condensing two units of hydroxquinolinylcarbaldehyde (7) and one unit of *p*-hydroquinone-2,5-dicarbophosphonium

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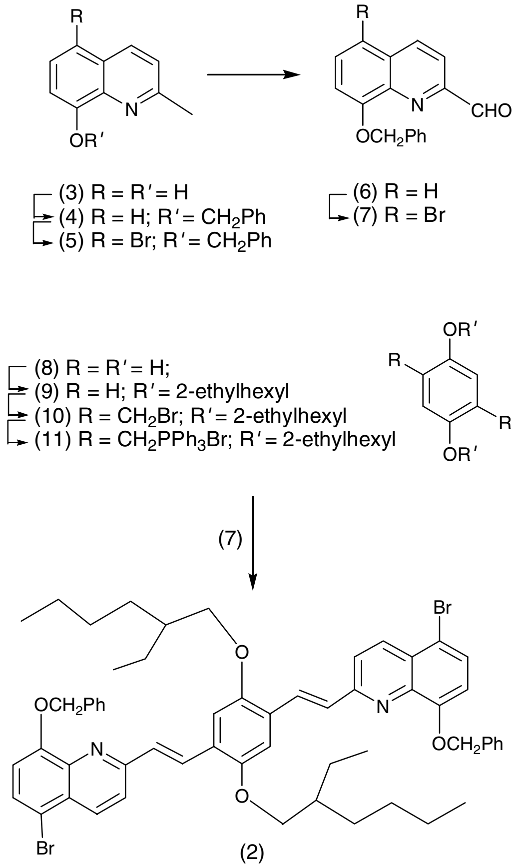

Scheme 1

bromide (11). The complete synthetic sequence is shown in Scheme 1.

The hydroxy group of 8-hydoxy-2-methylquinoline (3) was first converted into a benzyl group in (4). The subsequent transformation of (4) to (7) was accomplished through either of two pathways. The first way is to brominate first at C5 of (4), followed by oxidation of the methyl group at C2. The second way is to go through a reverted sequence, i.e. oxidation first followed by bromination. Both pathways are applicable, yet the former sequence resulted in a slightly higher overall yield. Bromination was achieved using *N*-bromosuccinimide (NBS), while oxidation was achieved using selenium dioxide in 1,2-dimethoxyethane (DME). Compound (7) was collected as yellowish crystals, of which the aldehyde group was confirmed by a stretching at 1710 cm^{-1} in the infrared (IR) and an signal at δ 193.5 in the ^{13}C nuclear magnetic resonance (NMR) spectrum.

Another segment of compound (2) was prepared starting from hydroquinone (8). Both the hydroxyl groups of (8) were alkylated to give (9) by heating an ethanolic solution of excess 2-ethylhexyl bromide in the presence of sodium hydroxide. Subsequent bromomethylation was accomplished by a reaction with paraformaldehyde in the presence of HBr in acetic acid. The symmetrical structure of (10) was evidenced by the number of ^{13}C peaks, e.g. three lines appeared in the aromatic region. Heating (10) with triphenylphosphine produced (11) in nearly quantitative yield. Connecting (7) and (11) was completed successfully by a double Wittig reaction to give (2). The twofold symmetry of the structure persisted as indicated by ^{1}H and ^{13}C NMR signals.

Polymerization of (2) was carried out by a Yamamoto homo-coupling reaction of aromatic halides utilizing Ni(COD)$_2$ in the presence of 2,2′-bipyridyl and cyclo-1,5-octadiene. The polymer was collected as an orange product in 54% yield. It showed a number-averaged molecular weight of 2.3 × 10^4 (M_n) and a weight-averaged molecular weight of 3.8 × 10^4 (M_w), with a polydispersity (M_w/M_n) of 1.67. It is readily soluble in most organic solvents, such as tetrahydrofuran (THF), benzene, and dichloromethane. This material shows a glass transition temperature (T_g) of 210°C by differential scanning calorimetry (DSC) analysis. The structure of (1) was confirmed by IR and NMR spectra. It exhibits good thermal stability, since no apparent decomposition can be observed up to 350°C under an oxygen atmosphere.

Physical Properties

The two adjacent quinoline rings, which are coupled by Ni, cannot be kept co-planar due to steric hindrance. The situation is similar to what happened for the structure of binaphthyl. Electron delocalization across two adjacent quinoline rings is limited, therefore the spectroscopic property of (1) is expected to be analogous to that of (2).[9] The ultraviolet (UV) absorption spectra of (1) and (2) are nearly identical (Fig. 1), indicating a close resemblance between these two chromophores. The emission spectra of the two also showed high similarity. Both emit blue light at λ_{em} 490 nm with good quantum yields, i.e. 0.27 for (1) and 0.42 for (2) (Fig. 1).

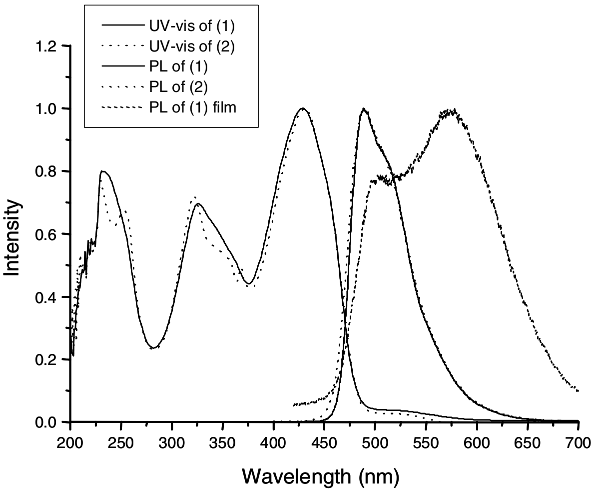

Fig. 1. The absorption (left with λ_{max} 427 nm) and emission (middle with λ_{em} 490 nm) spectra of (1) and (2), where PL indicates photoluminescence in THF. The broadband emission on the right (λ_{em} 573 nm) came from the solid film of (1).

The ethylhexyl and benzyl groups attached to the oxygen atoms of (1) were intended to help increase the solubility of the polymer. The solution of (1) therefore, can be easily spin-coated to form thin layers. It was also expected that the ethylhexyl side chains would be able to prevent local crystallization and aggregation while forming films. It was known that local crystallization may reduce the quantum yield of emission, and aggregation may result in both quenching as well as band broadening of luminescence. Although with such a design, it was unfortunate to see that the emission from the solid film of (1) did show a significant band broadening (Fig. 1). A broad new emission band at λ_{em} 573 nm was observed, which seems to be induced from some aggregated phase existing in the solid state.[10]

The redox behaviour of (1) was examined by cyclic voltammetry (CV) using a Pt working electrode on which a thin layer of the polymer was coated. Both reduction and oxidation waves were observed within the range of ± 2.00 V. A reduction peak appeared at –1.42 V, which is *quasi*-reversible and can be back-oxidized at –0.70 V. An oxidation peak appeared at +1.00 V, which is irreversible. The band gap thus measured is consistent with that measured on UV absorption (2.53 eV) within experimental uncertainty. The oxidative potential can be correlated to HOMO and LUMO levels by the equation IP = $E_{red} - E_g$ + 4.40 eV,[11] whereas –5.63 and –3.10 eV were depicted from the reduction onset (–1.30 V) of (1), respectively. These values are useful in designing LED device configuration. Compared with the known values of poly(2-methoxy-5-(2′-ethylhexoxy)-1,4-phenylenevinylene) (MEH-PPV) (–4.99 and –2.71 eV), our polymer has a wider band gap, yet is easier to reduce.

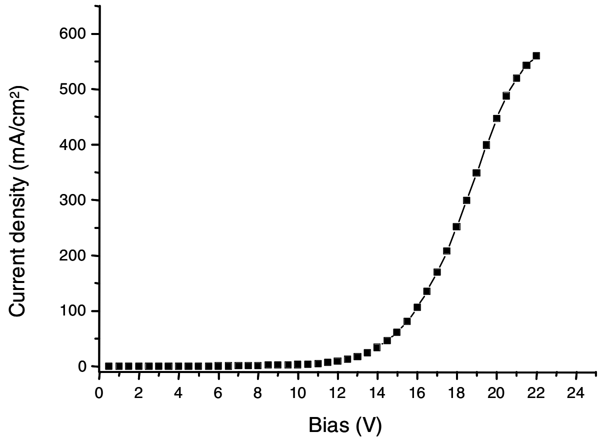

Fig. 2. The *I*–V plot for the device ITO/(1)/Al, which showed a turn-on voltage of 9 V. The brightness of this device was low (< 3 cd/m^2).

LED Fabrication

A single-layer LED device was fabricated by spin-coating a toluene solution of (1) (10 g/L) onto pre-treated indium tin oxide (ITO) glass. The film was then dried under vacuum, where it looked uniform and without pinholes. The film was then covered by a layer of aluminum (to act as a cathode) by vapour deposition. This simple device started emitting at 9 V, but with low intensity. The emission spectrum was quite close to that of the photoluminescence of the solid film (Fig. 1). It was evident that aggregation appeared in the film, which reduced the quantum efficiency of the device. A current versus voltage (*I*–V) plot of this device is shown in Figure 2. The current density increased steadily with increased applied voltage.

As shown by CV, the low reduction potential of (1) rendered it a good electron-transporting material. In order to enhance light emission, it seemed necessary to add a layer of hole-transporter. Charge recombination at the interface of two layers should result in more effective luminescence. Two commonly used hole-transporting materials, poly(vinylkarbazol) [poly(carbazolylethylene), PVK] and 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB), are considered in this regard. Three additional devices were then assembled, i.e. ITO/PVK/(1)/Ca/Al, ITO/PVK : (1)(3%)/(1)/Ca/Al, and ITO/NPB : (1)(3%)/(1)/ Ca/Al, in order to find out the optimal fabrication. Solutions of PVK (or NPB) in 1,2-dichloroethane were spin-coated onto ITO first. After sufficient drying in vacuum, a layer of (1) in toluene was spin-coated on top of the first layer. The amount of PVK (or NPB) re-dissolved in toluene during the second spin-coating process was limited due to its low solubility.

All three devices displayed electroluminescence upon applied voltage, while the spectra appeared identical to the photoluminescence of (1) in solution (Fig. 1). It was remarkable to observe the absence of broadband emission at λ_{em} 578 nm, which was derived presumably from aggregation. Upon the introduction of a hole-transporting layer, the charge recombination happened more effectively at the interface between two polymer layers. This phenomenon is also evidenced by the absence of short-wavelength emission of PVK (or NPB), which indicated that the charge recombination did not happen within the bulk of the PVK layer.

Among the three devices, the one without blending performed the best, i.e. ITO/PVK/(1)/Ca/Al. This device can be turned on at 6 V, and reached a maximum intensity of 250 cd/m^2 at 15 V (Fig. 3). Its optimal quantum efficiency was estimated to be 0.020% at 9 V.

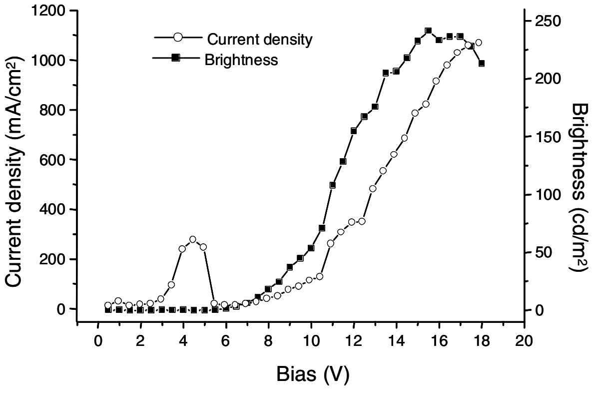

Fig. 3. The L(■)–I(○)–V plot for the device ITO/PVK/(1)/Ca/Al. The turn-on voltage is 6 V, while brightness reached a maximum intensity of 250 cd/m^2 at 15 V along with current density of 830 mA/cm^2. The optimal quantum efficiency was 0.020% at 9 V. A small current appearing at ca. 4 V was a spurious signal caused by initial charging of the device.

The electron-transporting property of (1) attracted our attention for it to be used in a wider range of applications. We went on testing the possibility by assembling it into a known LED device, i.e. the green-light device of coumarin-6. Two devices were fabricated for a comparison: (i) one without the addition of (1) as standard, ITO/coumarin-6(0.5%): PVK/Al; and (ii) one with an added layer of (1), ITO/coumarin-6(0.5%):PVK/(1)/Al. Both devices successfully displayed the green emission of coumarin-6 (Fig. 4). The latter one with an added layer of (1) performed much better than the standard. Its turn-on voltage at 8.5 V is lower than the standard at 11.5 V. At 14–16 V it showed a maximum brightness of 48 cd/m^2, which was about 10 times that of the standard, i.e. 5 cd/m^2 at 16 V. This experiment showed that polymer (1) can be used in the fabrication of OLED devices, not only as an effective emitting material, but also as a good electron-transporting material.

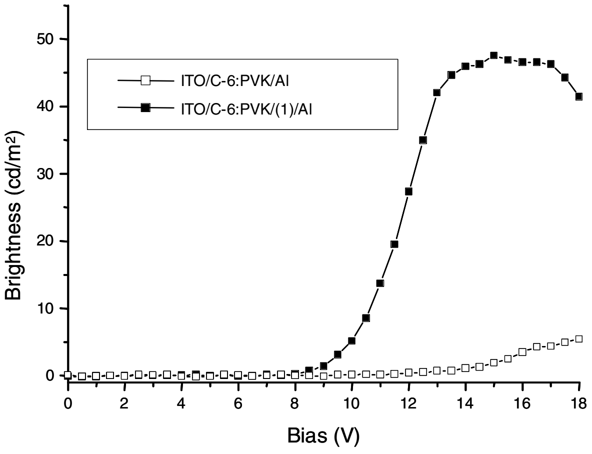

Fig. 4. The L–V plot for the devices ITO/coumarin-6(0.5%) : PVK/Al (□) and ITO/coumarin-6(0.5%) : PVK/(1)/Al (■).

Conclusion

The alkoxy side chains of polymer (1) increased its solubility in organic solvents, allowing films to be prepared readily by spin coating. The 5,5′-attachment of two adjacent quinoline moieties resulted in their rings being twisted out of plane, and therefore confined the conjugation within each monomer unit. The absorption and emission spectra of (1) are similar to those of (2). A LED device fabricated by two layers of polymers, i.e. ITO/PVK/(1)/Ca/Al, exhibited promising results; it showed a turn-on voltage at 6 V and maximum brightness 250 cd/m^2 at 15 V. Polymer (1) showed a low reductive potential on CV, which rendered it a good electron-transporting material. It can be fabricated into LED devices using coumarin-6 as the emitting material, in which it functions as an effective electron-injection layer.

Experimental

Device Fabrication

Prepatterned ITO substrates with an effective individual device area of 3.14 mm^2, and sheet resistance of < 50 ohms/mm^2, were cleaned by sonication in a detergent solution for 3 min and then washed with a large amount of doubly distilled water. Further sonication in ethanol for 3 min was performed before being blown dry with a stream of nitrogen. The ITO substrates were then treated with oxygen plasma for 1 min before use. Polymer films were spin-coated at 3000 rpm onto the substrate from a solution of the emitting material in toluene. The devices were placed under vacuum (4×10^{-4} torr) for 12 h to remove residual solvents. A 30 nm cathode layer was deposited by evaporation of Ca at 2×10^{-5} torr. The device was completed by capping with an Al layer with 120 nm thickness.

Instrumentation

^{1}H and ^{13}C NMR spectra were obtained on a Brucker APX-400 spectrometer. Chemical shifts of ^{1}H were measured downfield from tetramethylsilane (0) in δ units, while those of ^{13}C were recorded with the central peak of $CDCl_3$ at δ 77.00 as an internal reference. Mass spectra (MS) were carried out on a VG70-250S or a VG Trio-2000 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 682 infrared spectrophotometer. Absorption and emission spectra were recorded on a Hewlett–Packard 8453 absorption and a Hitachi F-4500 fluorescence spectrophotometer, emission quantum yields were measured with reference to 9,10-diphenylanthracene. Elemental analyses were obtained on a Perkin–Elmer 2400 CHN instrument. Melting Points were measured by a Thomas–Hoover melting point (m.p.) apparatus and were uncorrected. Light–current–voltage intensity (L–*I*–V) of LEDs were measured using a Keithley 2400 source meter and a Newport 1835C multifunction optical meter, equipped with a silicon photodiode (Newport, model 818-ST). The measurements of *I*–V–L were performed simultaneously through an IEEE interface to a computer. All measurements were made at ambient temperature and conditions.

1,4-Di(2′-ethylhexyloxy)-2,5-bis[2′-(8′-benzyloxy-5′-bromoquinolin-2′-yl)ethenyl]benzene (2)

To a Schlenk flask (100 mL) were added compounds (7) (0.99 g, 2.9 mmol) and (11) (1.4 g, 1.3 mmol) under a nitrogen atmosphere. To this was added freshly distilled DMF (5 mL) injected through a syringe, followed by sodium ethoxide (0.20 g, 2.9 mmol) against a nitrogen flow. The colour of the mixture turned from pale yellow to red. It was stirred with a magnetic bar at ambient temperature for 24 h while its colour changed gradually to orange-yellow. The mixture was poured into distilled water, and was extracted three times with dichloromethane (50 mL each). The combined organic portion was dried over anhydrous Na_2SO_4, and was concentrated. The orange residue was acidified with conc. HCl (36%, 0.5 mL). The brick-red precipitate was washed with ether to remove triphenylphosphine oxide. The remaining salt was dissolved in THF, and neutralized with saturated $NaHCO_3$ to give a yellow-green mixture. It was extracted several times with dichloromethane. The combined organic layer was dried over anhydrous Na_2SO_4, and was evaporated under vacuum. The residue was subjected to a silica gel chromatographic column eluted with hexane/ethyl acetate (2 : 1) to yield (2) as a yellow-orange solid. It was recrystallized from cyclohexane (850 mg, 0.84 mmol, 65% yield); m.p. 178–179°C. IR (KBr) ν_{max} 3452(br), 3063, 2957, 2927, 2869, 1592, 1500, 1453, 1390, 1221, 1202, 1000 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.95, m, 6H; 1.04, m, 6H; 1.35–1.50, m, 8H; 1.35–1.75, m, 8H; 1.91, m, 2H; 4.01, d, *J* 6 Hz, 4H; 5.51, s, 4H; 6.90, d, *J* 8 Hz, 2H; 7.30–7.35, m, 2H; 7.30–7.45, m, 6H; 7.50–7.60, m, 6H; 7.65, d, *J* 17 Hz, 2H; 7.92, d, *J* 9 Hz, 2H; 8.06, d, *J* 17 Hz, 2H; 8.46, d, *J* 9 Hz, 2H. ^{13}C NMR ($CDCl_3$) δ 11.57, 14.38, 23.39, 24.59, 27.16, 29.48, 31.20, 40.00, 71.45, 72.16, 110.51, 111.93, 112.73, 119.91, 127.17, 127.29, 127.53, 128.10, 128.88, 129.62 (2C), 136.05, 137.03, 141.45, 151.85, 154.19, 156.66. MS (FAB) *m/z* 1010 (M$^+$, 15%).

Polymerization of (2)

To a Schlenk flask was added compound (2) (300 gm, 0.30 mmol), $Ni(COD)_2$ (130 mg, 0.47 mmol), 2,2′-bipyridyl (81 mg, 0.52 mmol) and cycloocta-1,5-diene (COD, 0.10 mL) under a nitrogen atmosphere. To this was added freshly distilled DMF (10 mL) injected through a syringe, and the resulting mixture was stirred at 80°C for 24 h. It was poured into methanol (200 mL), and an orange precipitate formed. The precipitate was dissolved in dichloromethane, and re-solidified by pouring into methanol. This processes was repeated twice. The resulting polymer was extracted with acetone (100 mL) for 24 h using a Soxhlet extractor to remove contaminated monomer and oligomers of low molecular weight. Polymer (1) (0.136 gm) was collected in 54% yield; T_g 210°C and T_d 326°C. IR (KBr) ν_{max} 3400(br), 3032, 2923, 2927, 2865, 1596, 1557, 1498, 1449, 1376, 1312 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.86, br s, 6H; 0.95, br s, 6H; 1.33, br s, 8H; 1.50, br s, 8H; 1.82, br s, 2H; 3.99, br s, 4H; 5.44, br s, 4H; 7.24, br s, 2H; 7.30–7.80, br m, 20H; 8.20, br s, 2H. ^{13}C NMR ($CDCl_3$) δ 11.58, 14.42, 23.65, 24.83, 29.72, 31.41, 40.33, 71.68, 72.41, 110.43, 110.76, 119.24, 127.47, 128.48, 128.71, 129.27, 130.06, 130.32, 135.20, 137.69, 140.94, 152.11, 154.97, 156.13.

8-Benzyloxy-5-bromo-2-methylquinoline (5)

To a round-bottom flask were added a solution of 8-benzyloxy-2-methylquinoline (4) (1.00 g, 4.0 mmol) and NBS (1.4 g, 8.0 mmol) in chloroform (10 mL). The solution was stirred with a magnetic bar at ambient temperature for 5 h, while the reaction was monitored by thin-layer chromatography (TLC) till completion. It was poured into distilled water (30 mL), and the resulting mixture was extracted several times with dichloromethane. The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under vacuum. Compound (5) was isolated using a silica gel chromatographic column eluted with hexane/ethyl acetate (v/v, 6:1), and was crystallized from hexane to give a colourless wool-like *solid* (1.2 g, 3.6 mmol) in 91% yield, m.p. 108–109°C (Found: C, 62.2; H, 4.3; N, 4.3%. $C_{17}H_{14}BrNO$ requires C, 62.8; H, 4.1; N, 4.1%). IR (KBr) ν_{max} 3063, 3034, 2930, 2871, 1593, 1499, 1462, 1379, 1315, 1238, 1093 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.89, s, 3H; 5.46, s, 2H; 6.90, d, *J* 8 Hz, 1H; 7.31, d, *J* 7 Hz, 1H; 7.38, t, *J* 7 Hz, 2H; 7.44, d, *J* 8 Hz, 1H; 7.51, d, *J* 7 Hz, 2H; 7.57, d, *J* 8 Hz, 1H; 8.41, d, *J* 8 Hz, 1H. ^{13}C NMR ($CDCl_3$) δ 25.29, 53.62, 111.71, 112.41, 124.04, 126.96, 127.29, 128.14, 128.85, 129.53, 136.68, 159.19. MS (EI) *m/z* 329 (M^+, 5%), 252 (3), 239 (3), 223 (5), 210 (5).

8-Benzyloxy-5-bromoquinoline-2-carbaldehyde (7)

Method A. To a round-bottom flask were added a solution of 8-benzyloxyquinoline-2-carbaldehyde (6)[12] (0.50 g, 1.9 mmol) and NBS (0.68 g, 3.8 mmol) in chloroform (10 mL). The solution was stirred with a magnetic bar at ambient temperature for 48 h, while the reaction was monitored by TLC till completion. It was poured into distilled water (30 mL), and the resulting mixture was extracted several times with dichloromethane. The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under vacuum. Compound (7) was isolated using a silica gel chromatographic column eluted with hexane/ethyl acetate (v/v, 6:1), and was crystallized from hexane/dichloromethane to give yellowish crystals (0.46 g, 1.35 mmol) in 71% yield.

Method B. To a Schlenk flask a DME (50 mL) solution of compound (5) (3.3 g, 1.00 mmol) and SeO_2 (1.4 g, 33 mmol) was injected through a syringe under nitrogen atmosphere. The mixture was heated to 80°C for 2 h while a red precipitate formed. The solution was filtered through Celite and the filtrate was concentrated under vacuum. Product (7) was collected using a silica gel chromatographic column eluted with hexane/ethyl acetate (v/v, 6:1) in 82% yield (2.8 g, 0.82 mmol).

Physical data of (7). M.p. 114–115°C (Found: C, 68.5; H, 5.9; N, 2.5%. $C_{17}H_{12}BrNO_2$ requires C, 68.9; H, 6.2; N, 2.8%). IR (KBr) ν_{max} 3058, 2950, 2891, 2841, 1710, 1602, 1558, 1499, 1460 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.03, d, *J* 8 Hz, 1H; 7.35, d, *J* 7 Hz, 1H; 7.41, t, *J* 7 Hz, 2H; 7.54, d, *J* 7 Hz, 2H; 7.78, d, *J* 8 Hz, 1H; 8.14, d, *J* 8 Hz, 1H; 8.64, d, *J* 8 Hz, 1H; 10.71, s, 1H. ^{13}C NMR ($CDCl_3$) δ 71.50, 111.77, 112.47, 119.03, 127.30, 128.40, 128.96, 130.35, 132.98, 136.25, 137.30, 141.19, 151.97, 155.15, 193.47. MS (EI) *m/z* 343 (M^+, 10%), 214 (2), 253 (2), 237 (2), 196 (10).

1,4-Di(2′-ethylhexyloxy)benzene (9)

A solution of hydroquinone (8) (17.6 g, 0.16 mol) and KOH (25.6 g, 0.457 mol) in ethanol (150 mL) was heated to reflux, and 2-ethylhexyl bromide (92.5 g, 0.48 mol) was added. The mixture was heated overnight under a nitrogen atmosphere. The precipitates were filtered after being cooled. The filtrate was concentrated, and was passed through a silica gel chromatographic column eluted with hexane/ethyl acetate (v/v, 10:1) to remove unreacted hydroquinone. All non-polar portions were combined and the resulting solution was distilled under reduced pressure. Compound (9) was collected at 128°C at 0.1 torr (41.7 g, 0.125 mol) in 78% yield. IR (KBr) ν_{max} 2960, 2931, 2862, 1509, 1469, 1381, 1229 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.92, m, 12H; 1.33–1.69, m, 16H; 1.71, m, 2H; 3.81, d, *J* 9 Hz, 4H; 6.84, s, 4H. ^{13}C NMR ($CDCl_3$) δ 11.32, 14.29, 23.29, 24.10, 29.33, 30.78, 39.72, 71.45, 115.61, 153.70. MS (EI) *m/z* 334 (M^+, 50%), 222 (12).

2,5-Di(bromomethyl)-1,4-di(2′-ethylhexyloxy)benzene (10)

To a round-bottomed flask containing (9) (20 g, 60 mmol) and paraformaldehyde (4.0 g, 130 mmol) in acetic acid (50 mL) was added a solution of HBr (33% in acetic acid, 26 mL, 150 mL). The mixture was stirred with a magnetic bar at 100°C for 8 h, while a white precipitate formed. The mixture was poured into distilled water, and the precipitate was collected by filtration. The precipitate was dissolved in dichloromethane, and the solution was washed with saturated $NaHCO_3$. The organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was recrystallized from dichloromethane/methanol to give (10) (30 g, 58 mmol, 96% yield) as a white solid, m.p. 59–61°C. IR (KBr) ν_{max} 2960, 2921, 2872, 1509, 1469, 1411, 1317, 1229 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.93, m, 12H; 1.34, br s, 8H; 1.34–1.55, m, 8H; 1.78, m, 2H; 3.87, m, 4H; 4.53, s, 4H. ^{13}C NMR ($CDCl_3$) δ 11.47, 14.31, 23.28, 24.27, 28.96, 29.35, 30.87, 39.85, 71.20, 114.49, 127.63, 153.96. MS (EI) *m/z* 520 (M^+, 5%), 441 (6), 329 (10), 296 (12), 217 (15).

1,4-Di(2′-ethylhexyloxy)-2,5-bis[(triphenylphosphonio)methyl]-benzene Dibromide (11)

To a Schlenk flask (100 mL) fitted with a condenser was added (10) (5.2 g, 10.0 mmol) and triphenyl phosphine (5.8 g, 22 mmol) under a nitrogen atmosphere. To this was added freshly distilled DMF (40 mL) injected through a syringe, and the resulting solution was heated to reflux for 2 h. The solution was cooled and poured dropwise into ether, which was vigorously stirred. A white precipitate formed and was collected by filtration. It was dried under vacuum to give (11) (10.2 g, 9.8 mmol) in 98% yield, m.p. 263–266°C (dec.). IR (KBr) ν_{max} 3400(br), 3058, 2960, 2931, 2862, 2774, 1587, 1514, 1435, 1313, 1219, 1111 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.67, t, *J* 7 Hz, 6H; 0.88, t, *J* 7 Hz, 6H; 0.95–1.05, m, 16H; 1.22, m, 2H; 2.87, br s, 4H; 5.31, m, 4H; 7.60, m, 12H; 7.65, m, 12H; 7.76, t, *J* 7 Hz, 6H. ^{13}C NMR ($CDCl_3$) δ 14.20, 22.98, 23.40, 29.09, 30.26, 39.02, 70.82, 115.88, 116.37, 117.56, 118.42, 130.25, 134.25, 135.01, 150.86. MS (EI) *m/z* 1015 (0.2%), 965 ($[M-Br]^+$, 0.5%), 899 (0.5), 882 ($[M-2Br]^+$, 2.5), 823 (1.2).

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