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Synthesis and characterization of highly soluble blue emitting poly(2-vinylanthracene) with 9,10-di(2-naphthalenyl) and 9,10-di(3-quinolinyl) substituents

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ABSTRACT

Two new blue fluorescent polymers, poly(9,10-di(2-naphthalenyl)-2-vinylanthracene) (P(2ADN)) and poly(9,10-di(3-quinolinyl)-2-vinylanthracene) (P(3ADQ)), were polymerized from free radical solution addition polymerization with $M_n = 21,500$ and 15,400, respectively. The polymers are highly soluble in common organic solvents while P(3ADQ) is also soluble in polar solvents including a 1/1 mixture of ethanol/water. Both polymers are amorphous with excellent thermal stability (T_{g} (Midpoint) = 343 °C and 298 °C for P(2ADN) and P(3ADQ), respectively). P(2ADN) exhibited three prominent absorption bands in tetrahydrofuran (364, 383 and 403 nm) and is similar to that of P(3ADO) (369, 384 and 404 nm). The solid-state Commission Internationale d'Eclairage (CIE_{x,y}) color coordinates for illumination were (0.15, 0.10) for P(2ADN) and (0.15, 0.13) for P(3ADQ) which lied within the requirements for a true blue display color. The photoluminescence (PL) of the polymers red-shifted 16-17 nm from their respective pendant chromophore 2-methyl-9,10-di(2-naphthalenyl)anthracene (2MADN) and 2-methyl-9,10-di(3quinolinyl)anthracene (**3MADQ**) and can be attributed to partial $\pi - \pi$ stacking between the adjacent aromatic pendant groups in the polymer chains. The luminescences of **3MADQ** and **P(3ADQ)** are sensitive to pH and the pK_a for the alkalescent **3MADQ** and **P(3ADQ)** calculated was 2.4 and 2.7, respectively. Both polymers have similar band-gap energy (E_{g}) between 2.88 and 2.91 eV, while the LUMO/HOMO for **P(3ADQ)** is shifted slightly downward -0.06 to -0.03 eV compared to **P(2ADN)**. The mobility (μ_{hole}) of the two polymers were measured to be 4.0×10^{-7} and 10^{-8} cm²/(V-s) for P(2ADN) and P(3ADQ), respectively.

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1. Introduction

Over the past decade, the use of conductive polymers as lightemitting materials has received increasing attention in polymer electroluminescent devices [1–9]. Although there have been significant progress in red [10,11] and green [12–14] light-emitting polymers, there are only limited blue light-emitting polymers reported that can fulfill the requirements for a full-color display application [15,16]. Simultaneously, tremendous efforts have been concentrated in the development of blue emitting small molecules [17–29]. The majority of the blue emitters are 9,10-anthracene derivatives [30]. For example, **2MADN**, has been studied extensively due to its reasonable luminescence property, descent thermal stability and good ambipolar charge transporting ability [31– 35]. For electroluminescent devices employing **2MADN** as the host and 9-[4-(2-diphenylamino-9,9-diethylfluoren-7-yl)phenyl]-9-phenylfluorene as a dopant, a deep blue emission with CIE_{*x,y*} (0.15, 0.13), a luminous efficiency of 5.3 cd/A, a power efficiency of 2.9 lm/W and an external quantum efficiency of 4.8% at 20 mA/cm² were achieved [36]. Another small molecule quinoline whose half-wave reduction potential at -2.13 eV and its derivatives (e.g. 3PQMPT [37]) have also been applied as the emitters and electron transporters. These compounds all have good thermal stability ($T_g > 200$ °C and $T_d > 400$ °C [38]), high solubility (completely soluble in formic acid [38]), and excellent electron-accepting properties (EA 2.40–2.65 eV) [37–39].

However, the inherent mechanical weaknesses, the problematic recrystallization under thermal stress and the needs of the higher cost vacuum thin film deposition for small molecule materials demand further improvement for a successful full-color polymer light-emitting diode (PLED) application [40–46]. Most of the inherent drawbacks for small molecules mentioned above can be eliminated by binding the functional moieties covalently into a polymer. As a result, polymers based on **2MADN** and **3MADQ** were







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prepared with the goals of disrupting the symmetry for recrystallization and eliminating the chance of phase separation of the dopant from the matrix and at the same time without significantly altering the overall electrical (LUMO/HOMO) and optical properties ($CIE_{x,y}$).

In our previous work, a blue emitting vinyl polymer poly(9,10di(1-naphthalenyl)-2-vinylanthracene) (P(ADN)) based on 2methyl-9.10-di(1-naphthalenyl)anthracene (MADN) had shown to possess excellent thermal stability and retained most of the photoluminescent & electrochemical properties of the parent small molecule MADN [47]. However, the solubility of P(ADN) diminished when its molecular weight (MW) became higher than 13,000. In this paper, two novel blue fluorescent monomers Vinyl-2ADN and Vinyl-3ADQ rooted from the basic molecules 2MADN and **3MADQ** were synthesized. Their polymers **P(2ADN)** and **P(3ADQ)** were prepared using free radical solution addition polymerization. Besides of the consideration of the steric effects, the replacement of the heteroatom N to CH at the C-3 position of the 2-naphthalenyl group also enhance the solubility for **P(3ADQ)**. The chemistry and physical properties of the intermediates, the monomers and the resulting polymers were characterized using, nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC), fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS), ultraviolet-visible (UV-Vis) spectroscopy, PL spectroscopy, cyclic voltammetry (CV) and quantum yield measurements.

2. Experimental

2.1. Materials and instruments

Unless specified otherwise, all reactions were carried out under the nitrogen atmosphere using standard Schlenk techniques. The glassware was dried in a 120 °C oven. The analytical grade solvents were purified by distillation with appropriate drying agents and blanketed with inert nitrogen atmosphere prior to use. Benzoyl peroxide (BPO) and 2, 2'-azobisisobutyronitrile (AIBN) were recrystallized in a chloroform/methanol mixed solvent before use. All other chemicals (analytical grade) were purchased from commercial sources and were used as received.

Solid-state FT-IR spectra were recorded on a Nicolet Magna 550 Series II FT-IR spectrometer using KBr pellets. The ¹H and ¹³C NMR spectra were measured on a Bruker-AF301 AT 400 MHz spectrometer using deuterated solvents (CDCl₃ or dimethyl sulfoxided (DMSO-d)) and tetramethylsilane as the internal standard. MALDI-TOF MS spectra were carried out and recorded using an Autoflex Bruker MALDI-TOF mass spectrometer. The molecular weights and polydispersity of the homopolymers were determined by GPC on an HP 1050 series HPLC with a visible wavelength and fluorescent detectors (at 254 nm) using tetrahydrofuran (THF) as the mobile phase (HPLC column: Jordi Gel GBR Mixed Bed, 300 mm \times 7.8 mm). The GPC results were calibrated against polystyrene standards with molecular weight at 1350 (PDI = 1.03), 28,000 (PDI = 1.01), 87,000 (PDI = 1.02) and 410,000 (PDI = 1.03). Thermal analyses were carried out on a Perkin-Elmer Pyris Diamond DSC and Perkin–Elmer TGA6 thermal analyzers at a heating rate of 40 °C/min (DSC) and 20 °C/min (TGA) under nitrogen purge, respectively. UV-vis absorption spectra were obtained with a Varian Cary 200 spectrophotometer both in THF solution and in solid-state thin film. The PL spectroscopy was measured on a Perkin-Elmer LS55 Luminescence Spectrometer both in THF solution and in solid-state thin film. The fluorescence quantum efficiencies of the monomers and their homopolymers were determined in THF at room temperature against quinine sulfate (0.1 M H₂SO₄) standard (λ = 313 nm, φ_F = 0.48; λ = 334 nm, φ_F = 0.56) [48]. CV measurements were performed on a BAS CV-50W electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration including a platinum working electrode, an auxiliary electrode and an Ag/AgCl reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ([Bu₄N]PF₆) dissolved in acetonitrile (ACN). The measurements were calibrated with an internal standard, ferrocene/ferrocenium (Fc/Fc⁺) redox couple (taken HOMO of Fc/Fc⁺ = -4.8 eV).

2.2. Synthesis

2.2.1. 2-Methyl-1,4,4a,9a-tetrahydroanthracene-9,10-dione (Nad)

Nad was synthesized by the Diels–Alder reaction. 1,4-Naphthaquinone (10.00 g, 63.20 mmol) and isoprene (12.90 g, 189.60 mmol) were dissolved in 150 mL of methanol. The reaction solution was refluxed and stirred overnight under open atmosphere. Most of the solutions were evaporated under reduced pressure and the residue was filtered to obtain a white solid (95% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.06–8.02 (m, 2H), 7.77–7.73 (m, 2H), 5.44–5.41 (m, 1H), 3.44–3.32 (m, 2H), 2.54–2.42 (m, 2H), 2.26–2.15 (m, 2H), 1.69 (d, *J* = 0.56 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 193.26, 192.96, 129.02, 128.80, 128.75, 126.60, 121.61, 121.58, 113.30, 41.85, 41.19, 23.72, 19.59, 18.22. MS (MALDI-TOF) *m*/*z* = 222.1077 (M + H).

2.2.2. 2-Methyl-9,10-anthracenequinone (MAq)

To a 250 mL two-mouth round bottom flask, the compound **Nad** (5.00 g, 22.10 mmol) and KOH (4.00 g, 100.00 mmol) were dissolved in 100 mL methanol. Compress air was introduced to oxidize the **Nad**. The solution was heated to 45 °C and stirred overnight. The products were filtered and washed by methanol to obtain a yellowish solid (98% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.32–8.28 (m, 2H), 8.21 (d, *J* = 7.92 Hz, 1H), 8.11 (d, *J* = 0.44 Hz, 1H), 7.82–7.77 (m, 2H), 7.60 (dd, *J*₁ = 1.04 Hz, *J*₂ = 7.96 Hz, 1H), 2.54 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 183.37, 182.94, 145.27, 134.92, 134.03, 133.91, 133.54, 133.51, 133.33, 131.23, 127.47, 127.41, 127.13, 127.11, 21.91. MS (MALDI-TOF) *m*/*z* = 222.0644 (M+).

2.2.3. 2-Methylanthracene (MA)

To a 250 mL round bottom flask, **MAq** (4.00 g, 18.00 mmol), zinc powder (3.50 g, 72.00 mmol), cupric sulfate pentahydrate (0.10 g, 0.40 mmol) and ammonia solution (200.00 g) were added. The mixture was heated to 85 °C and it turned from red to colorless. After filtration, the residue was washed by acetone. The acetone was then evaporated and methanol was added, a white solid was precipitated by adding conc. HCl (87% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.37 (s, 1H), 8.31 (s, 1H), 7.99–7.96 (m, 2H), 7.91 (d, J = 8.68 Hz, 1H), 7.75 (s, 1H), 7.45–7.40 (m, 2H), 7.31 (dd, $J_1 = 1.60$ Hz, $J_2 = 8.68$ Hz, 1H), 2.55 (d, J = 0.40 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 134.88, 131.95, 131.80, 131.18, 130.29, 128.22, 128.15, 128.03, 127.93, 126.29, 125.91, 125.20, 125.13, 124.88, 21.98. MS (MALDI-TOF) m/z = 193.1024 (M + H).

2.2.4. 9,10-Dibromo-2-methylanthracene (MADBr)

To a 250 mL round bottom flask, the compound **MA** (1.00 g, 5.20 mmol), n-bromosuccinimide (NBS) (2.23 g, 12.00 mmol) and 200 μ L trifluoroacetic acid was dissolved in 20 mL chloroform. The solution was stirred overnight at room temperature. After reaction, most of chloroform was evaporated, methanol was then added, a yellow needle-like crystal was obtained (90% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.58–8.54 (m, 2H), 8.48 (d, *J* = 9.22 Hz, 1H), 8.34 (s, 1H), 7.64–7.58 (m, 2H), 7.46 (dd, *J*₁ = 1.52 Hz,

 $J_2 = 8.96$ Hz, 1H), 2.63 (d, J = 0.72 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 137.39, 131.04, 130.99, 130.40, 130.11, 129.61, 128.17, 128.07, 128.03, 127.22, 126.89, 126.34, 123.32, 122.34, 22.04. MS (MALDI-TOF) m/z = 349.9127 (M+).

2.2.5. 2-Naphthalenyl boronic acid (2NB)

To a two-neck 250 mL round bottom flask, triisopropyl borate (3.30 mL, 29.06 mmol) and 3-bromoquinoline (3.00 g, 14.49 mmol) was dissolved in dry THF (100 mL), then n-butyllithium (14.50 mL of a 2 M solution in hexane, 29.00 mmol) was added dropwise via a dropping funnel over 1 h under N₂ at -78 °C. After 2 h, the acetone/

dry ice bath was removed, and the reaction solution was allowed to warm to 0 °C. The reaction was then quenched with a 2 M HCl solution, and the pH value was adjusted to 7 with a solution of 2 M NaHCO₃. The resulting solution was extracted with ethyl acetate (EA) (3 × 100 mL). The combined organic layers were dried with MgSO₄ and evaporated to dryness. n-Hexane was then added to precipitated the product as a white solid (80% yield). ¹H NMR (400 MHz, DMSO-d): δ (ppm) 8.38 (s, 1H), 8.22 (s, 2H), 7.93–7.86 (m, 4H), 7.54–7.51 (m, 2H). ¹³C NMR (100 MHz, DMSO-d): δ (ppm) 134.88, 133.96, 132.36, 130.56, 128.28, 127.42, 126.55, 126.33, 125.70. MS (MALDI-TOF) *m*/*z* = 195.0588 (M + Na).



Scheme 1. Synthetic routes for the polymers P(2ADN) and P(3ADQ).



Fig. 1. FT-IR spectra of 2MADN, Vinyl-2ADN & P(2ADN) and 3MADQ, Vinyl-3ADQ & P(3ADQ).

2.2.6. 2-Methyl-9,10-di(2-naphthalenyl)anthracene (2MADN)

2MADN was synthesized by the Suzuki cross-coupling reaction. A two-necked flask containing the compound MADBr (1.00 g, 2.85 mmol), 2NB (1.70 g, 9.99 mmol), tetrakis(triphenylphosphine) palladium(0) (300 mg, 2.60 mmol), and 2 M K₂CO₃ (3 mL) and THF (40 mL) was equipped with a magnetic stirrer and a reflux condenser was heated to reflux overnight under a N₂ purge. The mixture was then poured into water and extracted with 50 mL dichloromethane (DCM). The combined organic layer was dried with anhydrous MgSO₄ and evaporated to dryness. The crude product was purified by silica-gel column chromatography using hexane as eluent affording the title compound as a pale yellow solid (80% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.12–8.01 (m, 6H), 7.97–7.95 (m, 2H), 7.75–7.61 (m, 9H), 7.49 (s, 1H), 7.31–7.26 (m, 2H), 7.17 (d, J = 8.8 Hz, 1H), 2.36 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 136.74, 136.01, 134.90, 133.50, 133.44, 132.78, 130.30, 130.24, 129.73, 129.63, 129.60, 128.74, 128.20, 128.14, 128.03, 127.97, 127.96, 127.94, 127.08, 126.99, 126.97, 126.45, 126.40, 126.23, 126.20, 125.16, 125.07, 124.76, 22.02. MS (MALDI-TOF) m/z = 444.1912(M+).

2.2.7. 2-(Bromomethyl)-9,10-di(2-naphthalenyl)anthracene (2ADN-CH₂Br)

To a 250 mL round bottom flask, **2MADN** (0.85 g, 1.89 mmol) and NBS (0.37 g, 2.08 mmol), BPO (13 mg, 0.054 mmol) was dissolved in 35 mL benzene. The mixture was refluxed under N_2 purge overnight. Methanol was added, filtered, a pale yellow product was obtained. The product was used directly for the following reactions without further purification.

2.2.8. 9,10-Di(2-naphthalenyl)anthracene-2-carbaldehyde (2ADN-CHO)

To a 250 mL round bottom flask, 2-nitropropane (0.80 g, 8.99 mmol), KOH (1.04 g, 22.61 mmol), were added to methanol (30 mL). The mixture was stirred until it became a clear solution. **2ADN-CH₂Br** (0.90 g, 1.72 mmol) dissolved in 30 mL dimethyl sulfoxide (DMSO) was added into above methanol solution. The

solution was stirred overnight at room temperature. Water was added to precipitate the crude product. The crude product was purified by silica-gel column chromatography using hexane/DCM (6:1) as the eluent. A yellow solid was obtained (92% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.89 (s, 1H), 8.25–5.26 (m, 1H), 8.16–8.04 (m, 5H), 8.01–7.96 (m, 3H), 7.84–7.73 (m, 4H), 7.67–7.60 (m, 6H), 7.44–7.37 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 191.20, 138.94, 136.54, 135.40, 134.67, 134.30, 132.43, 132.26, 132.21, 131.87, 131.76, 130.99, 130.53, 129.64, 129.21, 129.09, 128.07, 128.06, 127.95, 127.38, 127.24, 127.16, 127.06, 126.99, 126.90, 126.84, 126.43, 126.16,



Fig. 2. Chromatogram of P(2ADN) and P(3ADQ).

| Iddle I | |
|----------------------|----------------------|
| Summary of molecular | weight measurements. |

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| Polymers | Yield (%) | M_n^a | <i>M</i> _w ^a | PDI |
|----------|-----------|---------|------------------------------------|------|
| P(2ADN) | 85 | 21500 | 50300 | 2.34 |
| P(3ADQ) | 72 | 15400 | 41800 | 2.71 |

^a The weight-averaged (M_w) and number-averaged (M_n) molecular weights were determined by GPC calibrated against poly(styrene) MW standards. GPC conditions: UV–Vis detector wavelength 254 nm, mobile phase THF at 1 mL/min.

125.69, 125.56, 125.55, 125.39, 124.89, 119.29. MS (MALDI-TOF) m/z = 459.1820 (M + H).

2.2.9. 9,10-Di(2-naphthalenyl)-2-vinylanthracene (vinyl-2ADN)

Vinyl-2ADN was synthesized by the Witting reaction. To a 250 mL round bottom flask, methyltriphenylphosphonium bromide (1.26 g, 3.53 mmol) was dissolved in 30 mL freshly distilled THF. Potassium t-butyl oxide (0.40 g, 3.57 mmol) was added and stirred for 30 min in an ice bath. A yellow solution was resulted. 2ADN-CHO (0.65 g, 1.40 mmol) dissolved in THF was added to the ylide/t-butyl oxide solution under continuous stirring. The mixture was stirred at room temperature until the reaction was completed as indicated by thin layer chromatography. Hexane was added. The mixture was then filtered. The solvent was then evaporated under reduced pressure and the residue was purified by column chromatography using hexane as the eluent. A yellow solid was obtained with 88% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.11 (d, I = 2.40 Hz, 1H), 8.09 (d, I = 2.40 Hz, 1H), 8.06-8.03 (m, 2H), 8.00 (s, 2H), 7.95-7.94 (m, 2H), 7.74-7.69 (m, 3H), 7.64-7.58 (m, 7H), 7.52 (dd, $J_1 = 9.2$ Hz, $J_2 = 1.6$ Hz, 1H), 7.33–7.29 (m, 2H), 6.70 (dd, $J_1 = 17.6$ Hz, $J_2 = 10.8$ Hz, 1H), 5.72 (d, J = 10.8 Hz, 1H), 5.21 (d, I = 17.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 135.33, 135.30, 132.99, 132.28, 132.27, 131.66, 131.63, 129.40, 129.11, 129.06, 129.02, 128.55, 128.46, 128.35, 127.01, 126.95, 126.90, 126.88, 126.77, 126.37, 125.97, 125.89, 125.32, 125.12, 124.94, 124.19, 124.12, 120.86, 113.13. MS (MALDI-TOF) m/z = 456.1894 (M+).

2.2.10. 3-Quinolinyl boronic acid (3QB)

The procedures were the same as in **2NB**, except that NaHCO₃ was replaced by NaOH. 3-Bromoquinoline (2.00 g, 9.62 mmol), 1.5 M n-butyllithium (12.50 mL, 18.75 mmol) and trisisoproborate (4.60 mL, 20.01 mmol) were used. White crystal of **3QB** was obtained with 90% yield. ¹H NMR (400 MHz, DMSO-d): δ (ppm) 9.16 (d, *J* = 1.6 Hz, 1H), 8.71 (s, 1H), 8.50 (s, 2H), 8.01–7.96 (m, 2H), 7.79–



Fig. 3. TGA thermogram for P(2ADN) and P(3ADQ) and their parent small molecules 2MADN and 3MADQ at heating rate of 20 °C/min under nitrogen purge.



Fig. 4. DSC thermogram for P(2ADN) and P(3ADQ) under heating rate of 40 °C/min under nitrogen purge.

7.75 (m, 1H), 7.62–7.60 (m, 1H). ¹³C NMR (100 MHz, DMSO-d): δ (ppm) 154.77, 148.27, 142.91, 130.12, 128.58, 128.49, 127.21, 126.36.

2.2.11. 2-Methyl-9,10-di (3-quinolinyl) anthracene (3MADQ)

MADQ was synthesized by the Suzuki cross-coupling reaction. The procedures were the same as in **2MADN**, except that **MADBr** (0.65 g, 2.32 mmol), **3QB** (1.60 g, 9.30 mmol), tetrakis (triphenylphosphine) palladium (0) (0.27 g, 0.23 mmol), 2 M K₂CO₃ (3 mL) and THF (40 mL) were used. The crude product was purified by silica-gel column chromatography using hexane/EA/chloroform (8:1:1) as the eluent affording the **3MADQ** as a pale yellow solid (85% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.05 (t, *J* = 2.4 Hz, 2H), 8.35–8.31 (m, 4H), 7.99–7.95 (m, 2H), 7.91–7.86 (m, 2H), 7.73–7.61 (m, 5H), 7.44 (s, 1H), 7.39–7.35 (m, 2H), 7.25–7.22 (m, 1H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 152.98, 152.93, 152.86, 152.81, 147.62, 138.12, 138.08, 138.04, 138.00, 135.89, 133.63, 132.69, 132.16, 132.04, 130.72, 130.67, 129.96, 129.61, 129.58, 129.12, 128.84, 128.14, 128.08, 128.02, 127.92, 127.85, 127.31, 126.61, 126.49, 125.88, 125.56, 124.75, 22.04. MS (MALDI-TOF) m/z = 447.1842 (M + H).

2.2.12. 2-(Bromomethyl)-9,10-di (3-quinolinyl) anthracene (3ADQ-CH₂Br)

The procedures were the same as in **2MADN**, except that **2MADQ** (1.00 g, 2.24 mmol) and NBS (0.46 g, 2.58 mmol), BPO (27.00 mg, 0.11 mmol) and 35 mL benzene were used.

2.2.13. 9,10-Di (3-quinolinyl) anthracene-2-carbaldehyde (3ADQ-CHO)

The procedures were the same as in **2ADN-CH₂Br**, except that **2ADN-CH₂Br** (1.00 g, 1.91 mmol), 2-nitropropane (2.18 g,

| Table 2 | |
|--------------------|------------|
| Summary of thermal | properties |

| Materials | Onset T _d (°C) ^a | Weight lost (%) | Midpoint T _g (°C) ^b | ΔC_p (J/g °C) ^c | $T_{\mathrm{m}} (^{\circ}\mathrm{C})^{\mathrm{b}}$ |
|-----------|---|--------------------|--|---------------------------------------|--|
| 2MADN | 380 | 95.73 | 127 | 0.45 | 261 |
| P(2ADN) | 424 | 20.77 | 343 | 0.21 | |
| 3MADQ | 376 | 84.46 | 127 | 0.41 | 255 |
| P(3ADQ) | 414 | 45.60 | 298 | 0.24 | |

 $^a\,$ About 5 mg samples were used for TGA under nitrogen purge at a heating rate 20 $^\circ C\,$ min $^{-1}.$

^b About 20 mg samples were used for DSC under nitrogen purge at a heating rate 40 °C min⁻¹. τ_m is the peak melting temperature.

^c The change in specific heat capacity at $T_{\rm g}$ ($\Delta C_{\rm p}$ J/g °C).



Fig. 5. Extinction coefficient and PL spectra of 2MADN, Vinyl-2ADN and P(2ADN) in THF.

24.49 mmol), KOH (1.30 g, 23.21 mmol), methanol (30 mL) and DMSO (30 mL) were used. The crude product was purified by silicagel column chromatography using hexane/EA/chloroform (4:1:0.5) as the eluent. A yellow solid was obtained (80% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.49 (s, 1H), 9.09–9.04 (m, 2H), 8.40–8.33 (m, 4H), 8.21 (s, 1H), 8.00–7.91 (m, 4H), 7.82–7.73 (m, 6H), 7.50–7.49 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 191.92, 152.36, 152.31, 152.22, 152.16, 147.89, 147.75, 138.20, 138.12, 138.04, 136.71, 135.31, 134.43, 134.00, 132.38, 132.08, 131.19, 131.14, 130.87, 130.45, 130.28, 129.71, 129.67, 129.61, 129.51, 128.15, 128.08, 128.03, 127.70, 127.57, 127.08, 126.82, 121.41. MS (MALDI-TOF) *m*/*z* = 461.1653 (M + H).

2.2.14. 9,10-Di (3-quinolinyl)-2-vinylanthracene (vinyl-3ADQ)

Vinyl-3ADQ was synthesized by the Witting reaction. The procedures were the same as in **Vinyl-3ADQ**, except that **2ADN-CHO** (0.50 g, 1.09 mmol) methyltriphenylphosphonium bromide (0.97g, 2.72 mmol), potassium t-butyl oxide (0.31 g, 2.76 mmol) and THF (20 mL) were used. The product was purified by silica-gel column chromatography using hexane/EA/chloroform (8:1:1) as the eluent. A yellow solid was obtained with 89.5% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.07 (s, 2H), 8.36–8.32 (m, 4H), 7.96–7.85 (m, 4H), 7.70–7.67 (m, 5H), 7.58–7.54 (m, 2H), 7.38–7.35 (m, 2H), 6.67 (dd, $J_1 = 17.6$ Hz, $J_2 = 11.2$ Hz, 1H), 5.74 (d, J = 17.6 Hz, 1H), 5.24 (d, J = 11.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.70, 151.64, 151.57, 146.55, 146.52, 137.07, 136.99, 136.91, 135.44, 133.82, 132.77, 132.66, 130.70, 129.79, 129.50, 129.45, 128.95, 128.49, 128.47, 127.02, 126.96, 126.91, 126.76, 126.74, 126.72, 126.26, 125.91, 125.56, 125.46,

125.04, 124.94, 124.26, 121.77, 114.14. MS (MALDI-TOF) m/z = 459.1840 (M + H).

2.2.15. Poly(9,10-di(2-naphthalenyl)-2-vinylanthracene) (P(2ADN))

To a 10 mL one-mouth glass apparatus charged with a stirrer bar, **Vinyl-2ADN** (200.00 mg, 0.433 mmol) and free radical initiator AIBN (1.43 mg, 0.0087 mmol) was dissolved in 1 mL dried toluene. The reaction mixture was degassed by several freeze–pump–thaw cycles and then sealed off under nitrogen atmosphere. The reaction mixture was stirred at 75 °C for 10 h. Finally, a viscous yellowish polymer solution was resulted. The polymer was purified by redissolving in THF and re-precipitated in excess acetone. A yellow solid product was obtained (85% yield).

2.2.16. Poly(9,10-di(3-quinolinyl)-2-vinylanthracene) (P(3ADQ))

The procedures were the same as in **P(2ADN)**. **Vinyl-3ADQ** (200.00 mg, 0.437 mmol), AIBN (1.43 mg, 0.0087 mmol) and dried toluene (0.5 mL) were used. A yellow solid product was obtained (72% yield).

3. Results and discussion

3.1. Synthesis and characterization of the polymers

The synthetic pathway for the monomers **Vinyl-2ADN** & **Vinyl-3ADQ** and their polymers **P(2ADN)** & **P(3ADQ)** are shown in Scheme 1. Details on the reaction procedures and their characterizations have been given in above synthesis Section 2.2.

Table 3

| Optical properties of 2MAD | N, Vinyl-2ADN, P(2ADN), 3 | MADQ, Vinyl-3ADQ and | d P(3ADQ) in THF solut | ions and in solid thin films. |
|----------------------------|---------------------------|----------------------|------------------------|-------------------------------|
|----------------------------|---------------------------|----------------------|------------------------|-------------------------------|

| Materials | λ_{max} absorption maximum (nm) | λ_{max} emission maximum (nm) | FWHM (nm) | Life time (ns) | Quantum efficiencies (φ) | CIE |
|-------------------------|---|---------------------------------------|-----------|----------------|------------------------------------|--------------|
| Solution (in THF) | | | | | | |
| 2MADN ^a | 359, 378, 398 | 425.5 | 53.5 | 4.45 | 0.80 | (0.15, 0.05) |
| Vinyl-2ADN ^a | 360, 380, 400 | 435.5 | 56.5 | 3.95 | 0.56 | (0.15, 0.06) |
| P(2ADN) ^a | 364, 383, 403 | 442.5 | 59.5 | 6.54 | 0.43 | (0.14, 0.08) |
| 3MADQ ^a | 362, 380, 400 | 436 | 55.5 | 3.51 | 0.41 | (0.15, 0.06) |
| Vinyl-3ADQ ^a | 366, 382, 404 | 440 | 56 | 3.51 | 0.39 | (0.15, 0.07) |
| P(3ADQ) ^a | 369, 384, 404 | 452 | 63.5 | 3.80 | 0.24 | (0.14, 0.12) |
| Solid-state | | | | | | |
| 2MADN ^b | 362, 380, 401 | 434.5 | 45 | 1 | 1 | (0.15, 0.06) |
| P(2ADN) ^c | 367, 386, 404 | 447.5 | 56 | 1 | / | (0.15, 0.10) |
| 3MADQ ^b | 386, 406 | 441.5 | 49 | 1 | 1 | (0.15, 0.06) |
| P(3ADQ) ^c | 388, 406 | 453 | 61.5 | 1 | 1 | (0.15, 0.13) |
| | | | | | | |

^a THF solution (5 ppm).

^b Cast from 10 wt % PMMA in chloroform solution with dye/PMMA = 2 wt% on quartz.

^c Thin films solvent cast on quartz.



Fig. 6. Optical absorption and PL spectra of 2MADN in a PMMA solid solution and P(2ADN) thin film cast on quartz.

Solid-state FT-IR measurements were performed for the confirmation of the chemical structures. The spectrum for the polymer **P(2ADN)** in comparison with the vinyl monomer **Vinyl-2ADN** and a model compound **2MADN** was given in Fig. 1. The FT-IR spectra of **2MADN**, **Vinyl-2ADN** and **P(2ADN)** have the following similar structural attributes: 3052-3054 cm⁻¹ (ν , aromatic C–H stretching), 1629-1336 cm⁻¹ (ν , aromatic C=C stretching; δ , sp^3 C–H deformation) and 817-743 cm⁻¹ (δ , C–H out of plane deformation). In Fig. 1, **2MADN**, **Vinyl-2ADN** and **P(2ADN)** showed similar distinct peaks of aromatic C=C stretching vibration with little shift. **Vinyl-2ADN** showed a unique =C–H vibration at 987 and 912 cm⁻¹ due to the vinyl group. An intense sp^3 C–H stretching vibration at 2919 cm⁻¹ for **P(2ADN)** was attributed to the polymer hydrocarbon main chain.

The FT-IR spectra of **3MADQ**, **Vinyl-3ADQ** and **P(3ADQ)** were also given in Fig. 1. Common features of **3MADQ**, **Vinyl-3ADQ** and **P(3ADQ)** are attributed to the following structures/moieties: $3062-3059 \text{ cm}^{-1}(\nu, \text{ aromatic C-H stretching})$, $1620-1258 \text{ cm}^{-1}(\nu, \text{ aromatic C=C stretching; } \delta, sp^3$ C-H deformation) and 788–751 cm⁻¹ (δ , C-H out of plane deformation). Again, distinct peaks of =C-H vibration at 995 and 914 cm⁻¹ was detected for **Vinyl-3ADQ** and a strong sp^3 C-H stretching vibration due to the aliphatic main chain was observed for **P(3ADQ)**. **3MADQ**, **Vinyl-3ADQ** and **P(3ADQ)** all have similar distinct peaks for the aromatic C=C stretching vibration with slight shift.

The molecular weights of the polymers **P(2ADN)** and **P(3ADQ)** were determined using GPC with THF as the mobile phase and were calibrated against polystyrene MW standards (Fig. 2). The resulting yield and relative MW measurements were presented in Table 1.

The number-averaged molecular weights (M_n) of **P(2ADN)** and **P(3ADQ)** were found to be 21,500 and 15,400, with a relatively high PDI of 2.34 and 2.71, respectively. The high polydispersity could be a result of chain transfer to the aromatic moieties as well as stabilization of the radical species due to delocalization.

The solubility was compared by dissolving 1.00 mg of polymer in 10 mL of a solvent at room temperature in a supersonic bath for 20 min. Both **P(2ADN)** and **P(3ADQ)** were found to be soluble in common organic solvents including THF, CHCl₃, DCM, toluene et al. **P(3ADQ)** showed improved solubility as it can also be dissolved in ethanol and an ethanol/water ($\nu/\nu = 1/1$) mixture. In comparison with our previous work on **P(ADN)** based on 1-naphthalenyl, **P(2ADN)** have enhanced solubility which can be attributed to the lower steric hindrance for the 2-naphthalenyl substituted units.

3.2. Thermal properties

The thermal properties of the homopolymers were examined by TGA at a heating rate 20 °C min⁻¹ and DSC at a heating rate 40 °C min⁻¹, all under nitrogen purge. The results were summarized in Table 2, Fig. 3 and Fig. 4, respectively. Both **P(2ADN)** and **P(3ADQ)** possessed excellent thermal stabilities with glass transition temperatures (T_g midpoint) at 343 °C and 298 °C, respectively. This is significantly higher than the T_g previously reported for **P(ADN)** ($M_n = 17,600$ and $T_g = 237$ °C). The onset degradation temperature (T_d) for **P(2ADN)** and **P(3ADQ)** at 424 °C and 414 °C are also higher than that of the model small molecule **2MADN** ($T_d = 380$ °C) and **3MADQ** ($T_d = 376$ °C). Neither of the polymers **P(2ADN)** or **P(3ADQ)** showed melting nor crystalline-related



Fig. 7. Extinction coefficient and PL spectra of 3MADQ, Vinyl-3ADQ and P(3ADQ) in THF.



Fig. 8. Optical absorption and PL spectra of 3MADQ in a PMMA solid solution and P(3ADQ) thin film cast on quartz.

transitions upon repeated heating (up to 300 $^{\circ}$ C) and cooling indicating **P(2ADN)** and **P(3ADQ)** are completely amorphous.

3.3. Optical properties

The UV–Vis absorption and PL emission spectra for **2MADN**, **Vinyl-2ADN** and **P(2ADN)** in THF were given in Fig. 5 with the results summarized in Table 3. Three prominent bands of **2MADN** were observed at 359, 378 and 398 nm, which were all due to the $\pi \rightarrow \pi^*$ transition. A red-shift of about 5 nm for the same absorption peaks were found for **P(2ADN)**. The small molecule **2MADN** has an emission maximum at 425.5 nm, while **Vinyl-2ADN** has a broader emission peak at 435.5 nm. A red-shift of 17 nm in PL spectrum for **P(2ADN)** was found in comparison to **2MADN**. The red-shift is probably a result of short-range $\pi - \pi$ stacking interaction between adjacent **ADN** moieties [49]. The extinction coefficient of **P(2ADN)** decreased to only 62% to that of **2MADN**, which could be attributed to the exciton and dispersion–force interaction in the polymer with an ordered structure [40–52].

The solid-state UV—vis absorption and PL emission spectra of **2MADN** (dispersed in a poly(methyl methacrylate) (PMMA) solid thin film) and a solvent cast **P(2ADN)** solid thin film were shown in Fig. 6. The **2MADN**/PMMA solid thin film was cast at room temperature from a 10 wt% PMMA chloroform solution with the concentration **2MADN**/PMMA = 2 wt%. Both solid-state thin film and the THF solution have very similar $\pi \rightarrow \pi^*$ transition absorption bands. A smaller red-shift in the absorption and emission spectra was found for the solid thin films than those in THF solutions. Similarly, **P(2ADN)** exhibited the same behavior in THF solution and in solid thin film. The UV—vis absorption, PL emission spectra and CIE results indicated that the optical properties were preserved when **Vinyl-2ADN** was polymerized into **P(2ADN)**.

Figs. 7 and 8 showed the UV—vis absorption and PL emission spectra for **3MADQ**. Vinyl-3ADQ and **P(3ADQ)** in THF and in solid thin films. The results were also included in Table 3. The extinction coefficients of Vinyl-3ADQ and **P(3ADQ)** were only 65.5% and 51.6% of that of **3MADQ**. The UV—vis and PL spectra also showed a slight red-shifts for **P(3ADQ)** compared to **3MADQ**. Compared to the UV—vis absorption and PL emission spectra of **3MADQ** and **P(3ADQ)** in THF solution, both solid film spectra of **3MADQ** and **P(3ADQ)** showed some red-shifts. This phenomenon can be attributed to the difference in dielectric constant of the environment [30,53].

The lifetimes of **P(2ADN)** and **P(3ADQ)** were 6.54 and 3.80 ns, respectively, which were both higher than those of the small molecules **2MADN** (4.45 ns) and **3MADQ** (3.51 ns) (see Fig. 9). **Vinyl-2ADN** and **P(2ADN)** have similar fluorescence quantum efficiencies ($\varphi = 0.56$ and 0.43) and both were lowered than that of the

small molecule **2MADN** ($\varphi = 0.80$). However, **3MADQ** and **Vinyl-3ADQ** have similar fluorescence quantum efficiencies ($\varphi = 0.41$ and 0.39) and were both higher than that of the polymer **P(3ADQ)** ($\varphi = 0.24$). Both the CIE of **P(2ADN)** and **P(3ADQ)** are in the range of CIE_{x,y} (0.14–0.15, 0.08–0.13) either in solid-state form or in solution, indicating both **P(2ADN)** and **P(3ADQ)** are within the requirements for a true blue display color.

The sensitivity of fluorescent on pH for a 5 ppm **3MADQ** and **P(3ADQ)** in a mixed ethanol/water (v/v = 1/1) solution were indicated in Fig. 10(a, b). The pH values were adjusted by adding different amounts of HCl and NaOH. This pH sensitive phenomenon could be attributed to the acid-base ionization equilibrium of ground state and/or excited state quinoline groups suspended on the anthracene-core at low pH value environments (see Scheme 2) [54,55].

The PL intensity of **3MADQ** at 442 nm against pH is sigmoidal and was shown in Fig. 10(c). A similar sigmoidal relationship at 457 nm for **P(3ADQ)** was also given Fig. 10(d). According to the Henderson–Hasselbach equation (Eq. (1)), the pK_a of **3MADQ** and **P(3ADQ)** was calculated to be 2.4 and 2.7, respectively, indicating they are weak alkalis. The equation is given as

$$pK_{a} = pH - \log \frac{\left[I_{F_{max}} - I_{F}\right]}{\left[I_{F} - I_{F_{min}}\right]}$$
(1)



Fig. 9. PL life time spectra of 2MADN, Vinyl-2ADN, P(2ADN), 3MADQ, Vinyl-3ADQ and P(3ADQ).



Fig. 10. PL spectra of **3MADQ** (a) and **P(3ADQ)** (b) in a mixed ethanol/water ($\nu/\nu = 1/1$) solution with pH values adjusted by HCl and NaOH. The concentrations of **3MADQ** and **P(3ADQ)** were both 5 ppm. The spectra (c) and (d) were the PL intensity cross-section for **3MADQ** at 442 nm and **P(3ADQ)** at 457 nm against pH.

where the fluorescence signal $I_{F_{max}}$ is the max fluorescence value, $I_{F_{min}}$ is the minimum fluorescence value, and I_F is fluorescence value at a certain pH value.

At increasing pH, the PL intensity for **3MADQ** increased faster than that of **P(3ADQ)** indicating **P(3ADQ)** was less sensitive to pH than **3MADQ**. The observation could be related to the facts that the **P(3ADQ)** chains not being fully extended in the ethanol/water (ν / ν = 1/1) mixed solution.

3.4. Electrochemical and electrical properties

The ionization potential and redox stability of the model small molecules (2MADN and 3MADQ) and the polymers (P(2ADN) and P(3ADQ)) were investigated using CV. The CV of the small molecules 2MADN and 3MADQ were measured in ACN while the polymers P(2ADN) and P(3ADQ) measurements were effected by coating the polymers on the Pt working electrode. The first oxidation potential in the anodic sweep was used to determine the highest occupied molecular orbital (HOMO) energy level which was calculated by assuming the internal standard ferrocene was -4.8 eV with respect to the vacuum level. Hence, the HOMO of the polymers was estimated using the equations $E_{HOMO} = -(E_{ox} + 4.8)$ eV, where E_{ox} is the onset potential for first oxidation relative to the Fc/Fc⁺ couple. As a result, the lowest unoccupied molecular orbital (LUMO) energy level of the polymers was found by subtracting the band-gap energy (determined from the absorption edge of the UV-Vis absorption spectra) from the HOMO value.

The cyclic voltammograms for **2MADN**, **3MADQ**, **P(2ADN)** and **P(3ADQ)** were given in Fig. 11 with the results summarized in Table 4. The first oxidation wave of **2MADN** and **P(2ADN)** occurred at 1.15 and 1.18 V, respectively, which was lower than that of **3MADQ** (1.24 V) and **P(3ADQ)** (1.21 V). Both the small molecules and the polymers have similar band-gap energy (E_g) (2.95–2.98 eV for the small molecules and 2.88–2.91 eV for the polymers). The LUMO/HOMO for **3MADQ** and **P(3ADQ)** were both shifted slightly downward (from –0.06 to –0.03 eV) compared to **2MADN** and **P(2ADN)**. The results indicated the LUMO, HOMO and energy gap



Scheme 2. The equilibrium equations for 3MADQ and P(3ADQ) at different pH values.



Fig. 11. CV of 2MADN and 3MADQ in ACN, and P(2ADN) and P(3ADQ) thin film cast on the Pt working electrode.

| able 4 |
|--|
| lectrochemical and electrical properties of 2MADN, 3MADQ, P(2ADN) and P(3ADQ). |

| Materials | $E_{1/2}^{\text{ox}}$ (V, ferrocene) ^a | $E_{\text{oneset}}^{\text{ox}}$ (V, sample) ^a | HOMO (eV) ^b | UV–Vis absorption onset (nm) | $E_{\rm g}~({\rm eV})$ | LUMO (eV) ^c | Mobility ^d μ_{hole} (cm ² /(V s)) |
|-----------|---|--|------------------------|------------------------------|------------------------|------------------------|---|
| 2MADN | 0.46 | 1.15 | -5.49 | 416.5 | 2.98 | -2.51 | 6.5×10^{-4} |
| P(2ADN) | 0.46 | 1.18 | -5.52 | 426.5 | 2.91 | -2.61 | 4.0×10^{-7} |
| 3MADQ | 0.46 | 1.24 | -5.58 | 421.0 | 2.95 | -2.63 | 10 ⁻⁸ |
| P(3ADQ) | 0.46 | 1.21 | -5.55 | 430.0 | 2.88 | -2.67 | $< 10^{-8}$ |

^a Oxidation potentials were measured in 0.1 M [Bu₄N]PF₆ ACN solution relative to Ag/AgCl electrode.

^b Assuming the HOMO of ferrocene is –4.8 eV.

The LUMO was obtained by subtracting the HOMO from the band-gap energy which was deduced from the UV-Vis absorption onset.

^d The hole mobility was measured using a top-contact OFET method with MoO₃/Au as the contact electrodes. The small molecules were evaporated onto a PS dielectric layer and the polymers were spin coated on a SiO₂ layer.

were not altered significantly by converting the small molecules into polymers.

PLED devices based on the configuration ITO/MoO₃/P(2ADN) or P(3ADQ)/LiF/Al have been prepared by spin coating. The EL of the devices, however, was rather weak even under high biased voltage (>20 V). The causes were further investigated by studying the mobility of the polymers. The hole mobility (μ_{hole}) was measured using a top-contact OFET technique [56]. The mobility of the polymers were found to be 4.0×10^{-7} and $<\!10^{-8}~cm^2/(V~s)$ for P(2ADN) and P(3ADQ), respectively (see Table 4). The low mobility is consistent with the solid-state PL observation that a mere 12-13 nm red-shit in the λ_{max} and a slight broadening (5–9 nm) of the FWHM indicated only minimum or partial $\pi - \pi$ stacking between adjacent 2ADN and 3ADQ moieties in their polymers (see Table 3). The exception low mobility for **3MADQ** and **P(3ADQ)** could further be explained by the polar ADQ moieties can readily absorb moisture which are known traps for charges (especially electrons). A refine in the device configuration such as employing conductive dopants/emitters would need further investigation.

4. Conclusion

Two blue fluorescent polymers **P(2ADN)** and **P(3ADQ)** were synthesized successfully using free radical solution addition

polymerization. Both P(2ADN) and P(3ADQ) have excellent solubilities in common organic solvents compared to another blue emitting polymer poly(2-vinylanthracene) with 9,10-di(1-naphthalenyl) substituent. P(3ADQ) is also found to be dissolved in polar solvent including ethanol/water (v/v = 1/1) mixture. **P(2ADN)** and P(3ADQ) are both amorphous and possess excellent thermal stabilities as well as a longer PL life time than that of their model molecules 2MADN and 3MADQ. The quantum efficiencies of the polymers P(2ADN) and P(3ADQ), however, are 41% and 46% smaller than that of **2MADN** and **3MADQ**, respectively. Both polymers have similar band-gap energy while their LUMO/HOMO is lightly lower for P(3ADQ) compared to P(2ADN). Only a slight red-shift in the absorption and emission spectra of both the polymers P(2ADN) and P(3ADQ) was found in comparison with their model compounds suggesting weak $\pi - \pi$ interaction between adjacent pendant **ADN** or ADQ moieties in the polymer chains. The CIE coordinates (x = 0.15, y = 0.10 for P(2ADN); x = 0.15, y = 0.13 for P(3ADQ))remained closed to the values required for a true blue display color. The preliminary study on the electroluminescent of the polymers was rather weak as explained by their poor mobility. The wide band-gap polymers, however, can be used as a host for a range of dopants/emitters that need further investigation. The **3MADQ** and P(3ADQ) also shown to have remarkable pH sensitivity, suggesting their potential applications in pH and environmental monitoring.

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