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Synthesis of aminocarbazole–anthraquinone fused dyes and polymers

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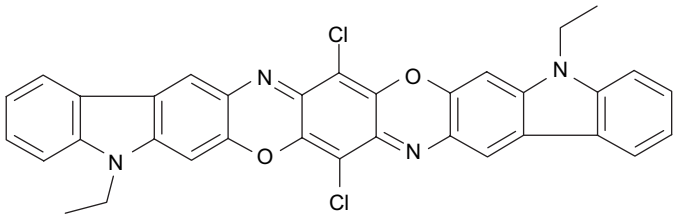
Abstract

A new series of dyes have been synthesized by Buchwald-type coupling of 3-aminocarbazole with various isomers of chloroanthraquinone. The absorption maxima of the resulting dyes were found to vary from 542 nm (violet) to 777 nm (green) depending on the extent of conjugation. Also, three different polymers have been synthesized by coupling of 3,6-diaminocarbazole with isomers of dichloroanthraquinone under palladium-catalyzed conditions. We demonstrated that the conjugation length in these polymers was largely confined to their monomer repeat units.

Keywords: Carbazole; Anthraquinone; Violet pigment; Red-emitting; Palladium catalysis; Polymer

1. Introduction

Carbazole is an attractive raw material for the synthesis of dyes since it is cheap and readily available. Carbazoledioxazine **1** (violet 23) is a representative compound of dioxazine pigments [1]. It is an important violet pigment, used as a coloring material for plastics and printing inks [2]. Violet 23 is synthesized from 3-amino-9-ethylcarbazole by initial condensation with *p*-chloroanil to generate dicarbazolylaminochlorobenzoquinone and subsequent cyclization of the quinone gives carbazoledioxazine. Recently, Ikeda et al. have confirmed the structure spectroscopically by attaching a long alkyl chain at the nitrogen center of carbazole [3–5]. As part of our efforts into developing cheap alternatives for violet 23, we have focussed on the coupling of two readily available substrates, 3-aminocarbazole and chloroanthraquinones. Both 3-aminocarbazole and 3,6-diaminocarbazole are easy to synthesize and dichloroanthraquinones are readily available in various isomeric forms. The synthesis of 3,6-bis(1-anthraquinonylamino)carbazole has been reported either by the condensation of 3,6-diaminocarbazole with 1-chloroanthraquinone or by condensation of the more readily available dihalocarbazoles with 1-aminoanthraquinone [6,7]. The resulting pigment was violet in color ($\lambda_{max} = 513$ nm) but the absorption maximum was too hypsochromic compared to violet 23 ($\lambda_{max} = 602$ nm). In the present study, we report on the synthesis and characterization of dyes and pigments based on the coupling of 3-aminocarbazole **2** with 1,4-, 1,5- and 1,8-dichloroanthraquinones, under palladium-catalyzed Buchwald–Hartwig type amination conditions [8]. This yielded materials ranging in color from violet to greenish-blue. The synthesis and characterization of a series of soluble polymers by coupling of diaminocarbazole with 1,4-, 1,5- and 1,8-dichloroanthraquinones are also presented.



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2. Experimental details

All solvents were purified and freshly distilled prior to use according to literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 250 (250 and 62.5 MHz, respectively). UV–vis data were recorded on a Perkin–Elmer Lamda 9 and the PL measurements in solution on a SPEX Fluorolog 2 type 212 steady-state fluorometer. Gel-permeation chromatography (GPC) analysis was performed with PL gel columns (10^3 and 10^4 Å pore widths) connected to a UV–vis detector against polystyrene standards with narrow weight distributions.

2.1. 9-(2-Ethylhexyl)carbazole

A 100 mL Schlenk flask was charged with carbazole (1.00 g, 5.9 mmol), NaH (0.33 g, 8.26 mmol) and 40 mL of DMF. The resulting mixture was stirred for 30 min. 2-Ethylhexylbromide (1.29 mL, 7.08 mmol) was then added under argon and the mixture was stirred overnight at room temperature. The reaction mixture was quenched with 20 mL of water and extracted three times with diethyl ether (40 mL each). The combined organic fractions were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Silica gel, 2% ethyl acetate in hexane as eluent). Isolated yield = 92%. ^{1}H NMR (250 MHz, $CDCl_3$), ppm: 8.04 (d, 2H, $J = 7.7$ Hz), 7.33 (m, 4H), 7.15 (d, 2H, $J = 7.7$ Hz), 4.11 (d, 2H, $J = 7.5$ Hz), 2.02 (m, 1H), 1.21–1.31 (m, 8H), 0.82–0.89 (m, 6H). FDMS: *m/z* 279.5.

2.2. 3-Nitro-9-(2-ethylhexyl)carbazole

$Cu(NO_3)_2 \cdot 2.5H_2O$ (0.41 g, 1.76 mmol) was added to a mixture of acetic acid (4 mL) and acetic anhydride (8 mL) at room temperature. The mixture was stirred for 10 min, and then 9-(2-ethylhexyl)carbazole (1 g, 3.55 mmol) was added slowly in portions over 5 min. Heat was generated during the addition, and an additional 4 mL of acetic acid was added. The mixture was stirred at this temperature for 15 min and then poured into distilled water (200 mL). Then the aqueous layer was extracted with DCM and dried over $MgSO_4$ and purified by column chromatography. Isolated yield = 72%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 9.02 (d, 1H, $J = 2.2$ Hz), 8.36 (dd, 1H, $J = 2.3$ Hz, $J = 9.1$ Hz), 8.18 (d, 1H, $J = 7.8$ Hz), 7.62–7.41 (m, 3H), 7.35 (t, 1H, $J = 7.4$ Hz), 4.23 (d, 2H, $J = 7.5$ Hz), 2.07 (m, 1H), 1.49–1.19 (m, 8H), 0.96–0.81 (m, 6H). ^{13}C NMR, ppm: 144.26, 142.41, 140.77, 127.58, 123.02, 122.67, 121.62, 121.10, 120.90, 117.30, 110.40, 108.96, 48.06, 39.69, 31.23, 29.04, 24.68, 23.33, 14.09, 10.97. FDMS: *m/z* 324.6.

2.3. 3-Amino-9-(2-ethylhexyl)carbazole (**2**)

Palladium on charcoal (10%, 356 mg) was added in portions to a hot solution of 3-nitro-9-(2-ethylhexyl)carbazole (2.7 g, 8.32 mmol) and hydrazine hydrate (3.1 mL) in ethanol (60 mL) and the mixture was heated under reflux for 2 h. The cooled mixture was filtered off and the filtrate was concentrated to give the title product **2**. Isolated yield = 72%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 7.97 (d, 1H, $J = 7.8$ Hz), 7.43–7.30 (m, 3H), 7.22 (d, 1H, $J = 8.6$ Hz), 7.12 (ddd, 1H, $J = 1.5$ Hz, $J = 6.6$ Hz, $J = 8.0$ Hz), 6.88 (dd, 1H, $J = 2.3$ Hz, $J = 8.6$ Hz), 4.10 (d, 2H, $J = 7.2$ Hz), 3.64 (s, 2H), 2.03 (m, 1H), 1.44–1.14 (m, 8H), 0.95–0.80 (m, 6H). ^{13}C NMR, ppm: 141.77, 139.84, 135.70, 125.70, 123.75, 122.57, 120.50, 118.22, 115.70, 109.99, 109.30, 105.91, 47.78, 39.84, 31.39, 29.23, 24.79, 23.50, 14.23, 11.11. FDMS: *m/z* 294.2.

2.4. 3,6-Dinitro-9-(2-ethylhexyl)carbazole

$Cu(NO_3)_2 \cdot 2.5H_2O$ (1.19 g, 5.1 mmol) was added into a mixture of acetic acid (5 mL) and acetic anhydride (10 mL) at room temperature. The mixture was stirred for 10 min, and 9-(2-ethylhexyl)carbazole (1 g, 3.55 mmol) was added slowly in portions over 5 min. Heat was generated during the addition, and an additional 5 mL of acetic acid was added. The mixture was stirred at this temperature for 15 min and then poured into distilled water (200 mL). The yellow precipitate was then collected by filtration, washed with water and dried under vacuum. The product was recrystallized from ethanol. Isolated yield = 70%. ^{1}H NMR (250 MHz, $CDCl_3$), ppm: 9.08 (d, 2H, $J = 2.2$ Hz), 8.4 (dd, 2H, $J = 2.2$ Hz, J = 9.2 Hz), 7.5 (d, 2H, $J = 9.2$ Hz), 4.28 (d, 2H, $J = 7.5$ Hz), 2.02 (m, 1H), 1.21–1.31 (m, 8H), 0.82–0.89 (m, 6H). ^{13}C NMR, ppm: 145.61, 142.16, 123.14, 122.81, 117.91, 110.44, 48.78, 39.86, 31.24, 29.04, 24.71, 23.32, 14.09, 10.98. FDMS: *m/z* 369.2.

2.5. 3,6-Diamino-9-(2-ethylhexyl)carbazole (**3**)

Palladium on charcoal (10%, 115 mg) was added in portions to a hot solution of 3,6-dinitrocarbazole (0.5 g, 1.35 mmol) and hydrazine hydrate (1 mL) in ethanol (40 mL) and the mixture was heated under reflux for 2 h. The cooled mixture was filtered off and the filtrate was concentrated to give 415 mg of title product. Isolated yield = 77%. ^{1}H NMR (250 MHz, $CDCl_3$), ppm: 7.25 (d, 2H, $J = 2.2$ Hz), 7.08 (d, 2H, $J = 8.5$ Hz), 6.8 (dd, 2H, $J = 2.5$ Hz, $J = 8.5$ Hz), 3.9 (d, 2H, $J = 9.0$ Hz), 3.50 (br s, 4H), 1.94 (m, 1H), 1.18–1.28 (m, 8H), 0.82–0.89 (m, 6H). ^{13}C NMR, ppm: 139.08, 136.33, 123.14, 115.67, 109.80, 105.88, 47.83, 39.87, 31.37, 29.20, 24.75, 23.45, 14.16, 11.06. FDMS: *m/z* 309.6.

2.6. 1,5-Bis[3-amino-9-(2-ethylhexyl)carbazole] anthraquinone (**4**)

3-Amino-9-(2-ethylhexyl)carbazole (2.2 g, 7.48 mmol), 1,5-dichloroanthraquinone (861 mg, 3.1 mmol), $Pd_2(dba)_3$ (76 mg), BINAP (153 mg), cesium carbonate (3.98 g) and toluene (15 mL) were mixed together and heated at 100 °C for 24 h. The reaction mixture was quenched with water (10 mL) and then extracted with 100 mL of DCM, washed with brine and dried over $MgSO_4$. Evaporation of solvent under vacuum resulted in a violet residue. The residue was purified by column

chromatography using ethyl acetate/hexane as eluent. Isolated yield = 72%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 11.46 (s, 2H), 8.12–8.03 (m, 4H), 7.70 (dd, 2H, $J = 1.0$ Hz, $J = 7.2$ Hz), 7.55–7.41 (m, 10H), 7.37 (dd, 2H, $J = 1.0$ Hz, $J = 8.6$ Hz), 7.23 (ddd, 2H, $J = 1.9$ Hz, $J = 6.1$ Hz, $J = 7.9$ Hz), 4.22 (d, 4H, $J = 7.4$ Hz), 2.11 (m, 2H), 1.35 (m, 16H), 0.95 (t, 6H, $J = 7.4$ Hz), 0.87 (t, 6H, $J = 7.0$ Hz). ^{13}C NMR, ppm: 184.61, 150.08, 140.77, 138.25, 135.41, 134.05, 130.04, 125.20, 123.15, 122.69, 121.59, 119.56, 118.06, 117.87, 116.46, 115.49, 112.71, 109.10, 108.55, 46.82, 38.71, 30.25, 28.06, 23.69, 22.31, 13.02, 9.95. FDMS: *m/z* 792.3. Elemental analysis: calculated C 81.78, H 7.12, N 7.06; found C 82.05, H 7.05, N 7.18.

*2.7. 1,5-Bis[3-amino-9-ethyl-carbazole]anthraquinone (**4a**)*

3-Amino-9-ethyl-carbazole (1.66 g, 7.94 mmol), 1,5-dichloroanthraquinone (1.00 g, 3.61 mmol), $Pd_2(dba)_3$ (88 mg), BINAP (178 mg), cesium carbonate (4.63 g) and toluene (15 mL) were mixed together and heated at 100 °C for 24 h. The reaction mixture was quenched with water (10 mL) and then extracted with DCM, washed with brine solution and dried over $MgSO_4$. Evaporation of solvent under vacuum resulted in a violet residue. The residue was purified by recrystallization from ethanol. Isolated yield = 63%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 11.46 (s, 2H), 8.12–8.03 (m, 4H), 7.70 (d, 2H, $J = 7.3$ Hz), 7.55–7.41 (m, 10H), 7.35 (d, 2H, $J = 8.6$ Hz), 7.23 (t, 2H, $J = 6.4$ Hz), 4.43 (q, 4H, $J = 7.2$ Hz), 1.47 (t, 6H, $J = 7.0$ Hz). FDMS: *m/z* 624.8.

*2.8. 1,8-Bis[3-amino-9-(2-ethylhexyl)carbazole] anthraquinone (**5**)*

3-Amino-9-(2-ethylhexyl)carbazole (509 mg, 1.73 mmol), 1,8-dichloroanthraquinone (200 mg, 0.722 mmol), $Pd_2(dba)_3$ (17.5 mg), BINAP (35 mg), cesium carbonate (926 mg) and toluene (5 mL) were mixed together and heated at 80 °C for 24 h. The reaction mixture was quenched with water (5 mL) and then extracted with DCM, washed with brine solution and dried over $MgSO_4$. Evaporation of solvent under vacuum resulted in a violet residue, which was purified by column chromatography using 0–20% ethyl acetate/hexane as eluent. Isolated yield = 76%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 11.43 (s, 2H), 8.10–8.04 (m, 4H), 7.63 (dd, 2H, $J = 2.8$ Hz, $J = 5.7$ Hz), 7.54–7.40 (m, 12H), 7.22 (ddd, 2H, $J = 2.1$ Hz, $J = 6.0$ Hz, $J = 7.9$ Hz), 4.16 (d, 4H, $J = 7.5$ Hz), 2.07 (m, 2H), 1.48–1.18 (m, 16H), 0.96–0.80 (m, 12H). FDMS: *m/z* 793.6.

*2.9. 1,4-Bis[3-amino-9-(2-ethylhexyl)carbazole] anthraquinone (**6**)*

3-Amino-9-(2-ethylhexyl)carbazole (509 mg, 1.73 mmol), 1,4-dichloroanthraquinone (200 mg, 0.722 mmol), $Pd_2(dba)_3$ (17.5 mg), BINAP (35 mg), cesium carbonate (926 mg) and toluene (5 mL) were mixed together and heated at 80 °C for 24 h. The reaction mixture was quenched with water (5 mL) and extracted with DCM, washed with brine solution and dried over $MgSO_4$. Evaporation of solvent under vacuum resulted in a violet residue, which was purified by column chromatography using 0–20% ethyl acetate/hexane as eluent. Isolated yield = 80%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 12.53 (s, 2H), 8.41 (dd, 2H, $J = 3.3$ Hz, $J = 5.9$ Hz), 8.04 (d, 2H, $J = 7.7$ Hz), 8.00 (s, 2H), 7.76 (dd, 2H, $J = 3.3$ Hz, $J = 5.9$ Hz), 7.51–7.36 (m, 10H), 7.19 (t, 2H, $J = 7.2$ Hz), 4.16 (d, 4H, $J = 7.5$ Hz), 2.07 (m, 2H), 1.48–1.18 (m, 16H), 0.96–0.80 (m, 12H). ^{13}C NMR, ppm: 182.94, 145.85, 141.87, 139.21, 135.00, 132.64, 131.19, 126.54, 126.33, 125.51, 124.04, 123.75, 122.66, 120.69, 119.17, 117.18, 110.75, 110.13, 109.66, 47.90, 39.81, 31.36, 29.17, 24.78, 23.43, 14.16, 11.06. FDMS: *m/z* 793.2. Elemental analysis: calculated C 81.78, H 7.12, N 7.06; found C 81.96, H 6.98, N 7.00.

*2.10. 1,4,5,8-Tetra[3-amino-9-(2-ethylhexyl)carbazole] anthraquinone (**7**)*

3-Amino-9-(2-ethylhexyl)carbazole (303 mg, 1.44 mmol), 1,4,5,8-tetrachloroanthraquinone (100 mg, 0.289 mmol), $Pd_2(dba)_3$ (15 mg), BINAP (29 mg), cesium carbonate (745 mg) and toluene (5 mL) were mixed together and heated at 100 °C for 72 h. The reaction mixture was quenched with water (10 mL) and then extracted with DCM, washed with brine solution, and dried over $MgSO_4$. Evaporation of the solvent under vacuum resulted in a violet residue. The residue was purified by recrystallization from ethanol. Isolated yield = 42%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 12.14 (s, 4H), 8.03 (d, 8H, $J = 7.8$ Hz), 7.45 (m, 18H), 7.17 (m, 6H), 4.16 (s, 8H), 2.05 (m, 4H), 1.47–1.15 (m, 32H), 0.98–0.76 (m, 24H). FDMS: *m/z* 1378.0. Elemental analysis: calculated C 81.94, H 7.61, N 8.13; found C 82.17, H 7.66, N 7.97.

*2.11. 3,6-Bis(1-anthraquinonylamino)-9-(2-ethylhexyl)carbazole (**8**)*

3,6-Diamino-9-(2-ethylhexyl)carbazole (100 mg, 0.32 mmol), 1-chloroanthraquinone (170 mg, 0.70 mmol), $Pd_2(dba)_3$ (5.9 mg), BINAP (12 mg), cesium carbonate (312 mg) and toluene (5 mL) were mixed together and heated at 100 °C for 24 h. The reaction mixture was quenched with water (5 mL) and extracted with DCM, washed with brine, and dried over $MgSO_4$. Evaporation of the solvent under vacuum resulted in a violet residue. The residue was purified by column chromatography using 0–10% ethyl acetate/hexane as eluent. Isolated yield = 80%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 11.44 (s, 2H), 8.34 (dd, 2H, $J = 1.3$ Hz, $J = 7.7$ Hz), 8.25 (dd, 2H, $J = 1.7$ Hz, $J = 7.4$ Hz), 8.03 (d, 2H, $J = 1.6$ Hz), 7.86–7.72 (m, 4H), 7.64 (dd, 2H, $J = 1.4$ Hz, $J = 6.9$ Hz), 7.55–7.36 (m, 8H), 4.25 (d, 1H, $J = 7.4$ Hz), 2.15 (m, 1H), 1.49–1.21 (m, 8H), 0.97 (t, 3H, $J = 7.4$ Hz), 0.89 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR, ppm: 185.43, 183.69, 151.30, 139.92, 135.29, 135.20, 134.91, 134.31, 133.47, 131.10, 127.06, 126.91, 124.73, 123.41, 120.17, 117.71, 117.20, 113.77, 110.52, 110.47, 48.07, 39.88, 31.34, 29.16, 24.81, 23.43, 14.16, 11.09. FDMS: *m/z* 722.1.

Elemental analysis: calculated C 79.87, H 5.45, N 5.82; found C 80.09, H 5.28, N 5.87.

2.12. Ring-closed product **9**

Compound **8** (500 mg, 0.69 mmol) was dissolved in sulfuric acid (10 mL) and heated at 150 °C for 6 h. The reaction mixture was quenched with ice-cold water and then extracted with dichloromethane. The organic layer was washed with NaOH, 2 N HCl, saturated $NaHCO_3$ and finally with brine. Evaporation of solvent under vacuum resulted in a black residue. The residue was purified by column chromatography using 0–50% ethyl acetate/hexane as eluent to give the title compound as a black solid. Isolated yield = 24%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 8.57 (dd, 2H, $J = 1.1$ Hz, $J = 7.1$ Hz), 8.39 (dd, 2H, $J = 0.9$ Hz, $J = 8.4$ Hz), 8.08 (s, 4H), 7.87 (dd, 2H, $J = 7.2$ Hz, $J = 8.4$ Hz), 7.58 (dd, 2H, $J = 1.1$ Hz, $J = 7.8$ Hz), 7.08 (d, 2H, $J = 7.9$ Hz), 6.34 (t, 2H, $J = 7.1$ Hz), 5.93 (t, 2H, $J = 7.7$ Hz), 4.61 (d, 2H, $J = 7.7$ Hz), 2.28 (s, 1H), 1.70–1.20 (m, 8H), 1.13–0.99 (m, 3H), 0.82 (t, 3H, $J = 6.9$ Hz). ^{13}C NMR, ppm: 181.63, 148.53, 145.19, 137.80, 135.47, 134.92, 132.31, 129.92, 129.60, 129.02, 128.95, 128.62, 128.31, 128.27, 127.40, 127.06, 120.67, 119.86, 117.81, 117.05, 48.78, 41.35, 41.18, 31.57, 31.46, 29.24, 29.13, 25.23, 25.13, 23.34, 23.24, 14.02, 11.26, 11.17. FDMS: *m/z* 686.2.

2.13. 9-(2-Decyltetradecyl)carbazole

A 250 mL Schlenk flask was charged with carbazole (2.00 g, 11.9 mmol), NaH (0.66 g, 16.5 mmol) and 80 mL of DMF. The resulting mixture was stirred for 30 min. 2-Decyltetradecanebromide (6.00 g, 14.28 mmol) was then added under argon and the mixture was stirred overnight at room temperature. The reaction mixture was then quenched with 20 mL of water and extracted three times with diethyl ether (50 mL each). The combined organic fractions were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Silica gel, hexane as eluent) Isolated yield = 88%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 8.20 (d, 2H, $J = 7.7$ Hz), 7.61–7.48 (m, 4H), 7.33 (t, 2H, $J = 7.2$ Hz), 4.24 (d, 2H, $J = 7.4$ Hz), 2.25 (s, 1H), 1.60–1.20 (m, 40H), 1.04 (t, 6H, $J = 6.5$ Hz). ^{13}C NMR, ppm: 141.48, 126.03, 123.27, 120.65, 119.18, 109.54, 48.20, 38.44, 32.56, 32.48, 30.55, 30.30, 30.23, 30.16, 30.02, 29.97, 27.16, 23.33, 14.55. FDMS: *m/z* 503.9.

2.14. 3,6-Dinitro-9-(2-decyltetradecyl)carbazole

$Cu(NO_3)_2 \cdot 2.5H_2O$ (2.21 g, 9.52 mmol) was added into a mixture of acetic acid (10 mL) and acetic anhydride (20 mL) at room temperature. The mixture was stirred for 10 min, and then 9-(2-decyltetradecyl)carbazole (4.00 g, 7.93 mmol) was added slowly in portions over 5 min. Heat was generated during the addition, and an additional 10 mL of acetic acid was added. The mixture was stirred at this temperature for 15 min and then poured into distilled water (200 mL). The yellow precipitate was collected by filtration, washed with water and dried under vacuum. The product was recrystallized from ethanol. Isolated yield = 70%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 9.10 (d, 2H, $J = 2.1$ Hz), 8.46 (dd, 2H, $J = 2.2$ Hz, $J = 9.1$ Hz), 7.55 (d, 2H, $J = 9.1$ Hz), 4.29 (d, 2H, $J = 7.6$ Hz), 2.12 (s, 1H), 1.40–1.12 (m, 40H), 0.87 (t, 6H, $J = 6.4$ Hz). ^{13}C NMR, ppm: 145.63, 142.20, 123.15, 122.84, 117.98, 110.45, 49.15, 38.39, 32.28, 32.16, 30.16, 30.02, 29.95, 29.91, 29.81, 29.73, 29.69, 26.84, 23.07, 14.26. FDMS: *m/z* 594.2.

2.15. 3,6-Diamino-9-(2-decyltetradecyl)carbazole (**12**)

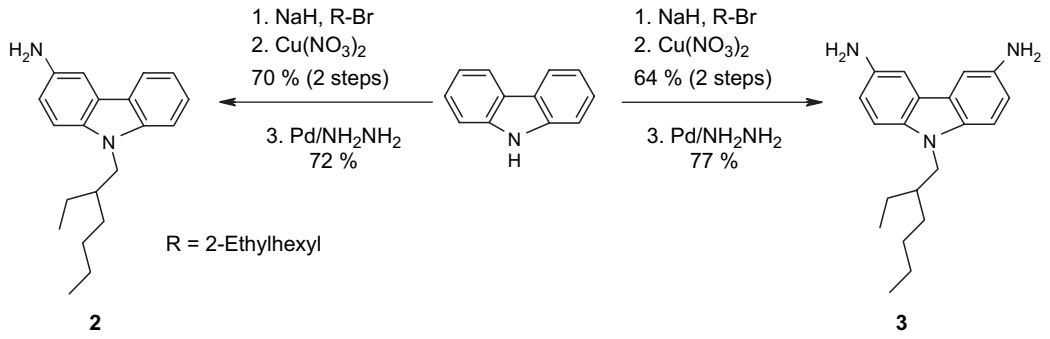
Palladium on charcoal (10%, 173 mg) was added in portions to a hot solution of 3,6-dinitrocarbazole (1.2 g, 2.02 mmol) and hydrazine hydrate (1.5 mL) in ethanol (60 mL) and the mixture was heated under reflux for 2 h. The cooled mixture was filtered and the filtrate was concentrated to give the title product **12**. Isolated yield = 70%. ^{1}H NMR (250 MHz, $CDCl_2$), ppm: 7.27 (d, 2H, $J = 2.1$ Hz), 7.13 (d, 2H, $J = 8.6$ Hz), 6.83 (dd, 2H, $J = 2.2$ Hz, $J = 8.6$ Hz), 4.01 (d, 2H, J = 7.4 Hz), 3.48 (br s, 4H), 2.04 (s, 1H), 1.40–1.10 (m, 40H), 0.88 (t, 1H, $J = 6.5$ Hz). ^{13}C NMR, ppm: 139.03, 136.33, 123.12, 115.65, 109.79, 105.87, 48.16, 38.42, 32.32, 32.23, 30.37, 30.04, 29.99, 29.95, 29.75, 29.73, 26.94, 23.08, 14.27. FDMS: *m/z* 534.4.

2.16. Polymer **13**

The 3,6-diamino-9-(2-decyltetradecyl)carbazole (192 mg, 0.36 mmol), 1,4-dichloroanthraquinone (100 mg, 0.36 mmol), $Pd_2(dba)_3$ (9 mg), BINAP (18 mg), cesium carbonate (462 mg) and toluene (5 mL) were mixed together and heated at 100 °C for 72 h. Then a solution of 1-chloroanthraquinone (10 mg) in 2 mL of toluene was added and the reaction mixture was heated at 100 °C for an additional 6 h. The reaction mixture was precipitated in methanol. The solid was filtered off, redissolved in THF and then reprecipitated from methanol. The polymer obtained was subjected to Soxhlet extraction for 24 h and then dried. Isolated yield = 71%. GPC analysis $M_n = 7 \times 10^3$ g mol^{-1} and PDI = 2.98 (PS standard).

2.17. Polymer **14**

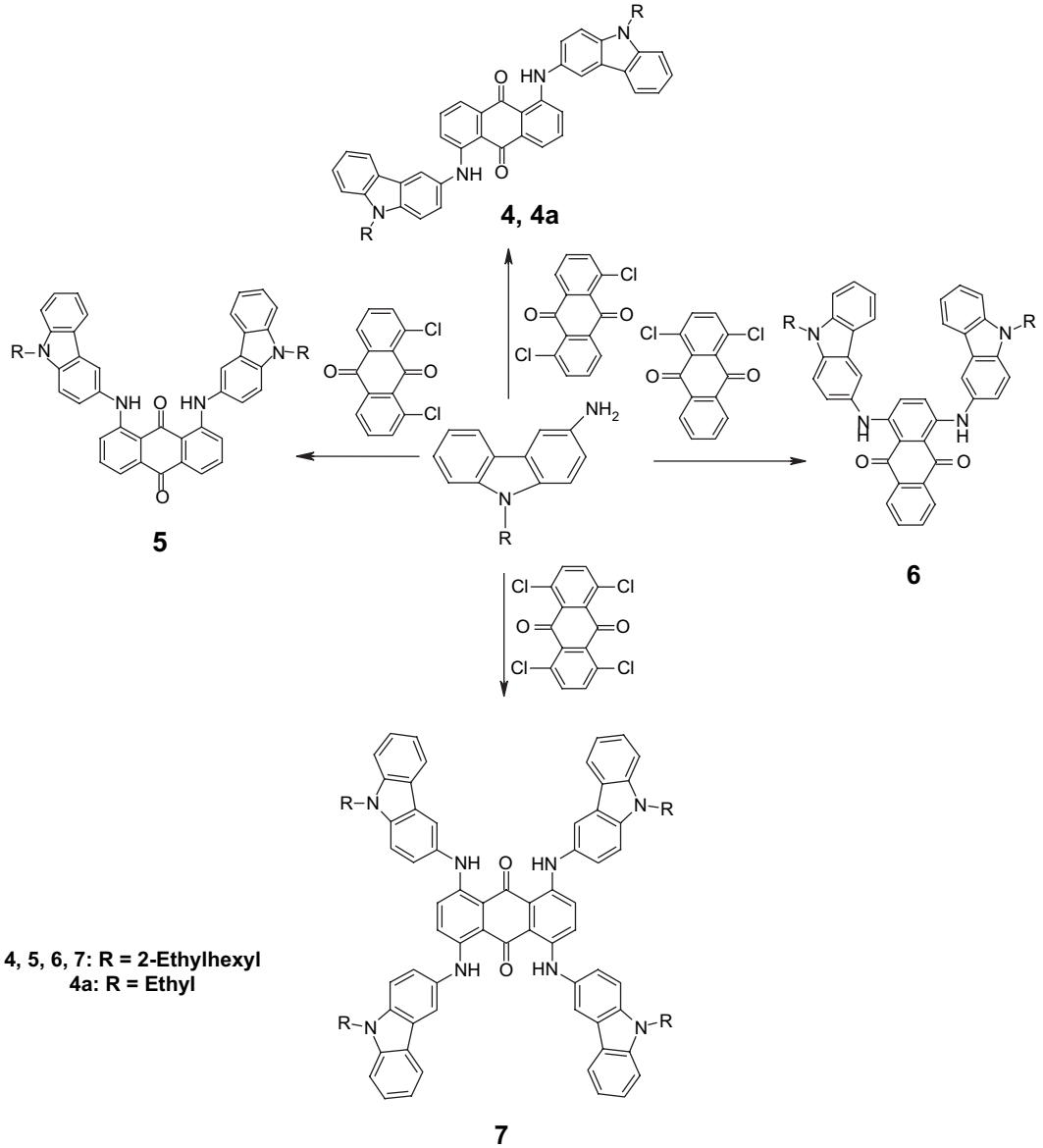
The 3,6-diamino-9-(2-decyltetradecyl)carbazole (96 mg, 0.18 mmol), 1,5-dichloroanthraquinone (50 mg, 0.18 mmol), $Pd_2(dba)_3$ (4.5 mg), BINAP (9 mg), cesium carbonate (231 mg) and toluene (3 mL) were mixed together and heated at 100 °C for 72 h. Then a solution of 1-chloroanthraquinone (5 mg) in 1 mL of toluene was added and the reaction mixture was heated at 100 °C for an additional 6 h. The reaction mixture was precipitated in methanol. The solid was filtered off and redissolved in THF and again precipitated from methanol. The polymer so obtained was subjected to Soxhlet extraction for 24 h and then dried. Isolated yield = 62%. GPC analysis: $M_n = 5.6 \times 10^3$ g mol^{-1} and PDI = 2.53 (PS standard).



Scheme 1. Synthesis of 3-amino and 3,6-diaminocarbazole.

*2.18. Polymer **15***

The 3,6-diamino-9-(2-decyltetradecyl)carbazole (96 mg, 0.18 mmol), 1,8-dichloroanthraquinone(50 mg, 0.18 mmol), $Pd_2(dba)_3$ (4.5 mg), BINAP (9 mg), cesium carbonate (231 mg) and toluene (3 mL) were mixed together and heated at 100 °C for 72 h. Then a solution of 1-chloroanthraquinone (5 mg) in 1 mL of toluene was added and the reaction mixture was heated at 100 °C for an additional 6 h. The reaction mixture was precipitated in methanol. The solid was filtered off and redissolved in



Scheme 2. Coupling of 3-aminocarbazole with chloroanthraquinones.

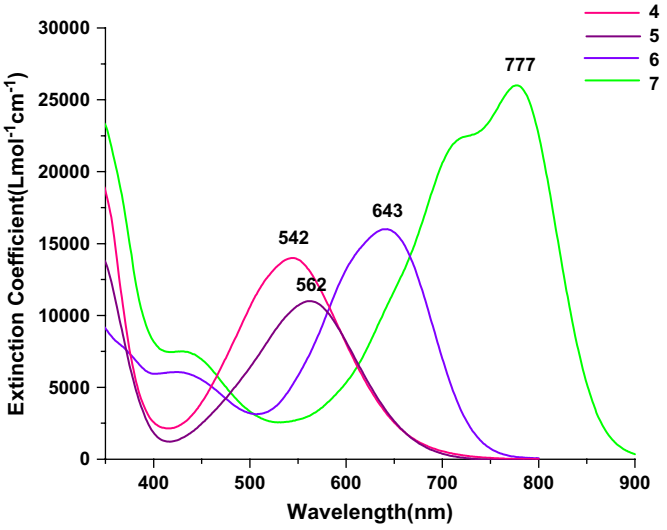


Fig. 1. Absorption spectra for compounds **4**, **5**, **6**, and **7** (THF solution).

THF and again precipitated from methanol. The polymer obtained was subjected to Soxhlet extraction for 24 h and then dried. Isolated yield = 52%. GPC analysis: $M_n = 5.0 \times 10^3$ g mol^{-1} and PDI = 2.30 (PS standard).

3. Results and discussion

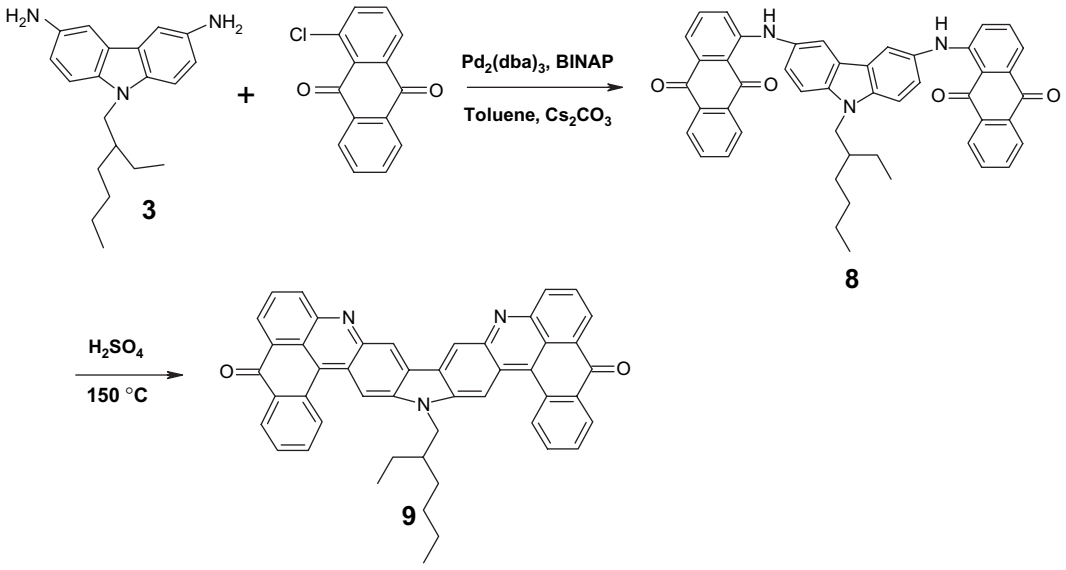
Starting from widely available carbazole, various dyes were synthesized, the structures and synthesis of which are presented below. The synthesis of 3-amino-9-(2-ethylhexyl)carbazole (**2**) and 3,6-diamino-9-(2-ethylhexyl)carbazole (**3**), two of the key intermediates in all the syntheses, are shown in Scheme 1. Carbazole was first alkylated with 2-ethylhexylbromide under argon using sodium hydride as a base in dry DMF in near quantitative yield. This was then selectively converted to either 3-nitro-9-(2-ethylhexyl)carbazole or 3,6-dinitro-9-(2-ethylhexyl)carbazole by varying the amount of the copper nitrate reagent. Finally the reduction of the nitro group with hydrazine in the presence of palladium on charcoal gave the desired 3-aminocarbazole **2** and 3,6-diaminocarbazole **3** in 50% and 49% overall yield, respectively.

The coupling of **2** with 1,5-dichloroanthraquinone under standard Buchwald-type conditions, using $Pd_2(dba)_3$ as catalyst and BINAP as a ligand in the presence of cesium carbonate, gave the dicoupled product **4** in 72% isolated yield (Scheme 2). Use of P(*t*-Bu)$_3$ as a ligand was equally successful. However, when the same reaction was carried out with sodium *tert*-butoxide as a base, only a trace amount of the product was observed. It was found that shorter alkyl chains on the nitrogen of carbazole gave lower yields. The temperature required for completion of the reaction was higher with ethyl than with the 2-ethylhexyl substituent. This can be attributed to the lower solubility of the precursor molecule with the ethyl moiety. Compound **4** was soluble in common organic solvents such as DCM and THF. The solubility was drastically decreased when the ethylhexyl alkyl chain was replaced with the ethyl group. Compound **4** gave a violet solution. The UV–vis absorption spectrum of **4** (Fig. 1) exhibited an absorption maximum at 542 nm and the extinction coefficient was calculated to be 1.40×10^4 L mol^{-1} cm^{-1}. The UV–vis spectrum of the ethyl substituted **4a** demonstrated that the absorption maximum was the same, while the extinction coefficient was found to be 2.05×10^4 L mol^{-1} cm^{-1}. The IR spectrum of **4** showed only one carbonyl stretch at 1617 cm^{-1}, which revealed that the imine of carbazole was interacting with the respective carbonyl group of anthraquinone and that the two carbonyl moieties were equivalent. However, the absorption maximum was blue-shifted compared to violet 23 (602 nm) and the extinction coefficient was five times lower (violet 23, $\varepsilon = 1.01 \times 10^5$ L mol^{-1} cm^{-1}).

To improve the conjugation within the molecule and to induce a red-shift in the absorption maximum, an analogous coupling of **2** with 1,8-dichloroanthraquinone was performed, which gave the product **5** in 76% isolated yield (Scheme 2). Compound **5** was soluble in common organic solvents like DCM and THF to give a violet solution. The UV–vis spectrum of **5** (Fig. 1) exhibited an absorption maximum at 562 nm, red-shifted by 20 nm compared to **4**. This suggested that the 1,8-isomer **5** was better conjugated than the 1,5-isomer **4**. The extinction coefficient of **5** was found to be 1.1×10^4 L mol^{-1} cm^{-1}, less than the value obtained for **4**. The IR spectrum of **5** revealed two bands in the carbonyl region at 1660 cm^{-1} and 1613 cm^{-1}, which suggested that the two carbonyl groups were different and that one was interacting more with the amine of carbazole as compared to the other. The absorption maximum and extinction coefficient of **5** was too hypsochromic and low, respectively, for use as a pure violet pigment. To further improve the conjugation between the two aminocarbazoles through anthraquinone, 1,4-dichloroanthraquinone was coupled with 3-aminocarbazole **2** to generate the product **6** in 80% isolated yield (Scheme 2). Compound **6** was soluble in common organic solvents such as DCM and THF, to give a greenish-blue solution. The UV–vis absorption spectrum (Fig. 1) of **6** exhibited an absorption maximum at 643 nm and an extinction coefficient of

Table 1
Optical and physical data for dyes (**4**, **4a**, **5**, **6**, and **7**)

Compound	Chloroanthraquinone	Substituent on nitrogen	λ_{max} (nm)	Extinction coefficient (L mol^{-1} cm^{-1}) $\times 10^{-4}$	Color
4	1,5-	2-Ethylhexyl	542	1.40	Violet
4a	1,5-	Ethyl	542	2.05	Violet
5	1,8-	2-Ethylhexyl	562	1.10	Violet
6	1,4-	2-Ethylhexyl	643	1.60	Greenish-blue
7	1,4,5,8-	2-Ethylhexyl	777	2.60	Green



Scheme 3. Synthesis of red-emitting material **9**.

1.60×10^4 L mol^{-1} cm^{-1}. The 1,4-isomer showed the highest bathochromic absorption maxima among the three isomeric coupling products, **4**, **5** and **6**. The same was true with extinction coefficients, which was highest for the 1,4-isomer. The IR spectrum of **6** revealed a single peak at 1599 cm^{-1} in the carbonyl region suggested that the secondary amine was interacting with the carbonyl group of anthraquinone stronger than in the 1,5- and 1,8-isomers.

The above results suggested that the substitution pattern on the anthraquinone has a significant impact on the absorption maximum of the resulting dye. To extend the concept, 1,4,5,8-tetrachloroanthraquinone was treated with an excess of 3-amino-9-(2-ethylhexyl)carbazole under standard Buchwald conditions to give the tetracoupled product **7** in 42% isolated yield (Scheme 2). In this case, the reaction took longer (72 h) time and required a higher temperature (100 °C) for the coupling to reach completion. Compound **7** was soluble in DCM and THF to yield a green solution. The UV–vis spectrum (Fig. 1) of **7** exhibited an absorption maximum at 777 nm and an extinction coefficient of 2.60×10^4 L mol^{-1} cm^{-1}. This

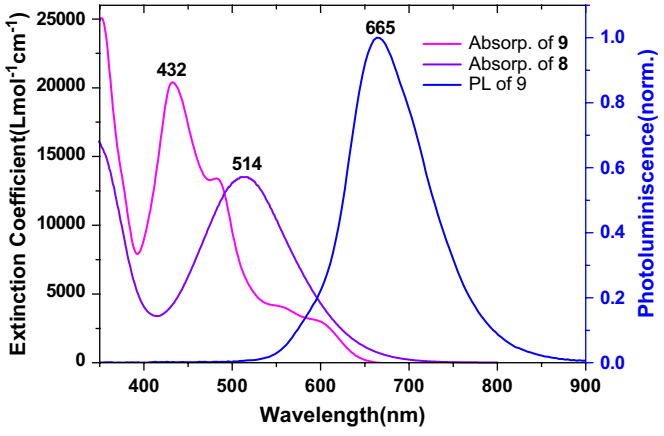


Fig. 2. Optical properties of **8** and **9**.

was the highest amongst the molecules synthesized in this investigation. This dye has potential for near infrared absorption applications.

All the results for dyes derived from 3-aminocarbazole and different isomers of dichloroanthraquinone and 1,4,5,8-tetrachloroanthraquinone are summarized in Table 1.

*3.1. Synthesis of a novel red-emitting material by double dehydration of 3,6-bis(1-anthraquinonylamino)-9-(2-ethylhexyl)carbazole (**8**)*

3,6-Diaminocarbazole was coupled with 1-chloroanthraquinone under standard Buchwald-type conditions to generate **8** in 80% yield (Scheme 3). Compound **8** was soluble in common organic solvents like THF and DCM. The UV–vis (Fig. 2) spectrum of **8** showed an absorption maximum at 513 nm, with an extinction coefficient of 1.35×10^4 L mol^{-1} cm^{-1}, and gave a pinkish-violet solution. In comparison with molecule **4**, the absorption maximum for molecule **8** was blue-shifted by 28 nm, which suggested that the increase in anthraquinone content led to a blue-shift in the absorption maximum. The IR spectrum exhibited two bands in the carbonyl region at 1669 cm^{-1} and 1627 cm^{-1} suggesting that the secondary amine of **8** was in poor conjugation with the carbonyl of the anthraquinone when compared with **4** (1617 cm^{-1}). In order to narrow the absorption band width, compound **8** was treated with sulfuric acid at 150 °C to generate the ring-closed product **9** in 24% yield (Scheme 3).

Compound **9** yielded a pale yellow solution and exhibited a fluorescence maximum at 665 nm, compared to the pinkish-violet color and absence of fluoresence for the precursor molecule **8**. Compound **9** was characterized by ^{1}H NMR, ^{13}C NMR, ^{1}H COSY, mass spectrometry, UV–vis and IR spectroscopy. Interestingly, two of the aromatic protons of **9** appeared at 6.34 and 5.93 ppm, which was more upfield than expected, and the aliphatic region in the ^{13}C NMR spectrum

showed two signals for each alkyl carbon. To understand this abnormality, theoretical calculations of **9** were undertaken (PC SPARTAN PRO Semi-Empirical Program (RHF/AM1)) to find out the different conformations possible for this molecule. The results revealed (Fig. 3) that the molecule was not planar and existed in two different conformations, viz., a *cis* and *trans* forms.

These calculations also explained the anomalies in ^{1}H NMR spectrum where the aromatic protons that appeared at high field were not in the plane of the carbazole ring, but instead were shielded by the aromatic π-system. This also accounted for certain anomalies in the ^{13}C NMR signals for the alkyl carbons, as two conformational isomers were possible. The UV–vis spectrum of **9** (Fig. 2) exhibited a strong absorption band at 432 nm with shoulder at a 482 nm and the extinction coefficient at 432 nm was found to be 2.04×10^4 L mol^{-1} cm^{-1}. The absorption maximum of **9** was blue-shifted by 82 nm in comparison with precursor molecule **8**, suggesting that the conjugation was hindered as a result of the dehydration reaction. The observed carbonyl stretch in IR spectrum of **9** at 1658 cm^{-1}, corresponding to the carbonyl group, implied weak conjugation with the rest of the molecule. The absorption maximum and the measured carbonyl stretch are consistent with the model compound **10** (Fig. 4) which absorbs at 356 nm ($\varepsilon_{max} = 1.54 \times 10^4$ L mol^{-1} cm^{-1}) and has its carbonyl stretch at 1664 cm^{-1} [9].

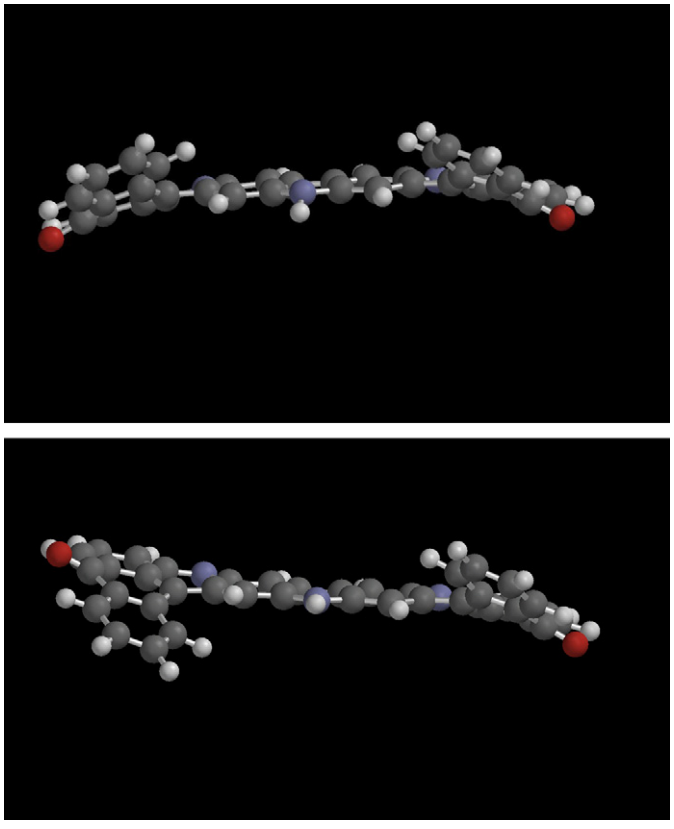


Fig. 3. *Cis* and *trans* conformers of compound **9** as calculated from "PC SPARTAN PRO Semi-Empirical Program (RHF/AM1)".

3.2. Polymers based on diaminocarbazole and dichloroanthraquinone

Polymers based on diaminocarbazole and dichloroanthraquinone were also synthesized to achieve the maximum possible conjugation length and thereby the maximum red-shift in absorption spectrum. The conditions for polymerization were optimized by varying the choice of catalyst and ligand, temperature and solvent. The best results were obtained when $Pd_2(dba)_3$ was used as a catalyst and BINAP as the ligand, at 100 °C in toluene. First, the polymerization was carried out with 3,6-diamino-9-(2-ethylhexyl)carbazole (**3**) with 1,5-dichloroanthraquinone. This resulted in an insoluble polymer, due to strong inter- and intrachain hydrogen bonding. However, when the polymerization was done with 3,6-diamino-9-(2-decyltetradecyl)carbazole (**12**), a polymeric material soluble in common organic solvents like DCM and THF was obtained. The longer branched alkyl chain was sufficient to overcome the inter- and intrachain hydrogen bonding by giving enough entropy to the polymer chain. The 3,6-diaminocarbazole **12** was synthesized by the same procedure as shown in Scheme 1.

Three additional polymers were synthesized by copolymerization of **12** with 1,4-dichloroanthraquinone, 1,5-dichloroanthraquinone and 1,8-dichloroanthraquinone to generate **13**, **14** and **15**, respectively, as shown in Scheme 4. Diaminocarbazole **12** was coupled with 1,4-dichloroanthraquinone in stoichiometric ratio with $Pd_2(dba)_3$ as the catalyst and BINAP as the ligand at 100 °C in toluene to give polymer **13** (71% yield), which was soluble in common organic solvents like DCM and THF. GPC analysis displayed a number average molecular weight (M_n) of 7.0×10^3 g mol^{-1} with a polydispersity index (PDI) of 3.0. This corresponds to a degree of polymerization of about 19. Further attempts to increase the molecular weight of the polymer by varying the monomer concentration, temperature and the catalyst ligand systems were not successful. The UV–vis absorption spectrum of **13** (Fig. 5) exhibited an absorption maximum at 645 nm with an extinction coefficient of 2.25×10^4 L mol^{-1} cm^{-1}. When compared to model compound **6**, the polymer showed no change in the absorption maximum suggesting that the chromophore was confined to the monomer unit.

An analogous polymerization of **12** with 1,5-dichloroanthraquinone under the same conditions resulted in polymer **14** in 62% yield. GPC analysis demonstrated an M_n value of 5.6×10^3 g mol^{-1} with a PDI of 2.5, which corresponds to

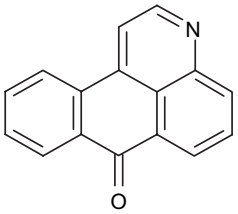


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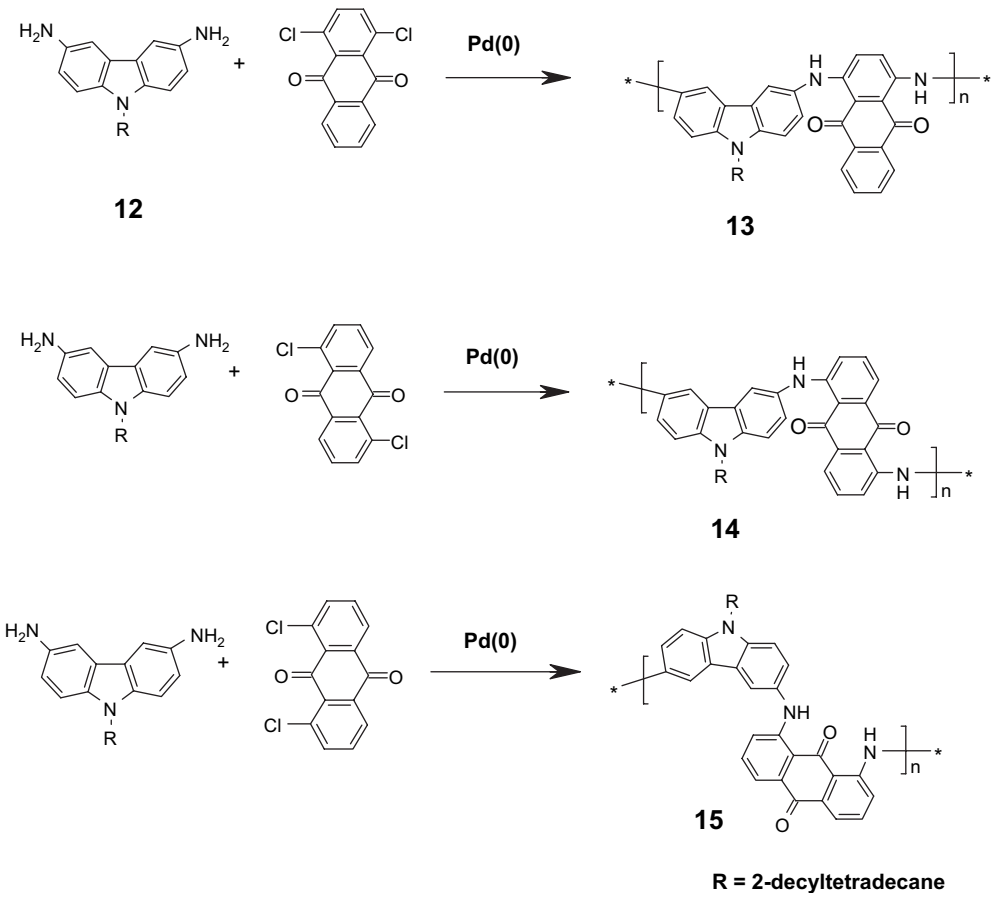
Fig. 4. Model compound **10**.



Scheme 4. Synthesis of polymers **13**, **14**, and **15**.

a degree of polymerization of about 15. The UV–vis (Fig. 5) spectrum of **14** exhibited an absorption maximum at 543 nm, with an extinction coefficient of 1.4×10^4 L mol^{-1} cm^{-1}, and gave a violet solution. Again, in comparison with model compound **4**, polymer **14** displayed no change in the absorption maximum or the extinction coefficient. Similar results were observed when **12** was polymerized with 1,8-dichloroanthraquinone. GPC analysis showed an M_n value of 5.00×10^3 g mol^{-1} with a PDI of 2.3, which corresponds to a degree of polymerization of about 14. The results obtained for all three copolymers are summarized in Table 2.

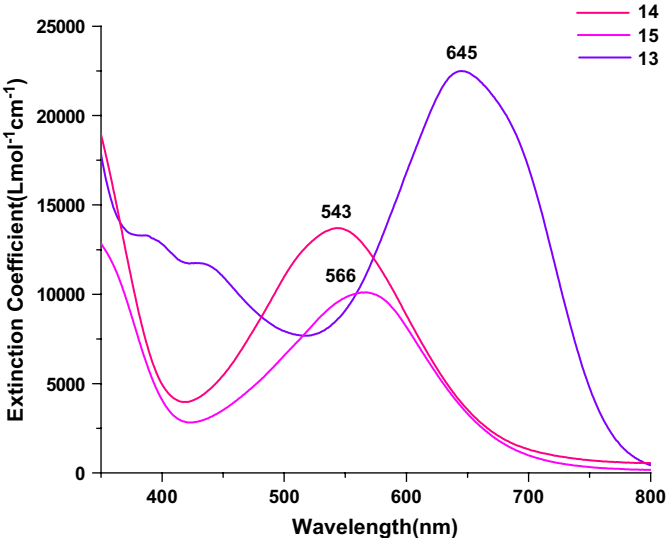


Fig. 5. Absorption spectra of compounds **13**, **14** and **15**.

4. Conclusions

In conclusion, a series of carbazole-based dyes have been synthesized by Buchwald-type coupling of 3-amino and 3,6-diaminocarbazole with various isomers of chloro- and dichloroanthraquinone. With increasing carbazole content, the absorption maxima of the resulting dye was found to vary from 513 nm (pinkish-violet) to 777 nm (green). When diaminocarbazole was coupled with 1-chloroanthraquinone, the resulting product underwent double dehydration upon treatment with sulfuric acid to generate a red-emitting

Table 2
Optical and physical data for polymers (**13**, **14**, and **15**)

Polymer	$M_n \times 10^{-3}$[a]	PDI	λ_{max} (nm)	Extinction coefficient (L mol^{-1} cm^{-1}) $\times 10^{-4}$	Color
13	7.0	3.0	645	2.25	Greenish-blue
14	5.6	2.5	543	1.37	Violet
15	5.0	2.3	566	1.01	Violet

[a] Calibrated against PS standard.

material. Also, a series of soluble polymers were synthesized by coupling of diaminocarbazole with 1,4-, 1,5- and 1,8-dichloroanthraquinone. The resulting polymers showed absorption maxima similar to their model compounds suggested that the conjugation in these materials were largely confined to their monomer units.

Acknowledgement

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