

Supporting Information

Synthesis and Reduction of Nitrogen-Substituted Diaryl Dihydrophenazine Diradical Dications

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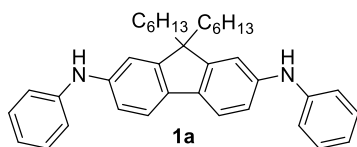
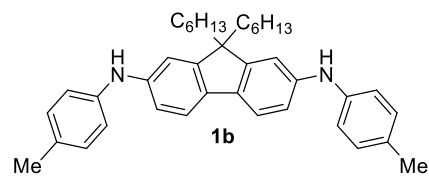
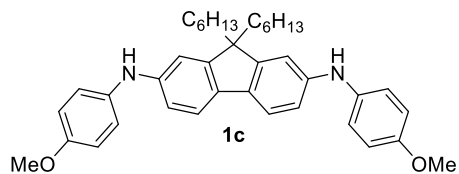
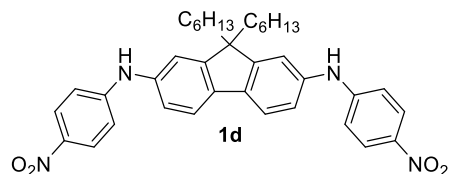
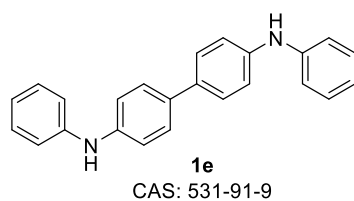
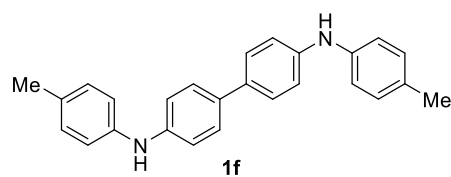
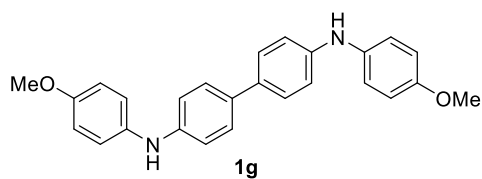
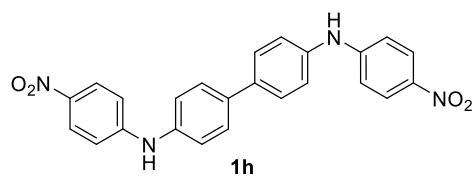
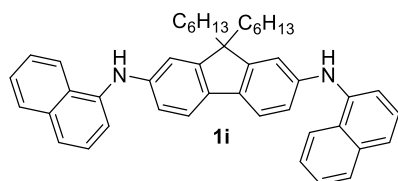
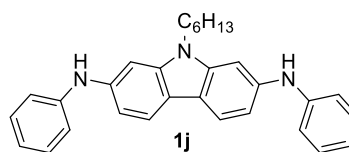
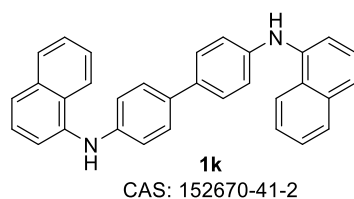
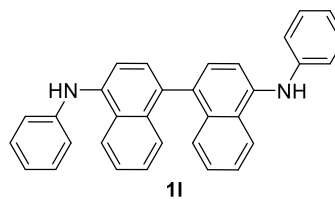
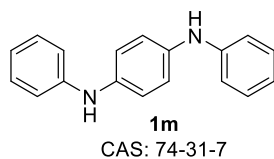
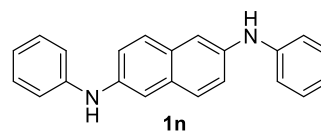
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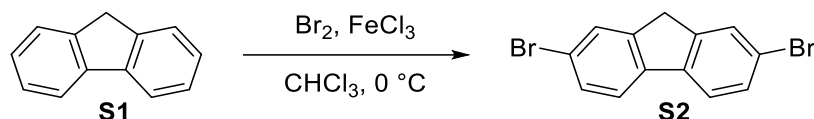
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General Considerations

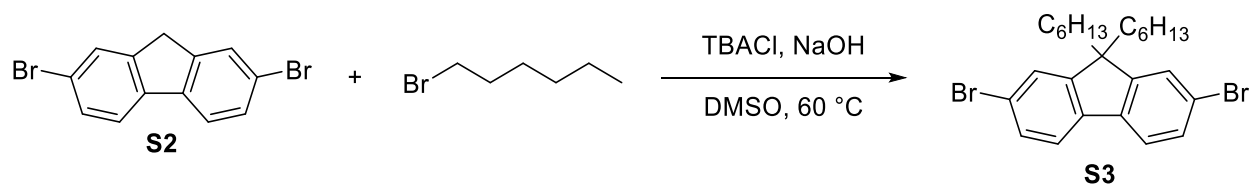
All reactions were performed under nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Commercial chemicals were purchased from suppliers including Sigma-Aldrich, TCI, Alfa Aesar, Fisher Scientific, Combi-Block and others and were used directly without further purification unless otherwise noted. Compounds synthesized following literature procedures matched the analytical data reported (by ^1H and ^{13}C NMR). Automated preparative chromatography was performed with a Yamazen Smart Flash AI-580S-Premium chromatography system. ^1H NMR and ^{13}C NMR were recorded on Bruker AV-III-400 and Bruker Avance-III-800 instruments with chemical shifts reported relative to residual solvent. HRMS data were obtained on a Thermo LTQ-Orbitrapmass spectrometer with a FTMS analyzer. Ultraviolet-Visible Light (UV-Vis) spectra were measured with an Agilent Technologies Cary 6000i UV-Vis-NIR Spectrophotometer using a 1-cm, two-window quartz cuvette. Solutions were prepared in tetrahydrofuran (THF) at a concentration of 1.5×10^{-4} mM. Electrochemical measurements, cyclic voltammetry (CV) and differential pulse voltammetry (DPV), were carried out on a Biologic SP-150 potentiostat in a three-electrode cell at a scan rate of 40 mV/s, at 1.5×10^{-4} mM with 0.2 M TBAPF₆ in THF as the supportive electrolyte, a platinum button working electrode, a platinum wire as the counter electrode, and a leakless Ag/AgCl electrode as reference electrode inside a nitrogen-filled glovebox. The voltammograms are reported in IUPAC convention, at 1mM analyte concentration with 0.2 M TBAPF₆ in THF as the supportive electrolyte, a platinum button working electrode, a platinum wire as the counter electrode, and a leakless Ag/AgCl electrode as reference electrode. The voltage was scanned from -1.0 to 1.0 V vs Ag/AgCl. The spectroelectrochemical experiments were measured using a Biologic SP-150 potentiostat in combination with the Agilent Technologies Cary 6000i UV-Vis-NIR Spectrophotometer. Electron paramagnetic resonance (EPR) measurements were performed on a Bruker EMX EPR Spectrometer at room temperature (RT) in THF. The molecular weight and polydispersity data were collected on a TOSOH Bioscience EcoSEC 8320GPC equipped with a Bryce-type double path refractive index detector and two TSKgel SuperMultiporeHZ-M columns. For the molecular weight and dispersity characterizations, tetrahydrofuran (THF) at 40 °C was used as the mobile phase at a flow rate of 0.35 mL/min. Density Functional Theory calculation were carried out using the Gaussian16¹ program suite with the hybrid functional B3LYP (the Becke three parameter exchange functional² and Lee–Yang–Parr correlation functional³) with all electron 6-31+G(d,p) basis set. The optimized geometry of the molecules with no imaginary frequency confirmed the global minima in the potential energy surface. Vertical excitation energies were computed using Time-Dependent DFT (TD-DFT)⁴ calculations using the same functional and basis set used to compute the optimized geometries. All calculations were carried out considering an isolated molecule in THF solvent and the solvation model used was IEFPCM.⁵

Synthesis & Characterization of Diamine Precursors

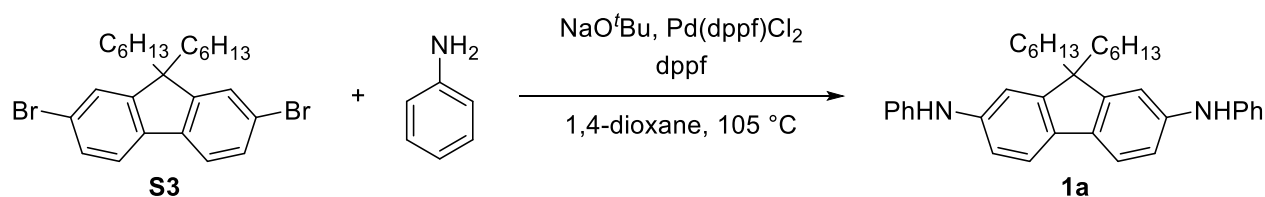




2,7-Dibromo-9H-fluorene S2 was synthesized following a literature procedure⁶: Fluorene **S1** (10.0 g, 60.2 mmol, 1.0 eq) and FeCl₃ (0.15 g, 1.20 mmol, 0.02 eq) were dissolved into chloroform (50 mL). To the reaction, a premix solution of Br₂ (6.5 mL, 126.3 mmol, 2.1 eq) in chloroform (20 mL) was added dropwise at 0 °C. The reaction was warmed to RT and stirred for 2 h. The reaction was then quenched with a saturated aqueous solution of sodium hydrogen sulfite. The reaction was then extracted with dichloromethane (3 x 30 mL). The organic layer was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The resulting white solid was used without further purification (17.8 g, 92% yield).



2,7-dibromo-9,9-di-hexyl-9H-fluorene S3 was synthesized following a literature procedure⁷: 2,7-Dibromo-9H-fluorene **S2** (8.0 g, 24.7 mmol, 1.0 eq) and tetrabutylammonium chloride (0.82 g, 2.96 mmol, 0.12 eq) were dissolved in DMSO (64 mL). The reaction was heated in an oil bath to 60 °C to fully dissolve the solids. Then, 1-bromohexane (8.8 mL, 64.2 mmol, 2.6 eq) was added dropwise and the reaction was cooled to room temperature. Once at room temperature aqueous NaOH (50% w/w, 40 mL) was added to the reaction. After 24 h, hexane (50 mL) and water (200 mL) were added to the reaction. The organic layer was collected, washed with 1M HCl and water. The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The crude product was purified by column chromatography (100% hexanes) to give a white solid (10.3 g, 85% yield).



9,9-di-hexyl-*N,N'*-diphenyl-9H-fluorene-2,7-diamine 1a was synthesized by the following procedure adapted from the literature⁸: To a 10-mL Schlenk tube, **S3** (0.50 g, 1.0 mmol, 1.0 eq), sodium *tert*-butoxide (0.39 g, 4.1 mmol, 4.0 eq), Pd(dppf)Cl₂ (74 mg, 0.10 mmol, 0.1 eq), and dppf (0.14 g, 4.1 mmol, 0.25 eq) were added. The reactor was evacuated and backfilled with N₂ three times. Under positive pressure, degassed aniline (0.37 mL, 4.1 mmol, 4.0 eq) and anhydrous 1,4-dioxanes (5.0 mL) were added via syringes. The reactor was sealed and heated in an oil bath at 105 °C. After 48 h, the reactor was cooled to room temperature, and the reaction quenched with water (5 mL). The reaction was then extracted with dichloromethane (3 x 30 mL). The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The pure compound was isolated by flash column chromatography (7:3 hexanes:DCM) which resulted

in an off-white solid (0.46 g, 88%). ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 8.17 (s, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.20 (t, J = 8.4 Hz, 4H), 7.07-7.00 (m, 8H), 6.78 (t, J = 7.3 Hz, 2H), 1.87-1.83 (m, 4H), 1.12-1.04 (m, 12H), 0.75 (t, J = 6.8 Hz, 6H), 0.68-0.57 (m, 4H); ^{13}C NMR (101 MHz, DMSO- d_6): δ (ppm) 150.8, 144.1, 141.4, 133.6, 129.1, 119.4, 119.1, 116.4, 116.0, 112.0, 54.2, 31.0, 29.0, 23.5, 22.0, 13.8; HRMS (ESI+) $[\text{M}]^+$ calcd. or $\text{C}_{37}\text{H}_{44}\text{N}_2$: m/z = 516.3504, Found: m/z = 516.3480.

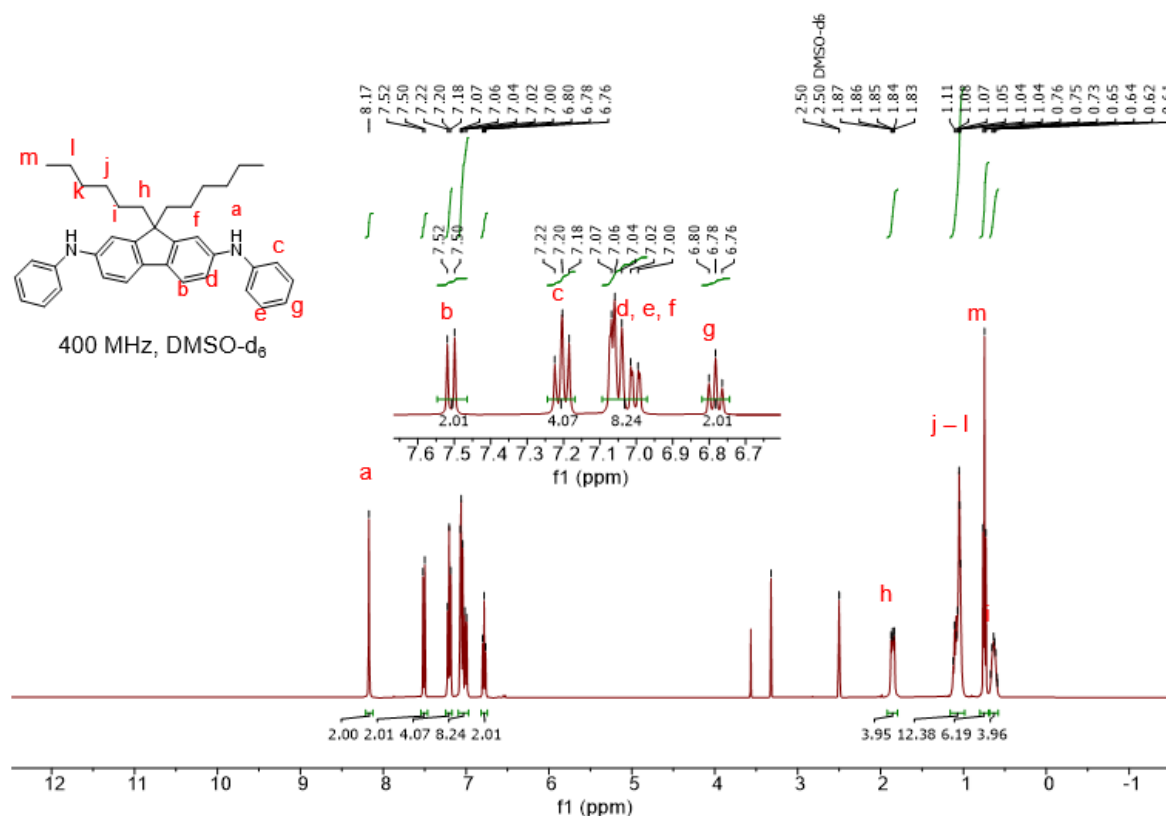


Fig S1. ^1H NMR of **1a**.

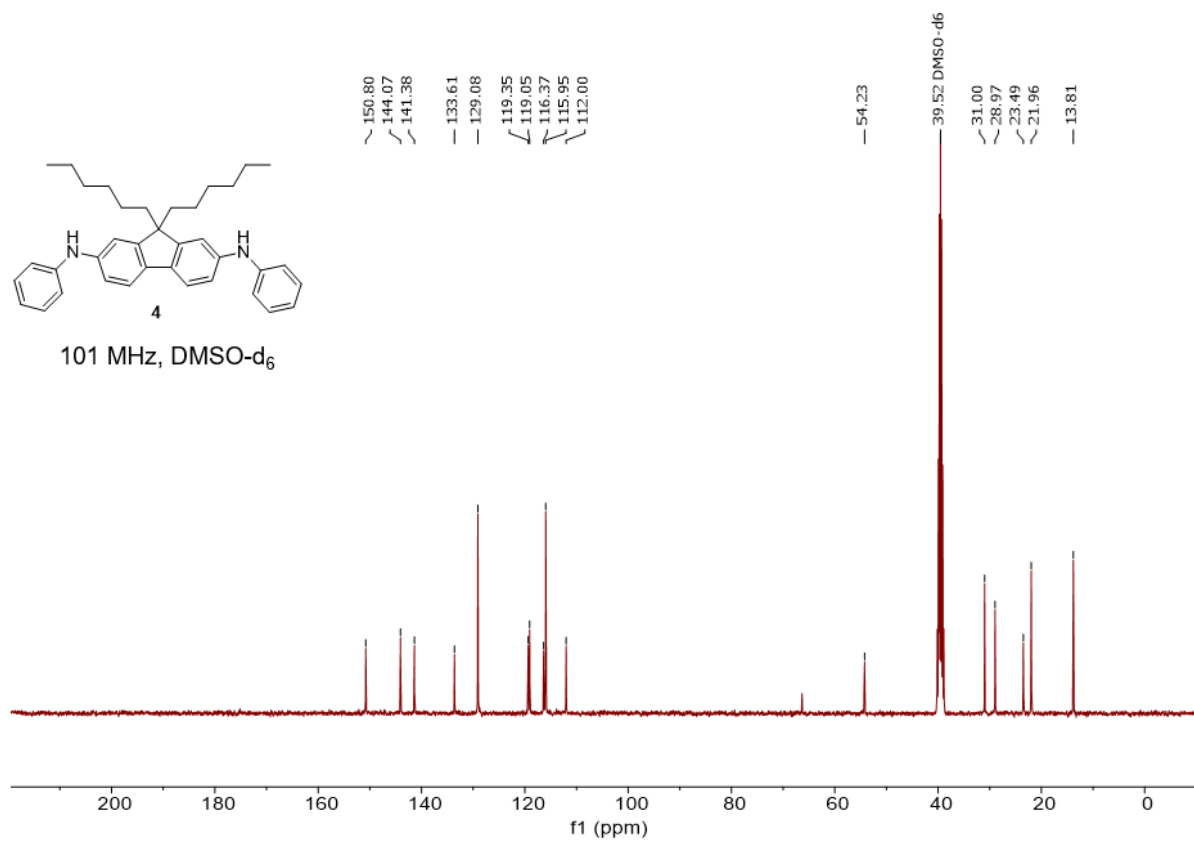
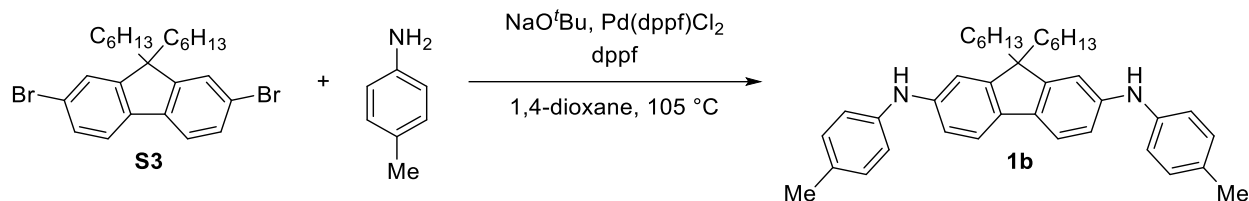


Fig S2. ^{13}C NMR of **1a**.



9,9-dihexyl-*N*²,*N*⁷-di-*p*-tolyl-9H-fluorene-2,7-diamine **1b** was synthesized by the following procedure adapted from the literature⁸: To a 10-mL Schlenk tube, **S3** (0.15 g, 0.30 mmol, 1.0 eq), *p*-toluidine (0.13 g, 1.22 mmol, 4.0 eq), sodium *tert*-butoxide (0.12 g, 1.22 mmol, 4.0 eq), Pd(dppf)Cl₂ (22 mg, 0.031 mmol, 0.1 eq), and dppf (42 mg, 0.76 mmol, 0.25 eq) were added. The reactor was evacuated and backfilled with N₂ three times. Under positive pressure, anhydrous 1,4-dioxane (1.5 mL) was added via syringe. The reactor was sealed and heated in an oil bath at 105 °C. After 48 h, the reactor was cooled to room temperature, and the reaction quenched with water (5 mL). The reaction mixture was then extracted with dichloromethane (3 x 30 mL). The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The pure compound was isolated by flash column chromatography (1:1 hexanes:DCM) which resulted in an off-white viscous syrup that solidified after three days (0.16 g, 94%). ¹H NMR (800 MHz, DMSO-*d*₆): δ (ppm) 8.01 (s, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.06-6.91 (m, 12H), 2.22 (s, 6H), 1.85-1.78 (m, 4H), 1.14-0.99 (m, 12H), 0.75 (t, *J* = 7.5 Hz, 6H), 0.66-0.60 (m, 4H); ¹³C NMR (201 MHz, DMSO-*d*₆): δ (ppm) 150.7, 142.0, 141.4, 133.1, 129.5, 128.0, 119.2, 116.7, 115.5, 111.20, 66.3, 54.1, 32.0, 27.0, 23.5, 22.0, 20.2, 13.8; HRMS (ESI⁺) [*M*]⁺ calcd. or C₃₉H₄₈N₂: *m/z* = 544.3818, Found: *m/z* = 544.3813.

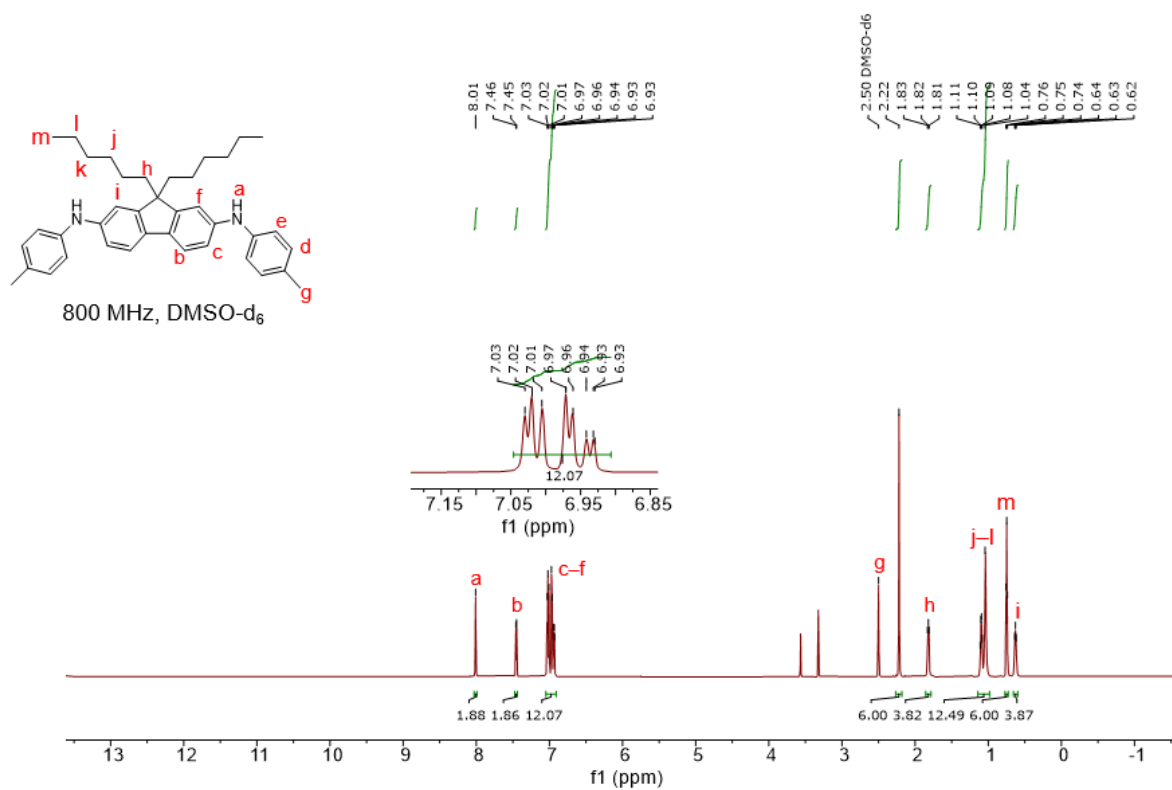


Fig S3. ^1H NMR of **1b**.

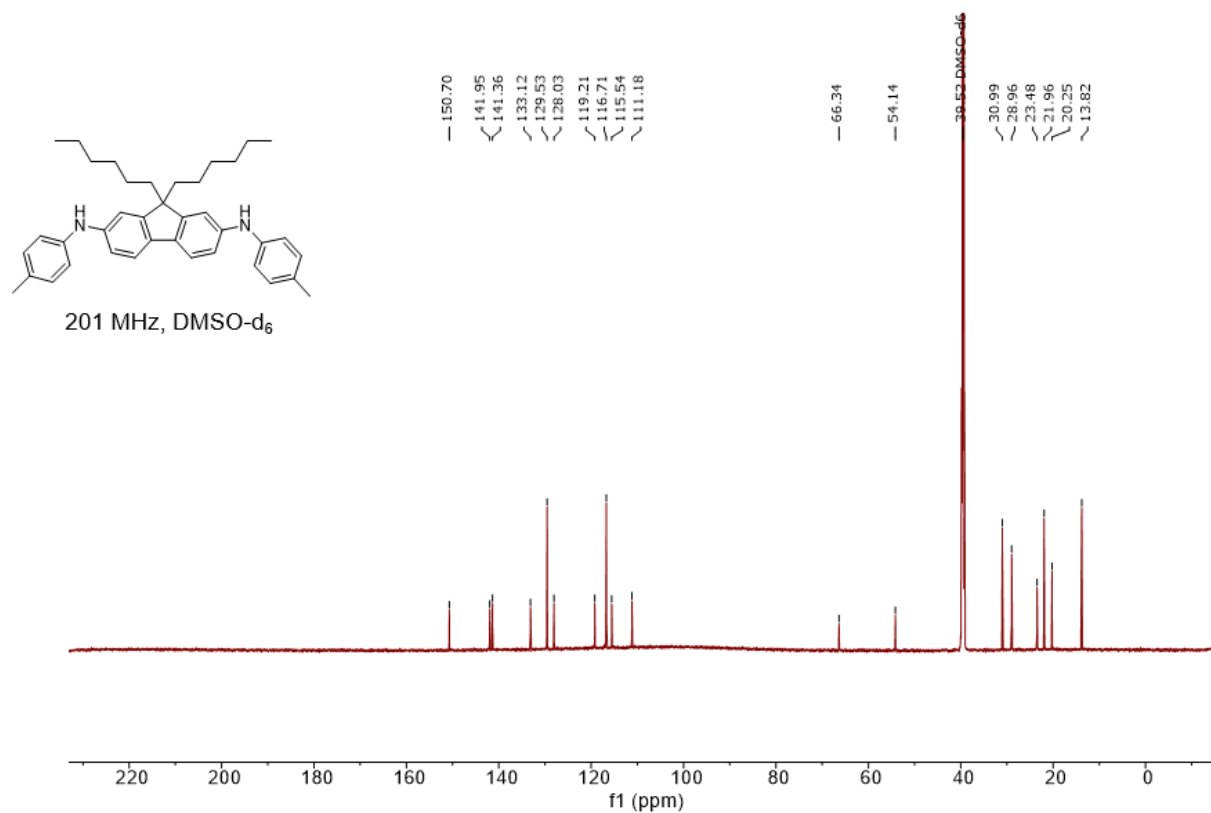
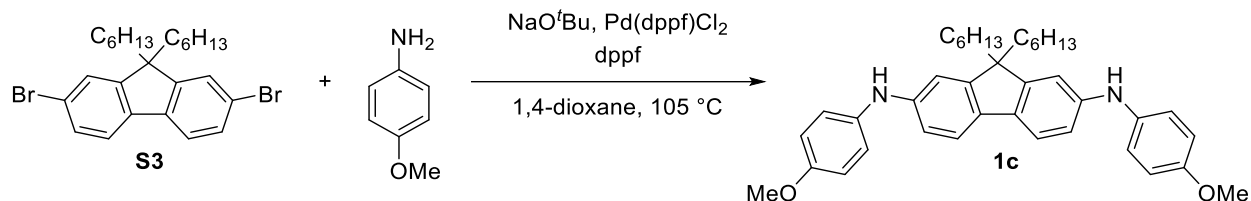


Fig S4. ¹³C NMR of **1b**.



9,9-dihexyl-*N*²,*N*⁷-bis(4-methoxyphenyl)-9*H*-fluorene-2,7-diamine **1c** was synthesized by the following procedure adapted from the literature⁸: To a 10-mL Schlenk tube, **S3** (0.15 g, 0.30 mmol, 1.0 eq), *p*-anisidine (0.15 g, 1.22 mmol, 4.0 eq), sodium *tert*-butoxide (0.12 g, 1.22 mmol, 4.0 eq), Pd(dppf)Cl₂ (22 mg, 0.030 mmol, 0.1 eq), and dppf (42 mg, 0.076 mmol, 0.25 eq) were added. The reactor was evacuated and backfilled with N₂ three times. Under positive pressure, anhydrous 1,4-dioxane (1.5 mL) was added via syringe. The reactor was sealed and heated in an oil bath at 105 °C. After 48 h, the reactor was cooled to room temperature, and the reaction quenched with water (5 mL). The reaction mixture was then extracted with dichloromethane (3 x 30 mL). The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The pure compound was isolated by flash column chromatography (1:2 hexanes:DCM) which resulted in a yellow viscous syrup that solidified after three days (0.16 g, 94%). ¹H NMR (800 MHz, DMSO-*d*₆): δ (ppm) 7.84 (s, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 4H), 6.93 (s, 2H), 6.88-6.82 (m, 6H), 3.71 (s, 6H), 1.82-1.78 (m, 4H), 1.12-0.99 (m, 12H), 0.75 (t, *J* = 7.5 Hz, 6H), 0.66-0.60 (m, 4H); ¹³C NMR (201 MHz, DMSO-*d*₆): δ (ppm) 153.3, 150.7, 142.9, 137.0, 132.6, 119.2, 119.1, 114.5, 114.3, 110.1, 66.3, 55.2, 54.1, 31.0, 29.0, 23.5, 22.1, 13.9; HRMS (ESI+) [*M*]⁺ calcd. for C₃₉H₄₈N₂O₂: *m/z* = 576.3716, Found: *m/z* = 576.3711.

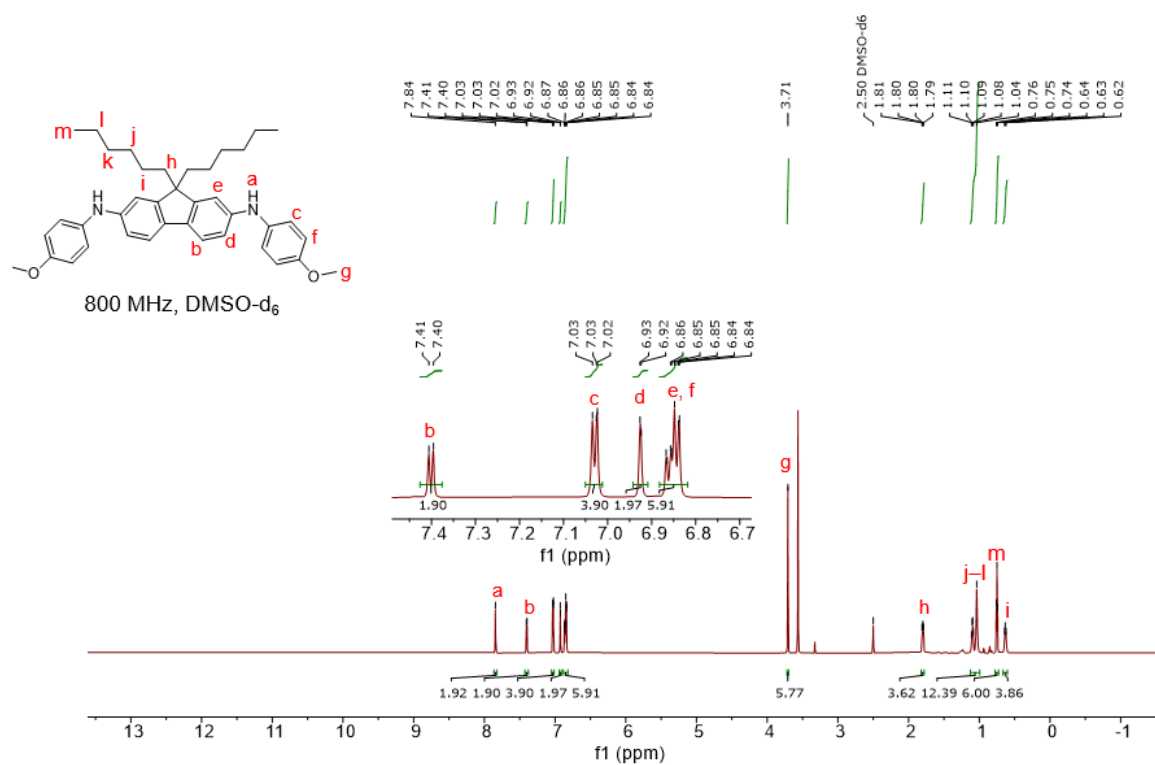


Fig S5. ^1H NMR of **1c**.

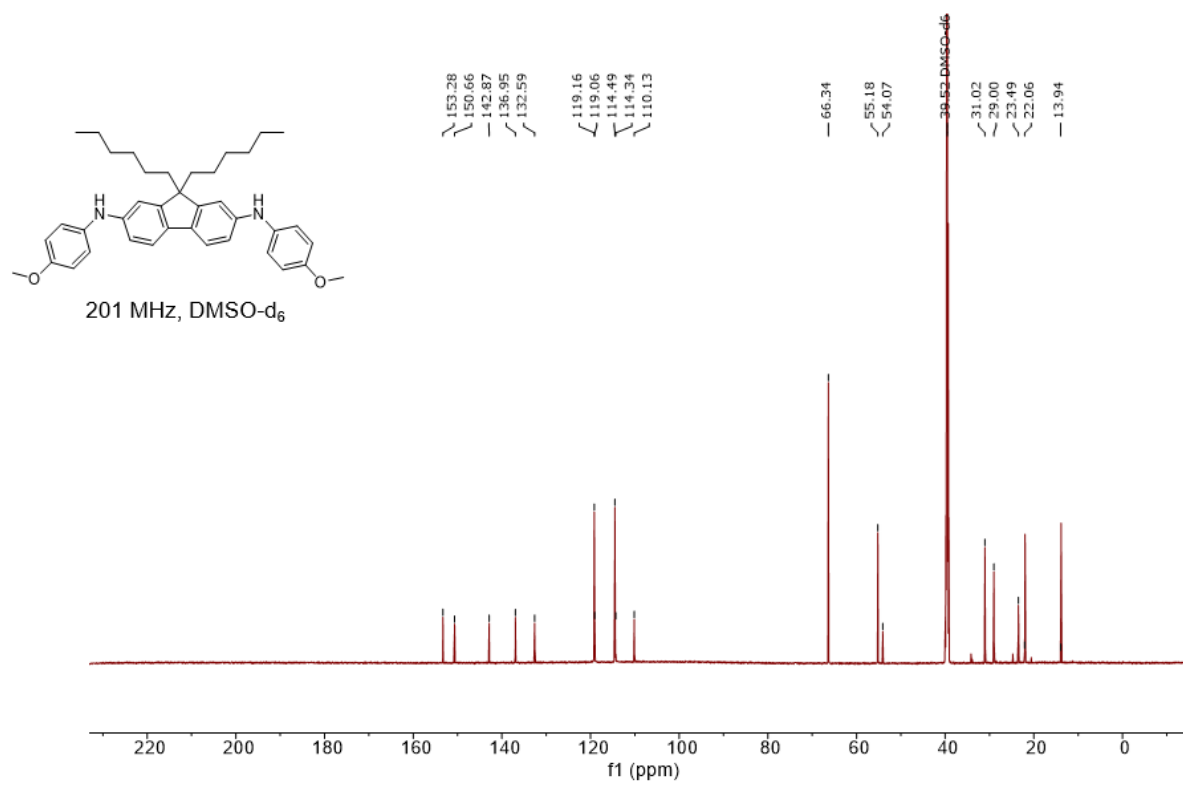
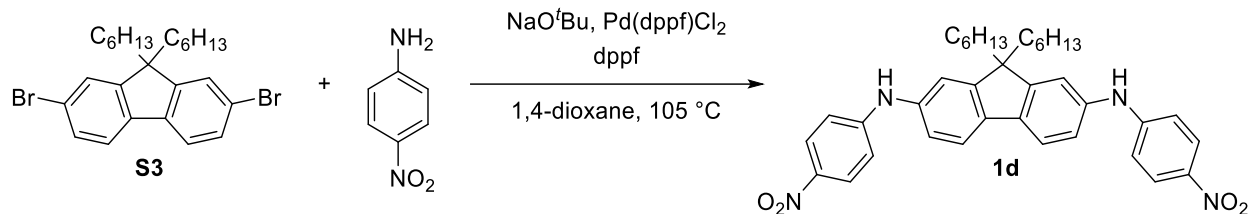


Fig S6. ^{13}C NMR of **1c**.



9,9-dihexyl-*N*²,*N*⁷-bis(4-nitrophenyl)-9*H*-fluorene-2,7-diamine **1d** was synthesized by the following procedure adapted from the literature⁸: To a 10-mL Schlenk tube, **S3** (0.15 g, 0.30 mmol, 1.0 eq), 4-nitroaniline (0.17 g, 1.22 mmol, 4.0 eq), sodium *tert*-butoxide (0.12 g, 1.22 mmol, 4.0 eq), Pd(dppf)Cl₂ (22 mg, 0.030 mmol, 0.1 eq), and dppf (42 mg, 0.076 mmol, 0.25 eq) were added. The reactor was evacuated and backfilled with N₂ three times. Under positive pressure, anhydrous 1,4-dioxane (1.5 mL) was added via syringe. The reactor was sealed and heated in an oil bath at 105 °C. After 48 h, the reactor was cooled to room temperature, and the reaction was quenched with water (5 mL). The reaction was then extracted with dichloromethane (3 x 30 mL). The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The pure compound was isolated by flash column chromatography (1:4 hexanes:DCM) which resulted in an orange solid (0.20 g, 54%). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 9.41 (s, 2H), 8.08 (d, *J* = 8.7 Hz, 4H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 1.1 Hz, 2H), 7.21 (dd, *J* = 8.2 Hz, 2.0 Hz, 2H), 7.05 (d, *J* = 9.5 Hz, 4H), 2.01-1.90 (m, 4H), 1.12-0.98 (m, 12H), 0.74 (t, *J* = 6.7 Hz, 6H), 0.65-0.56 (m, 4H); ¹³C NMR (101 MHz, DMSO-*d*₆): δ (ppm) 151.6, 151.1, 138.7, 137, 136.2, 126.2, 120.3, 120.1, 115.8, 113.2, 54.8, 31.0, 28.9, 23.5, 22.0, 13.8; HRMS (ESI⁺) [M]⁺ calcd. for C₃₇H₄₂N₄O₄: *m/z* = 606.3206, Found: *m/z* = 606.3194.

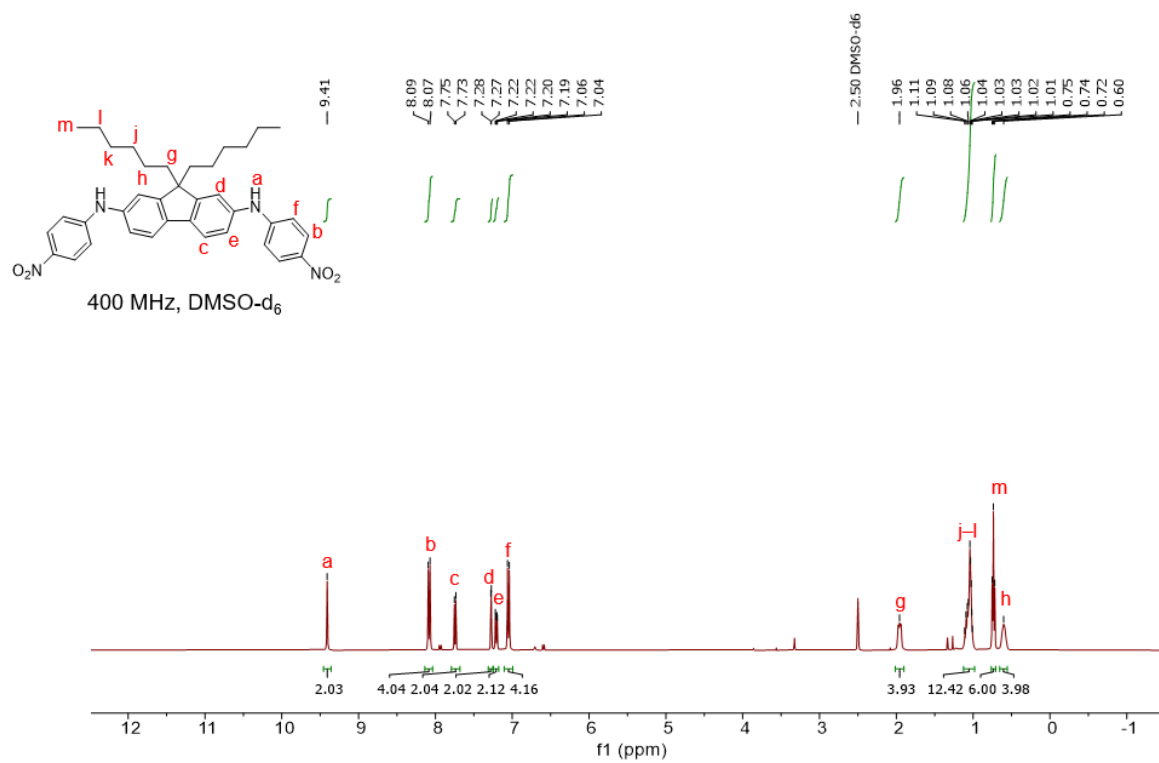


Fig S7. ^1H NMR of **1d**.

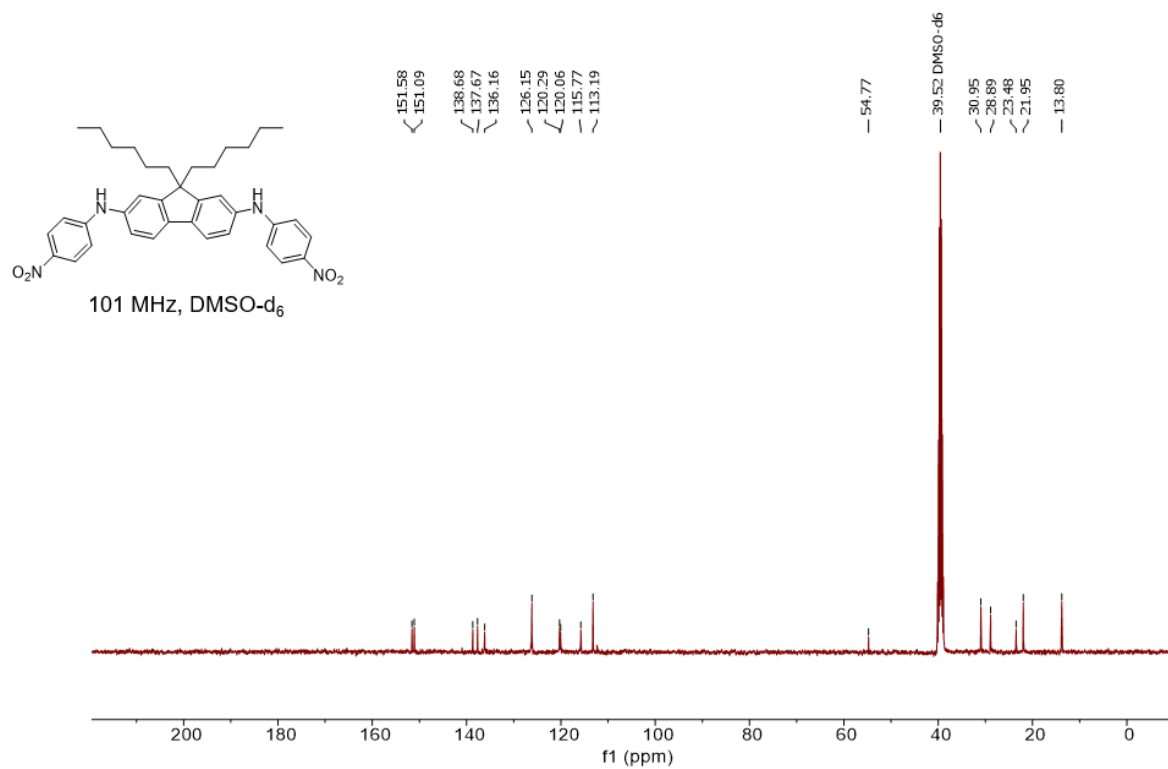
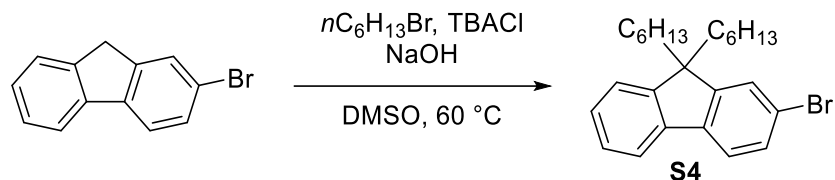
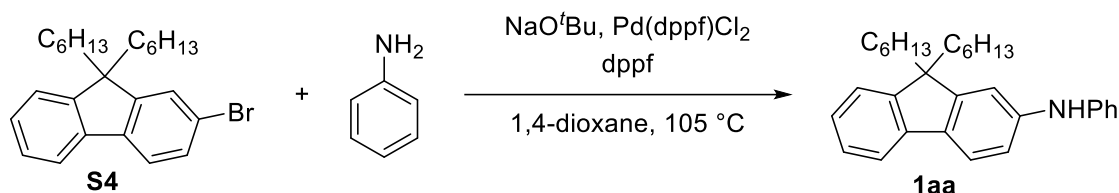


Fig S8. ^{13}C NMR of **1d**.



2,7-dibromo-9,9-dihexyl-9H-fluorene S4 was synthesized following literature procedures^{7,9}: 2-bromofluorene (3.0 g, 12.2 mmol, 1.0 eq) and tetrabutylammonium chloride (0.41 g, 1.47 mmol, 0.12 eq) were dissolved in DMSO (32 mL). The reaction was heated in an oil bath to 60 °C to fully dissolve the solids. Then, 1-bromohexane (4.4 mL, 31.8 mmol, 2.6 eq) was added dropwise and the reaction was cooled to room temperature. Once at room temperature aqueous NaOH (50% w/w, 15 mL) was added to the reaction. After 24 h, hexane (50 mL) and water (200 mL) were added to the reaction. The organic layer was collected, washed with 1M HCl and water. The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The crude product was purified by column chromatography (100% hexanes) to give a white solid (4.0 g, 80% yield).



9,9-dihexyl-N-phenyl-9H-fluoren-2-amine 1aa was synthesized by the following procedure adapted from the literature⁸: To a 10-mL Schlenk tube, previously reported **S4**⁹ (0.20 g, 0.48 mmol, 1.0 eq), sodium *tert*-butoxide (0.46 g, 1.93 mmol, 4.0 eq), Pd(dppf)Cl₂ (88 mg, 0.048 mmol, 0.1 eq), and dppf (0.17 g, 0.12 mmol, 0.25 eq) were added. The reactor was evacuated and backfilled with N₂ three times. Under positive pressure, degassed aniline (0.42 mL, 1.93 mmol, 4.0 eq) and anhydrous 1,4-dioxanes (6.0 mL) were added via syringe. The reactor was sealed and heated in an oil bath at 105 °C. After 48 h, the reactor was cooled to room temperature, and the reaction quenched with water (5 mL). The reaction mixture was then extracted with dichloromethane (3 x 30 mL). The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The pure compound was isolated by flash column chromatography (7:3 hexanes:DCM) which resulted in a viscous amber oil (0.39 g, 76%). ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 8.27 (s, 1H), 7.63 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 7.1 Hz, 2H), 7.28-7.15 (m, 4H), 7.12-6.99 (m, 4H), 6.82 (t, J = 7.9 Hz, 1H), 2.0-1.79 (m, 4H), 1.18-0.92 (m, 12H), 0.73 (t, J = 6.7 Hz, 6H), 0.65-0.45 (m, 4H); ¹³C NMR (101 MHz, DMSO-d₆): δ (ppm) 151.4, 149.4, 143.7, 142.7, 140.9, 132.9, 129.1, 126.7, 125.6, 122.4, 120.5, 119.4, 118.5, 116.4, 116.0, 111.4, 54.3, 30.9, 28.93, 23.3, 21.9, 13.8; HRMS (ESI+) [M+H]⁺ calcd. for C₃₁H₃₉N: m/z = 426.3161, Found: m/z = 426.3160.

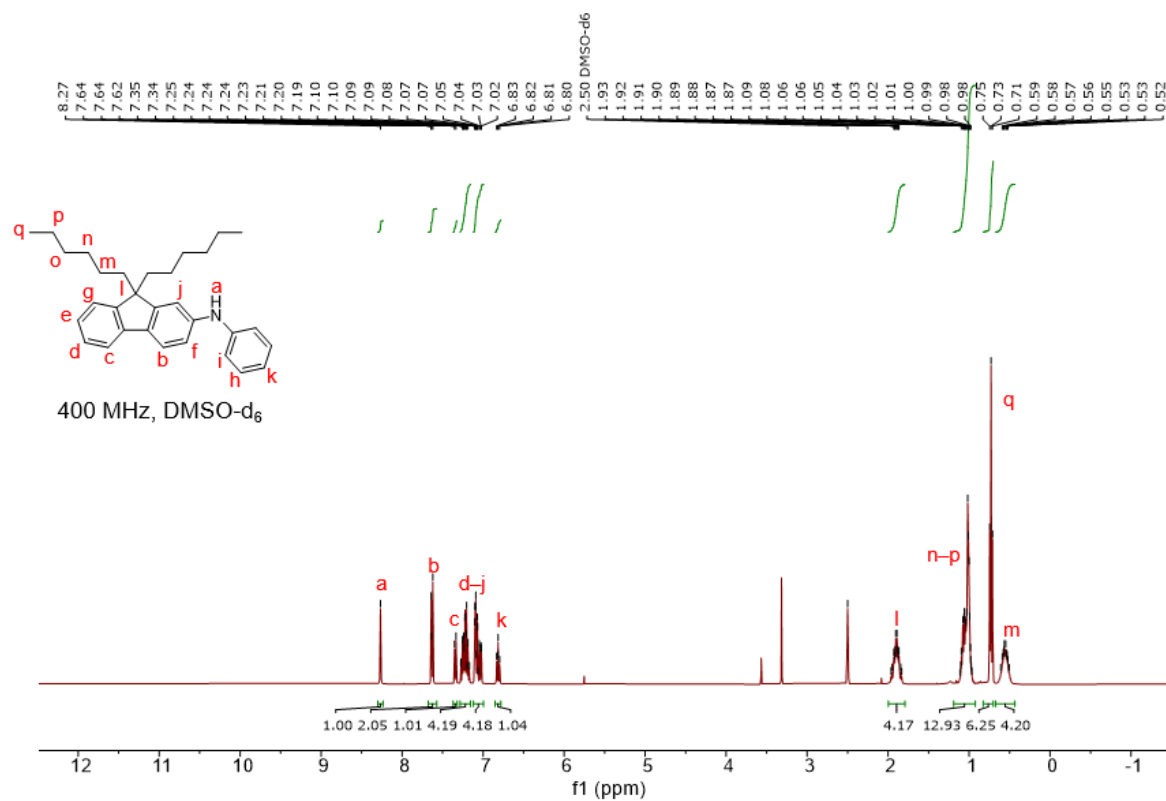


Fig S9. ¹H NMR of **1aa**.

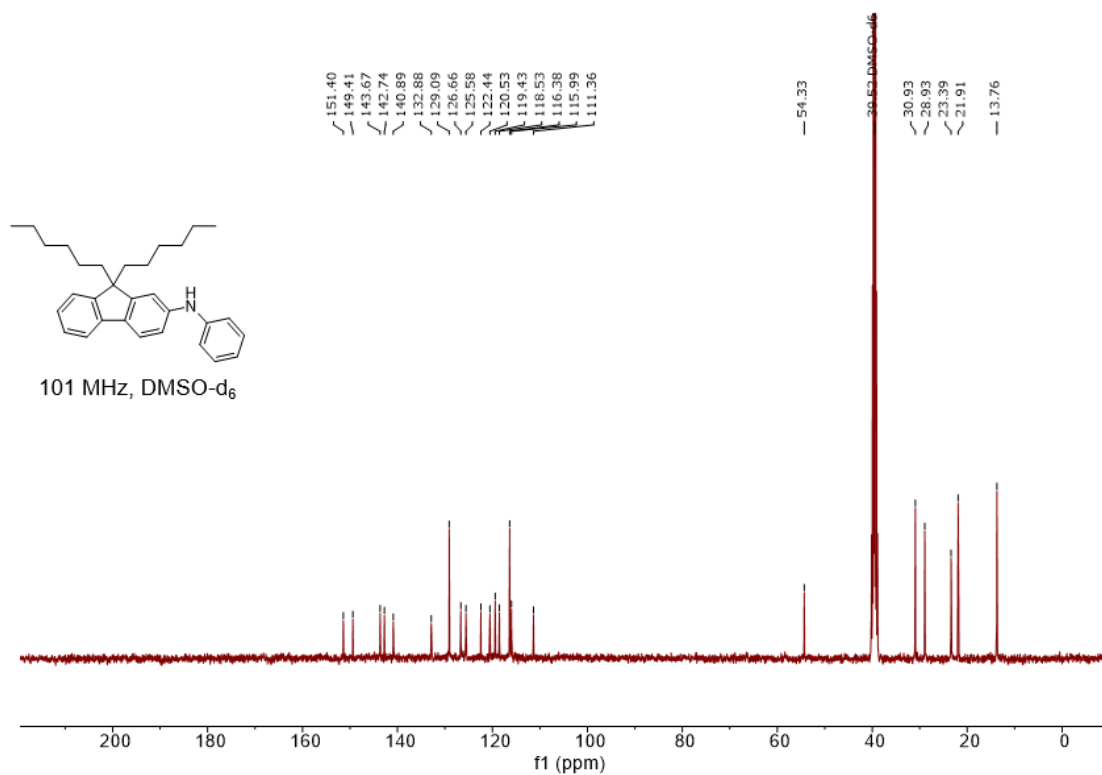
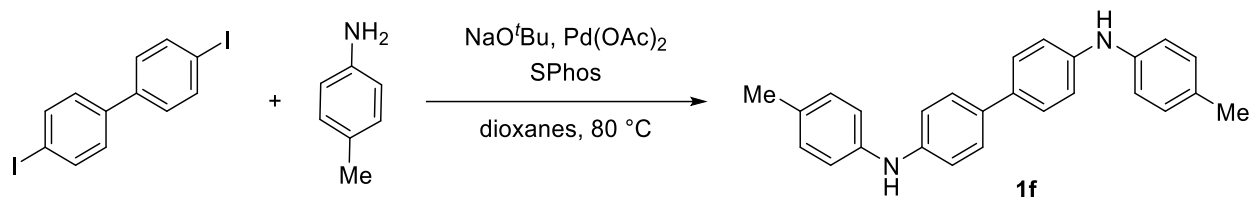
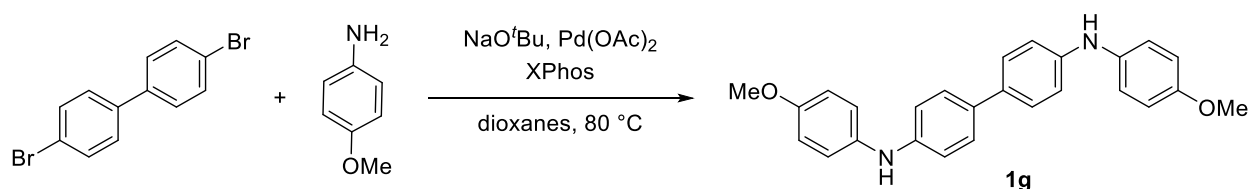


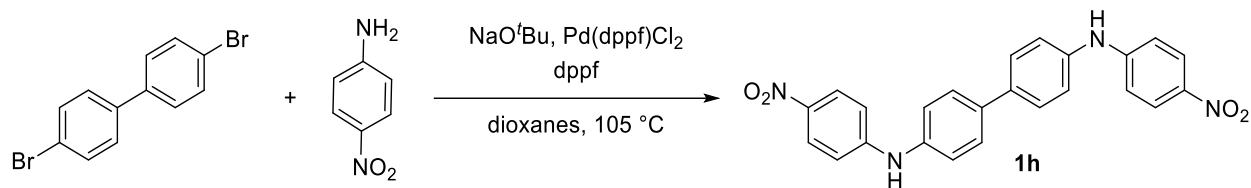
Fig S10. ^{13}C NMR of **1aa**.



***N*⁴,*N*^{4'}-di-*p*-tolyl-[1,1'-biphenyl]-4,4'-diamine 1f** was synthesized by the following procedure adapted from the literature^{10,11}: To a 10-mL Schlenk tube 4,4'-diiodobiphenyl (1.0 g, 2.5 mmol, 1.0 eq), *p*-toluidine (0.54 g, 5.2 mmol, 2.1 eq), sodium *tert*-butoxide (0.66 g, 9.9 mmol, 4.0 eq), Pd(OAc)₂ (5 mg, 0.025 mmol, 0.01 eq), and Dicyclohexyl(2,6-dimethoxy[1,1'-biphenyl]-2-yl)phosphane (SPhos, 30 mg, 0.074 mmol, 0.03 eq) were added. The reactor was evacuated and backfilled with N₂ three times. Under positive pressure, anhydrous 1,4-dioxane (5.0 mL) was added via syringe. The reactor was sealed and heated in an oil bath at 80 °C. After 14 h, the reactor was cooled to room temperature, the reaction mixture diluted with THF, and filtered through a pad of Celite. The resulting mixture was concentrated via rotary evaporation. The residue was dissolved into hot ethyl acetate, filtered hot, and cooled to room temperature. Off-white, sheet-like crystals began to grow. The crystals were placed into a -20 °C freezer for 16 h. The crystals were collected by filtration, washed with cold hexanes, and dried under vacuum which resulted in off-white crystals (0.65 g, 71%).



***N*⁴,*N*^{4'}-bis(4-methoxyphenyl)-[1,1'-biphenyl]-4,4'-diamine 1g** was synthesized by the following procedure adapted from the literature¹⁰: To a 10-mL Schlenk tube 4,4'-dibromobiphenyl (1.0 g, 3.2 mmol, 1.0 eq), *p*-anisidine (0.81 g, 6.7 mmol, 2.1 eq), sodium *tert*-butoxide (0.86 g, 12.8 mmol, 4.0 eq), Pd(OAc)₂ (7.2 mg, 0.032 mmol, 0.01 eq), and Dicyclohexyl[2,4,6-tris(propan-2-yl)[1,1'-biphenyl]-2-yl]phosphane(XPhos, 0.46 g, 0.096 mmol, 0.03 eq) were added. The reactor was evacuated and backfilled with N₂ three times. Under positive pressure, anhydrous 1,4-dioxane (6.5 mL) was added via syringe. The reactor was sealed and heated in an oil bath at 80 °C. After 14 h, the reactor was cooled to room temperature, the reaction mixture diluted with THF:triethylamine (98:2 v/v) and filtered through a pad of Celite. The resulting mixture was concentrated via rotary evaporation. The residue was dissolved into hot ethyl acetate, filtered hot, and cooled to room temperature. White, flakey crystals began to grow. The crystals were placed into a -20 °C freezer for 16 h. The crystals were collected by filtration, washed with cold hexanes, and dried under vacuum which resulted in white crystals (0.69 g, 54%).



N,N'-bis(4-nitrophenyl)-[1,1'-biphenyl]-4,4'-diamine **1h** was synthesized by the following procedure adapted from the literature⁸: To a 10-mL Schlenk tube, 4,4'-dibromobiphenyl (0.30 g, 0.96 mmol, 1.0 eq), 4-nitroaniline (0.53 g, 3.8 mmol, 4.0 eq), sodium *tert*-butoxide (0.37 g, 3.8 mmol, 4.0 eq), Pd(dppf)Cl₂ (70 mg, 0.096 mmol, 0.1 eq), and dppf (0.13 g, 0.24 mmol, 0.25 eq) were added. The reactor was evacuated and backfilled with N₂ for three cycles. Under positive pressure, anhydrous 1,4-dioxane (4.8 mL) was added via syringe. The reactor was sealed and heated in an oil bath at 105 °C. After 48 h, the reactor was cooled to room temperature, and the reaction was quenched with water (5 mL). The reaction was then extracted with dichloromethane (3 x 30 mL). The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The pure compound was isolated by flash column chromatography (1:4 hexanes:DCM) which resulted in a red solid (0.16 g, 41%). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 9.40 (s, 2H), 8.11 (d, *J* = 9.2 Hz, 4H), 7.69 (d, *J* = 8.2 Hz, 4H), 7.33 (d, *J* = 8.2 Hz, 4H), 7.12 (d, *J* = 9.2 Hz, 4H); ¹³C NMR (101 MHz, DMSO-*d*₆): δ (ppm) 150.5, 139.2, 138.0, 134.4, 127.2, 126.2, 190.9, 113.6; HRMS (ESI⁺) [*M*]⁺ calcd. or C₂₄H₁₈N₄O₄: *m/z* = 426.1328, Found: *m/z* = 426.1318.

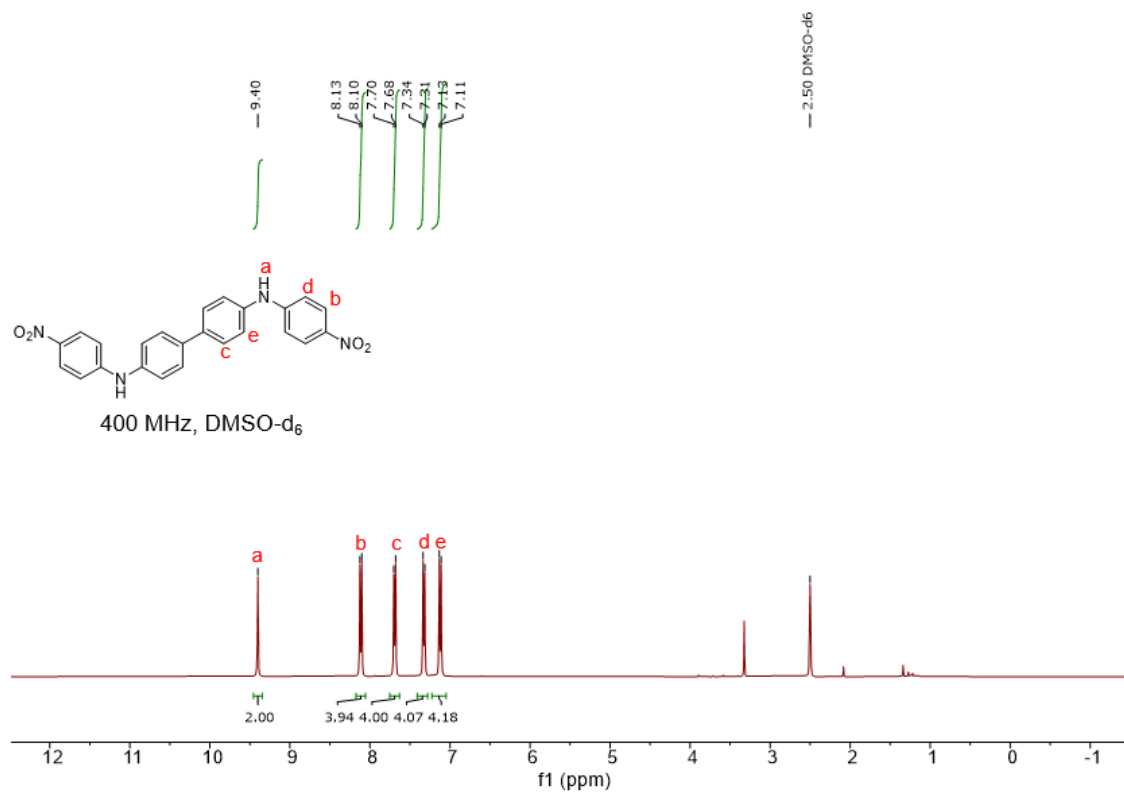


Fig S11. ¹H NMR of **1h**.

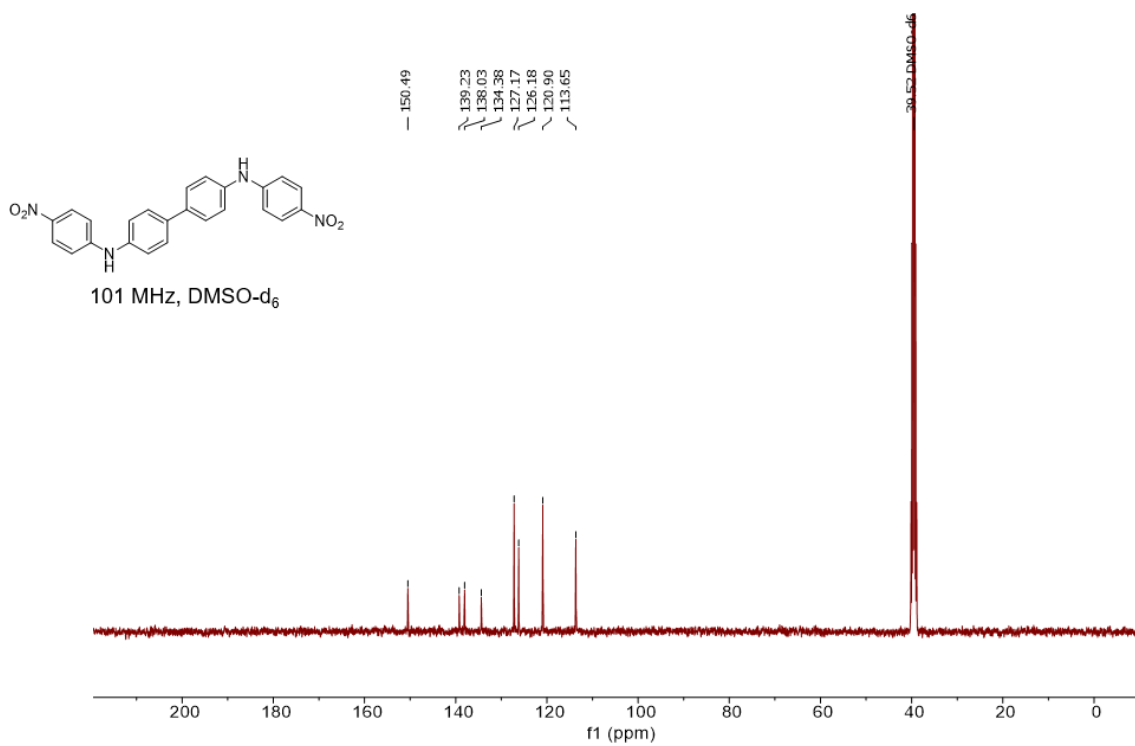
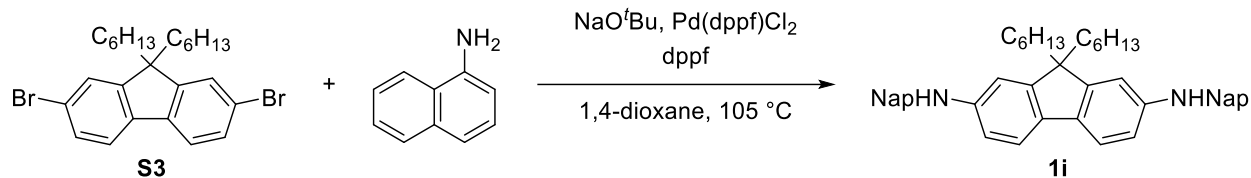


Fig S12. ¹³C NMR of **1h**.



9,9-dihexyl-*N*²,*N*⁷-di(naphthalen-1-yl)-9*H*-fluorene-2,7-diamine 1i was synthesized by the following procedure adapted from the literature⁸: To a 10-mL Schlenk tube, **S3** (0.25 g, 0.51 mmol, 1.0 eq), 1-naphthylamine (0.29 g, 2.0 mmol, 4.0 eq), sodium *tert*-butoxide (0.20 g, 2.0 mmol, 4.0 eq), Pd(dppf)Cl₂ (37 mg, 0.051 mmol, 0.1 eq), and dppf (70 mg, 0.13 mmol, 0.25 eq) were added. The reactor was evacuated and backfilled with N₂ three times. Under positive pressure, anhydrous 1,4-dioxane (5.0 mL) was added via syringe. The reactor was sealed and heated in an oil bath at 105 °C. After 48 h, the reactor was cooled to room temperature, and the reaction quenched with water (5 mL). The reaction was then extracted with dichloromethane (3 x 30 mL). The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The pure compound was isolated by flash column chromatography (7:3 hexanes:DCM) which resulted in a yellow solid (0.28 g, 89%). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.26-8.19 (m, 4H), 7.86 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.57-7.43 (m, 8H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 6.9 Hz, 2H), 7.08 (d, *J* = 2.0 Hz, 2H), 7.04 (dd, *J* = 8.1, 1.9 Hz), 1.81-1.74 (m, 4H), 1.15-0.99 (m, 12H), 0.75 (t, *J* = 6.7 Hz, 6H), 0.70-0.62 (m, 4H); ¹³C NMR (101 MHz, DMSO-*d*₆): δ (ppm) 150.8, 142.7, 140.4, 134.4, 133.8, 128.1, 126.2, 126.0, 124.8, 122.70, 120.4, 119.3, 117.4, 112.87, 112.1, 54.2, 31.0, 28.9, 23.5, 22.0, 13.8; HRMS (ESI+) [*M*]⁺ calcd. for C₄₅H₄₈N₂: *m/z* = 616.3815, Found: *m/z* = 616.3812.

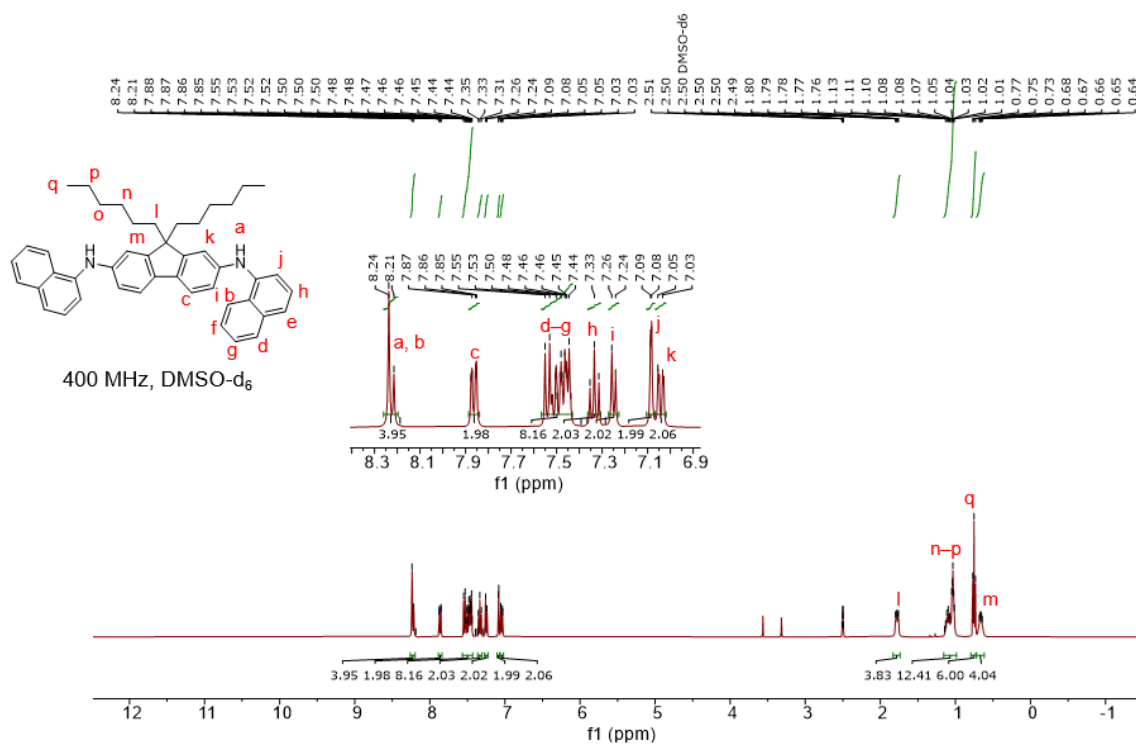


Fig S13. ^1H NMR of **1i**.

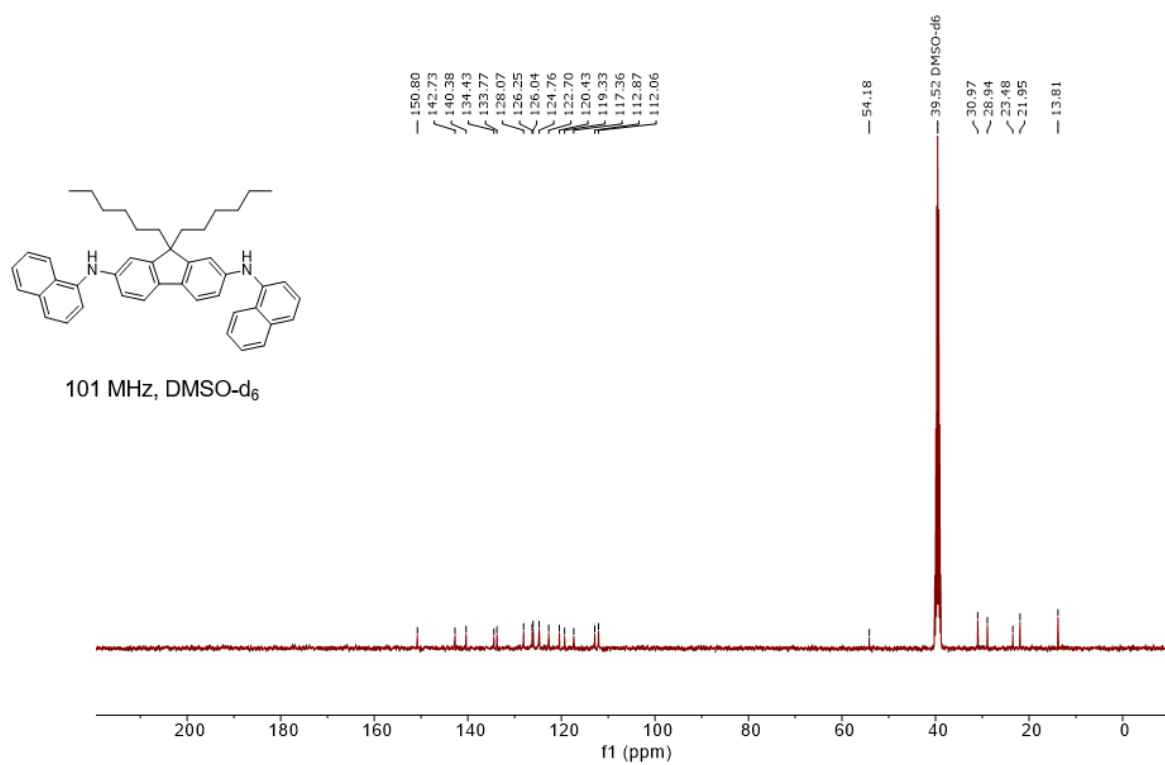
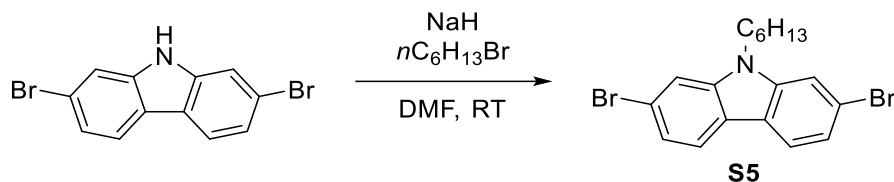
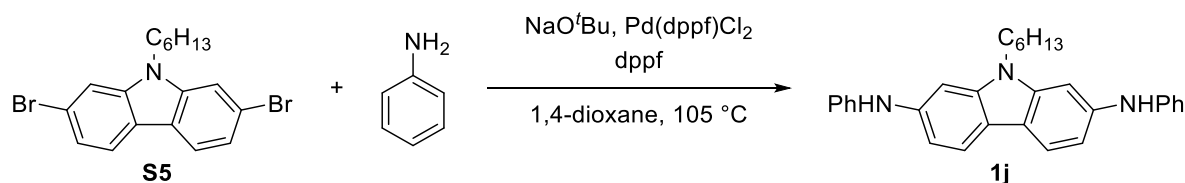


Fig S14. ^{13}C NMR of **1i**.



2,7-dibromo-9-hexyl-9H-carbazole S5 was synthesized following a literature procedure¹²: 2,7-dibromocarbazole (1.0 g, 3.1 mmol, 1.0 eq) was dissolved into anhydrous DMF (10 mL) under a nitrogen atmosphere. After complete dissolution, NaH (60% in mineral oil, 0.17 g, 4.3 mmol, 1.4 eq) was added to the reactor. After 0.5 h, 1-bromohexane (0.56 mL, 4.0 mmol, 1.3 eq) was added dropwise to the reactor. The reaction was stirred at room temperature. After 16 h, the reaction was diluted with water (10 mL). The reaction was then extracted with dichloromethane (3 x 30 mL). The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The pure compound was isolated by flash column chromatography (8:2 hexanes:ethyl acetate) which resulted in a white solid (1.17 g, 93%).



9-hexyl-*N*²,*N*⁷-diphenyl-9H-carbazole-2,7-diamine 1j was synthesized by the following procedure adapted from the literature⁸: To a 10-mL Schlenk tube, **S5** (0.25 g, 0.61 mmol, 1.0 eq), sodium *tert*-butoxide (0.24 g, 2.4 mmol, 4.0 eq), Pd(dppf)Cl₂ (45 mg, 0.061 mmol, 0.1 eq), and dppf (85 mg, 0.15 mmol, 0.25 eq) were added. The reactor was evacuated and backfilled with N₂ three times. Under positive pressure, degassed aniline (0.22 mL, 2.4 mmol, 4.0 eq) and degassed 1,4-dioxane (3.0 mL) were added via syringe. The reactor was sealed and heated in an oil bath at 105 °C. After 48 h, the reactor was cooled to room temperature, and the reaction quenched with water (5 mL). The reaction mixture was then extracted with dichloromethane (3 x 30 mL). The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The pure compound was isolated by flash column chromatography (7:3 hexanes:DCM) which resulted in a white solid (0.23 g, 86%). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 7.41 (s, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.71 (t, *J* = 8.1 Hz, 4H), 6.34–6.29 (m, 6H), 6.09 (dd, *J* = 8.4 Hz, *J* = 1.8 Hz, 2H), 5.98 (t, *J* = 7.2 Hz, 2H), 3.35 (t, *J* = 7.2 Hz, 2H), 0.93 (q, *J* = 7.0 Hz, 2H), 0.59–0.37 (m, 6H), 0.00 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, DMSO-*d*₆): δ (ppm) 144.3, 141.3, 140.6, 129.1, 119.7, 119.0, 116.5, 116.0, 110.7, 97.2, 42.0, 31.0, 28.2, 26.3, 22.0, 13.8; HRMS (ESI+) [*M*]⁺ calcd. for C₃₀H₃₁N₃: *m/z* = 433.2520, Found: *m/z* = 433.2493.

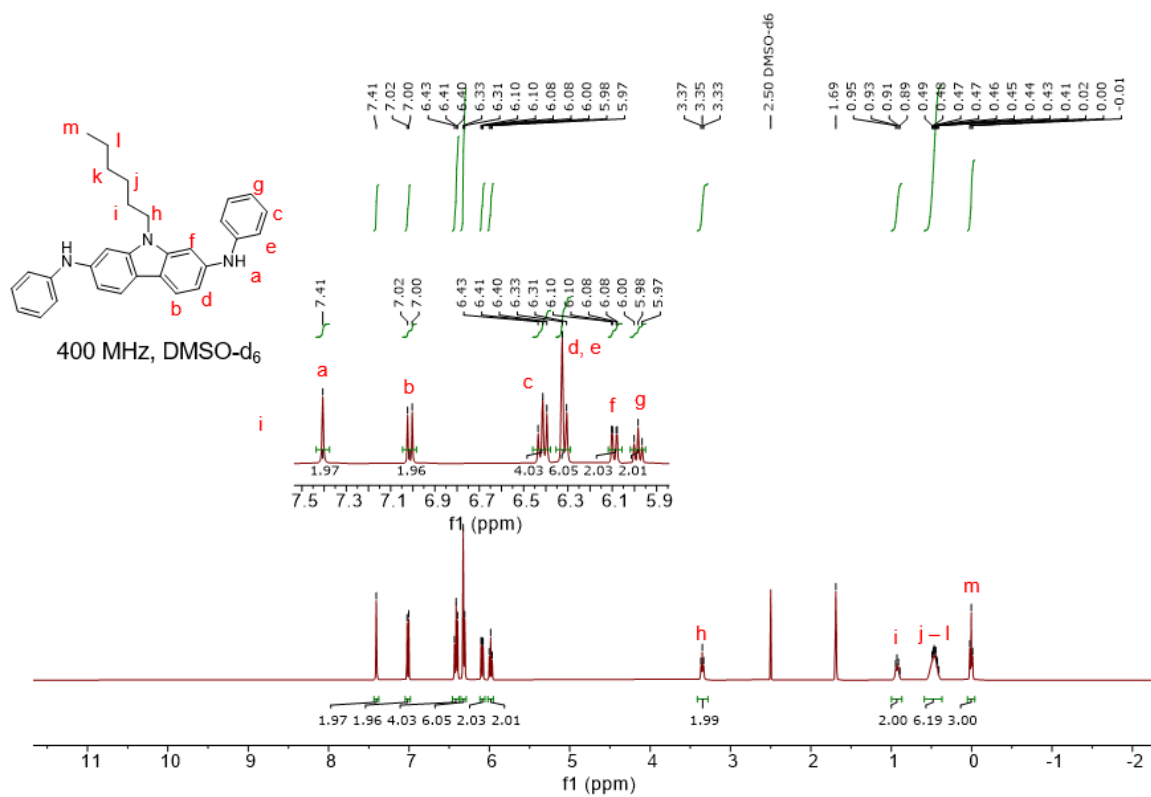


Fig S15. ^1H NMR of **1j**.

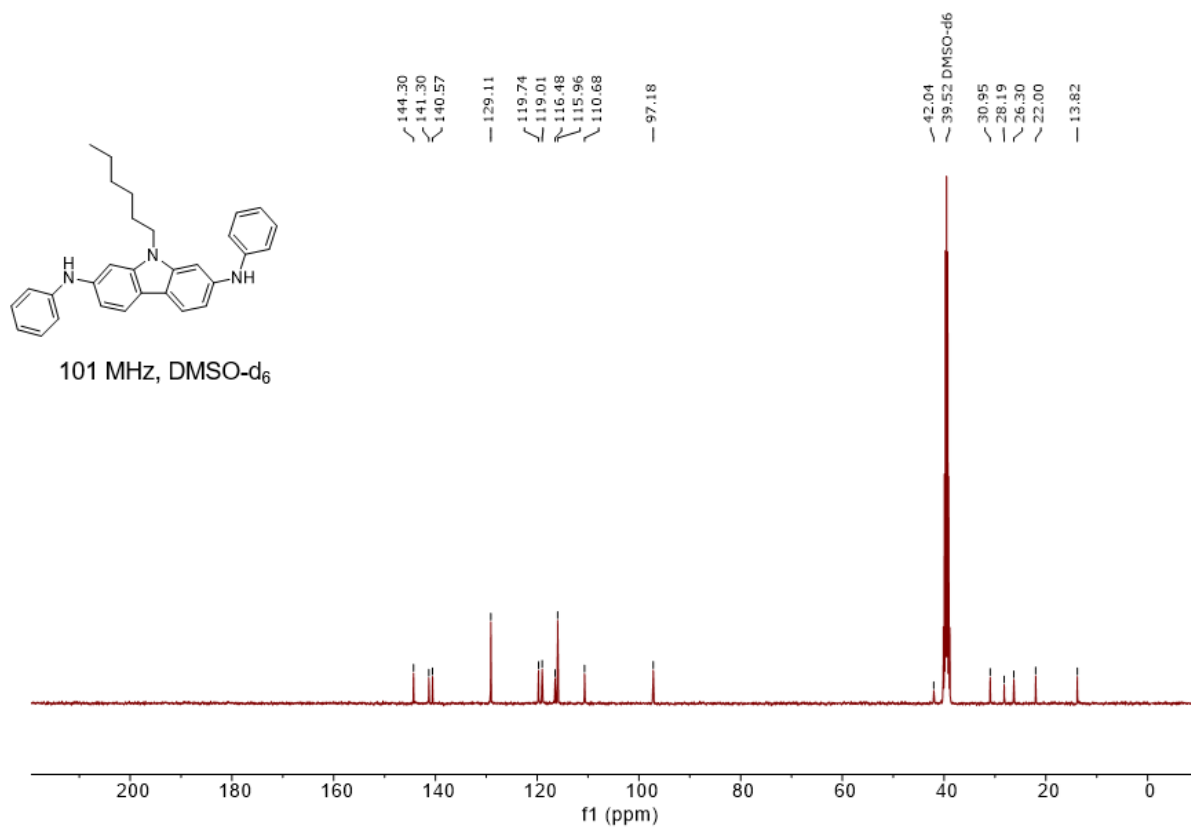
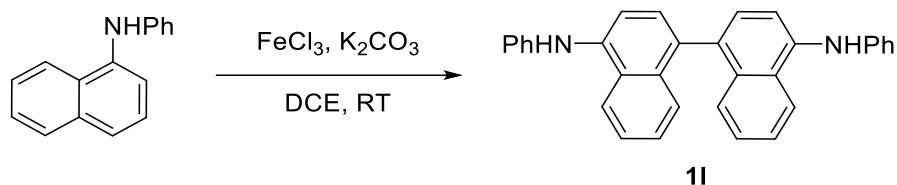
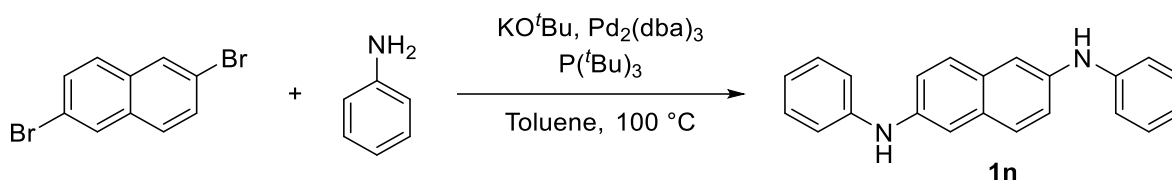


Fig S16. ¹³C NMR of **1j**.



***N*⁴,*N*^{4'}-diphenyl-[1,1'-binaphthalene]-4,4'-diamine 11** was synthesized following a literature procedure¹³: **S6** (0.22 g, 1.0 mmol, 1.0 eq) and K₂CO₃ (0.14 g, 1.0 mmol, 1.0 eq) were dissolved into 1,2-dichloroethane (6.0 mL) under a nitrogen atmosphere. The mixture was stirred for 5 min at room temperature. Next, FeCl₃ (0.20 g, 1.2 mmol, 1.2 eq) was added at once and the reaction was stirred at room temperature for 1 h. The reaction was quenched by adding 1 mL of triethylamine. The reaction mixture was filtered through a pad of silica gel, washed with ethyl acetate (3 x 20 mL). The collected organic phase was concentrated via rotary evaporation. The pure compound was isolated by flash column chromatography (1:1 hexanes:DCM) which resulted in an off-white solid (0.21 g, 35%).



***N*²,*N*⁶-Diphenylnaphthalene-2,6-diamine 1n** was prepared according to the following procedure: To an oven-dried 10 mL Schlenk tube 2,6-dibromonaphthalene (0.10 g, 0.35 mmol, 1.0 eq.), potassium *tert*-butoxide (0.19 g, 1.4 mmol, 4.0 eq), Pd₂(dba)₃ (32 mg, 0.035 mmol, 0.1 eq), and tri-*tert*-butylphosphine (P(*t*Bu)₃, 14 mg, 0.070 mmol, 0.2 eq) were added. The reactor was evacuated and backfilled with N₂ three times. Under positive pressure, degassed aniline (0.16 mL, 1.4 mmol, 4.0 eq) and anhydrous toluene (2.0 mL) were added. The reactor was sealed and heated in an oil bath at 100 °C. After 16 h, the reactor was cooled to room temperature, and quenched with water (5 mL). The reaction was extracted with ethyl acetate (3 x 30 mL) and washed with water (3 x 20 mL). The collected organic phase was dried with sodium sulfate, filtered, and concentrated via rotary evaporation. The pure compound was isolated by flash column chromatography (3:1, Hexanes: DCM) to give product as a white solid (51 mg, 48%). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.20 (s, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 2.4 Hz, 2H), 7.26-7.23 (m, 4H), 7.19 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 4H), 6.81 (t, *J* = 7.2 Hz, 2H); ¹³C NMR (101 MHz, DMSO-*d*₆): δ (ppm) 143.9, 138.8, 129.4, 129.2, 127.3, 120.8, 119.4, 116.4, 110.9; HRMS (ESI) [*M*]⁺ calcd. for C₂₂H₁₈N₂: *m/z* = 310.1470, found *m/z* = 310.1471.

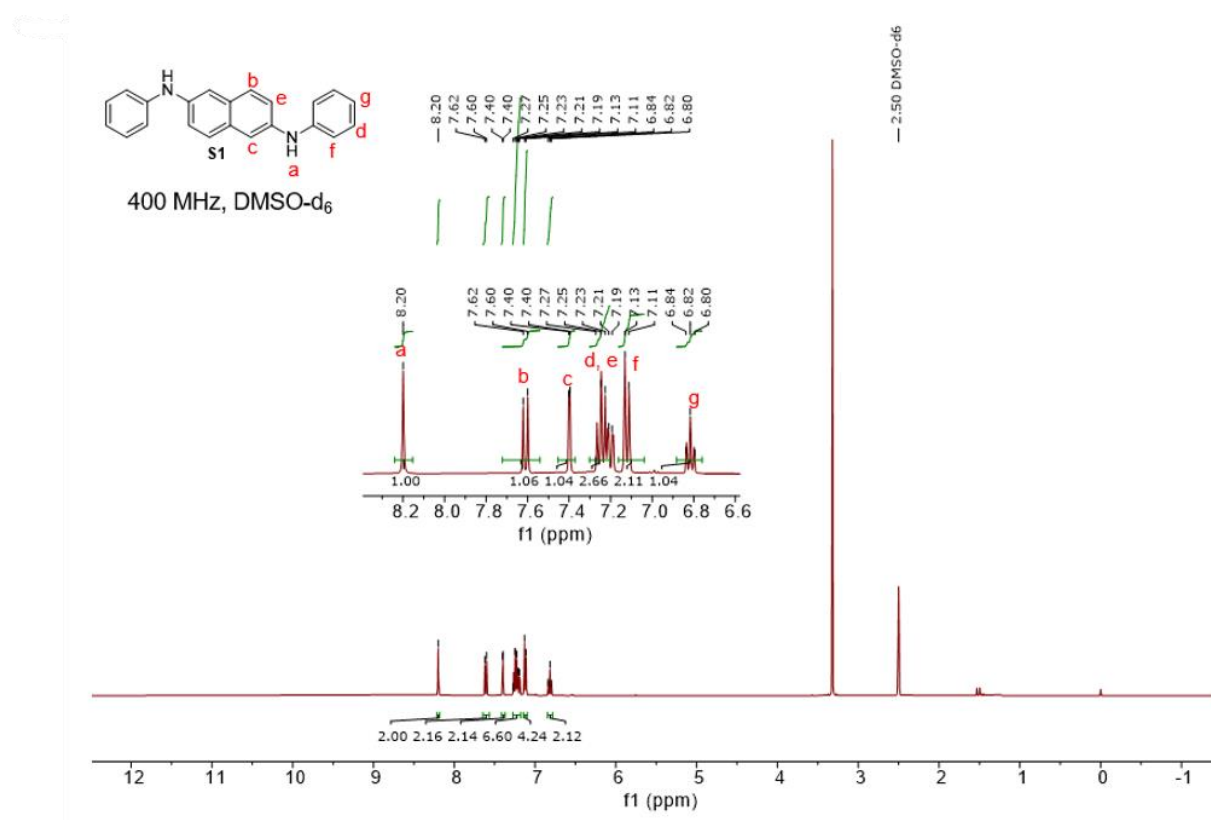


Fig S18. ^1H NMR of **1n**.

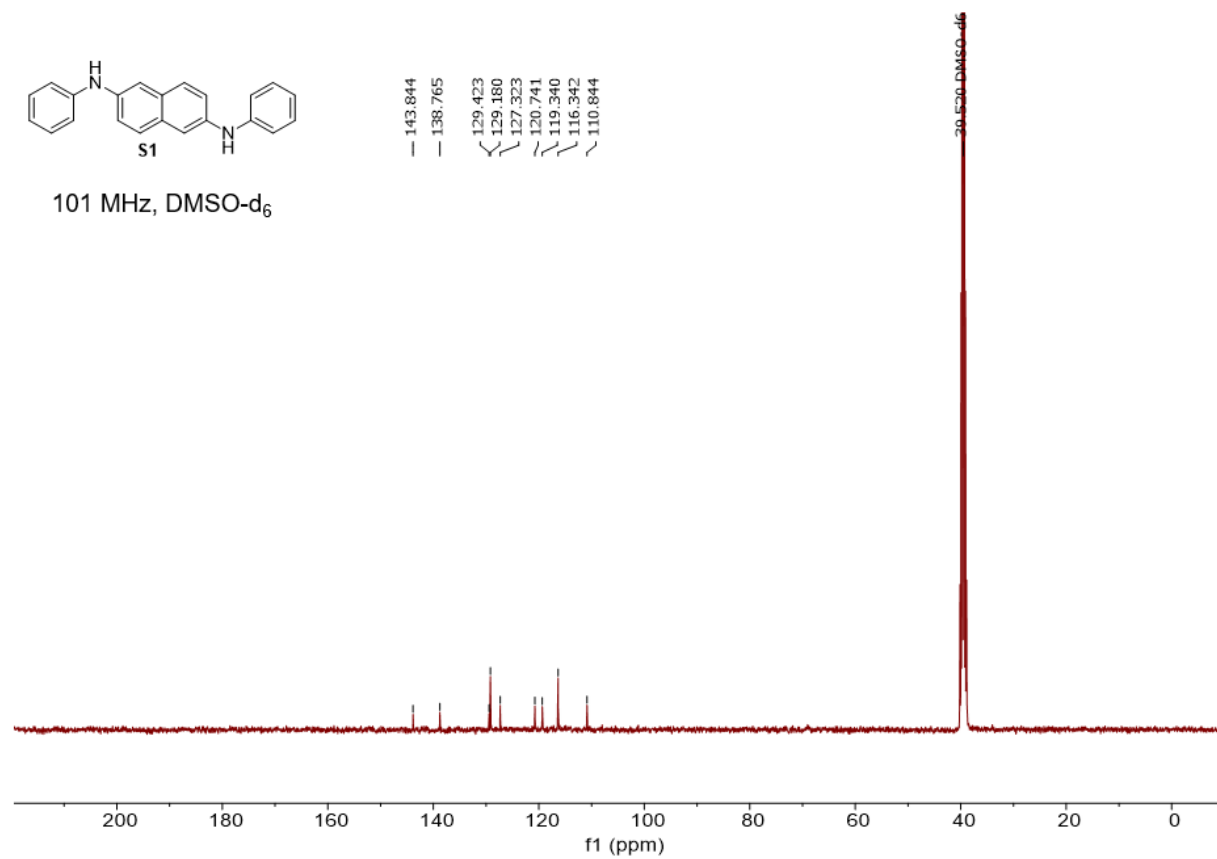
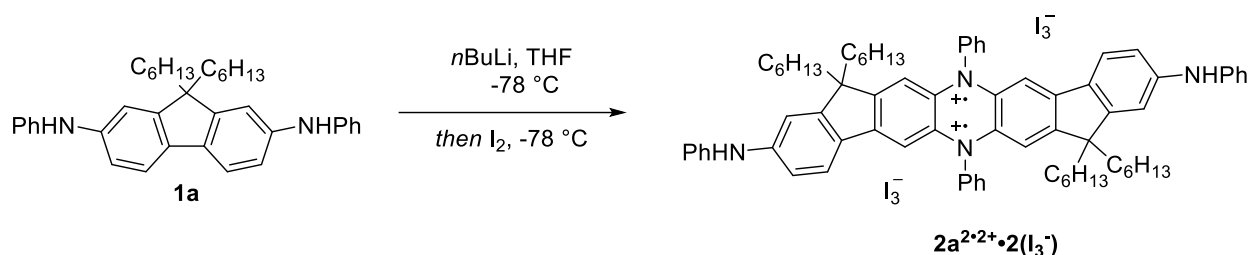


Fig S18. ¹³C NMR of **1n**.

Synthesis & Characterization of *N, N'*-Disubstituted Diphenyl Dihydrophenazines Diradical Dication Triiodide Salts



Diradical Dication Triiodide Diaryl Dihydrophenazine Salt 2a²⁺·2(I₃⁻) was synthesized by the following procedure with slight modification¹⁴: **1a** (0.2 g, 0.38 mmol, 1 eq) was dissolved into THF (24 mL) at room temperature. The reaction was cooled to $-78\text{ }^\circ C$ for 30 min. At $-78\text{ }^\circ C$, *n*BuLi (0.32 mL, 2.5 M, 0.81 mmol, 2.1 eq) was added dropwise. After complete addition, the reaction was warmed to RT for 30 min. After 30 min, the reaction was cooled to $-78\text{ }^\circ C$, and solid iodine (0.49 g, 1.9 mmol, 5 eq) was added in several portions. After complete addition, the reaction was stirred at $-78\text{ }^\circ C$ for an additional 1 h. After 1 h, the reaction was quenched with 10% potassium carbonate solution and warmed to RT. The reaction solution was then extracted with ethyl acetate (20 mL). The organic phase was combined, washed with 10% potassium carbonate aqueous solution (30 mL x 2) and water (30 mL x 2), and dried over anhydrous sodium sulfate. The solids were filtered off and the filtrate concentrated via rotary evaporation. The resulting residue was dissolved in a minimum amount of THF and precipitated into hexanes (300 mL). The solids were collected by filtration, washed with hexanes, and dried to yield a brown solid (0.47 g, 68%). HRMS (ESI+) [M]⁺ calcd for C₇₄H₈₄I₆N₄²⁺ *m/z* = 514.3348, Found: *m/z* = 514.3330.

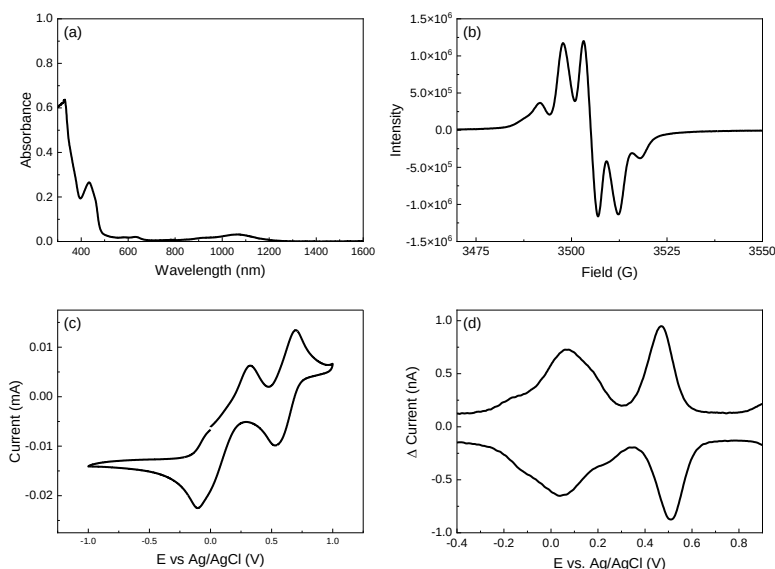
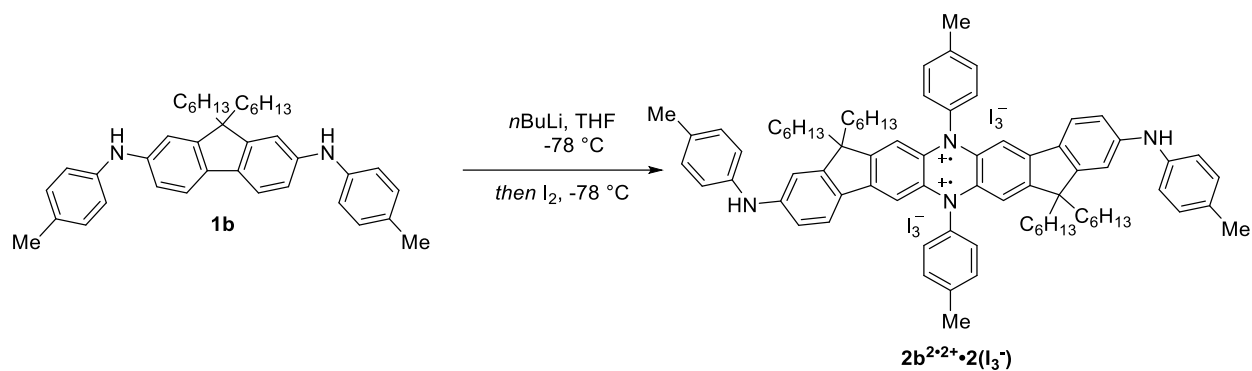


Fig S19. (a) UV-Vis, (b) RT EPR, (c) CV, and (d) DPV of **2a²⁺·2(I₃⁻)**.



Diradical Dication Triiodide Diaryl Dihydrophenazine Salt $2b^{2+2+} \cdot 2(I_3^-)$ was synthesized from compound **1b** following the same procedure for the synthesis of **2a²⁺²⁺·2(I₃⁻)**. Compound **2b²⁺²⁺·2(I₃⁻)** was obtained as a dark green solid (0.17 g, 62%). HRMS (ESI) $[M]^+$ calcd. for $C_{78}H_{92}I_6N_4^{2+2+}$: 542.3661, Found: 542.3655.

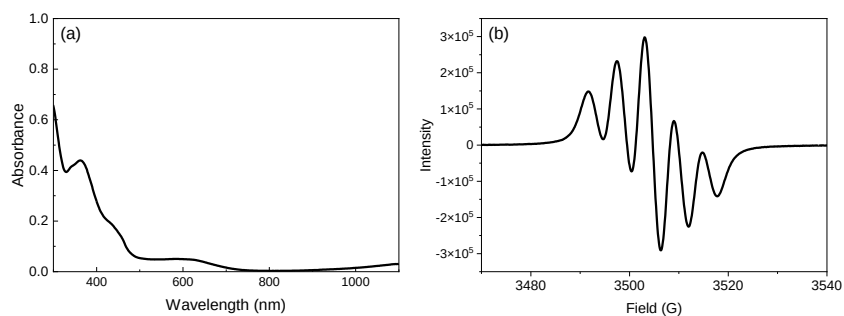
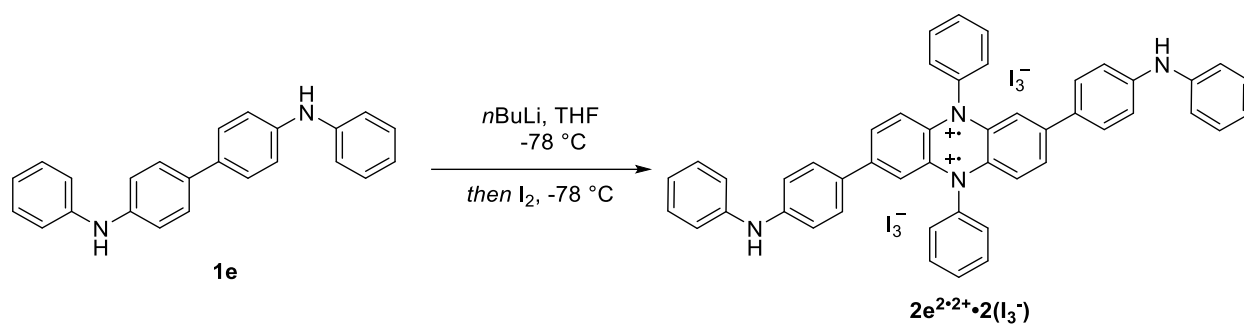


Fig S20. (a) UV-Vis and (b) RT EPR of **2b²⁺²⁺·2(I₃⁻)**.



Diradical Dication Triiodide Diaryl Dihydrophenazine Salt $2\text{e}^{2\cdot 2+} \cdot 2(\text{I}_3^-)$ was synthesized from compound **1e** following the same procedure for the synthesis of **2a**^{2•2+}·2(I₃[−]). Compound **2d**^{2•2+}·2(I₃[−]) was obtained as an obtained as a black solid (54 mg, 56%). HRMS (ESI) [M+H]⁺ calcd. for C₄₈H₃₆I₆N₄²⁺: m/z = 335.1548, Found: m/z = 335.1546.

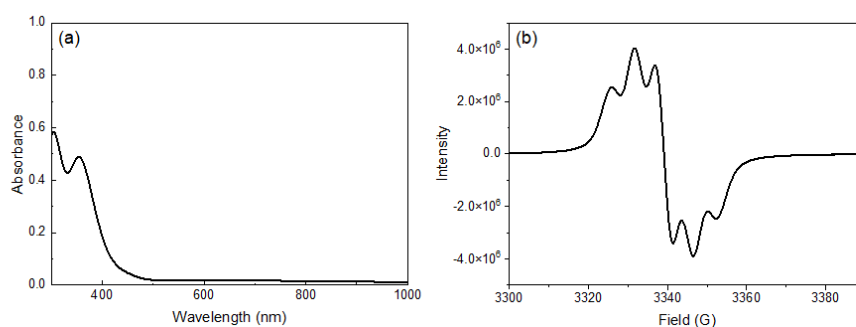
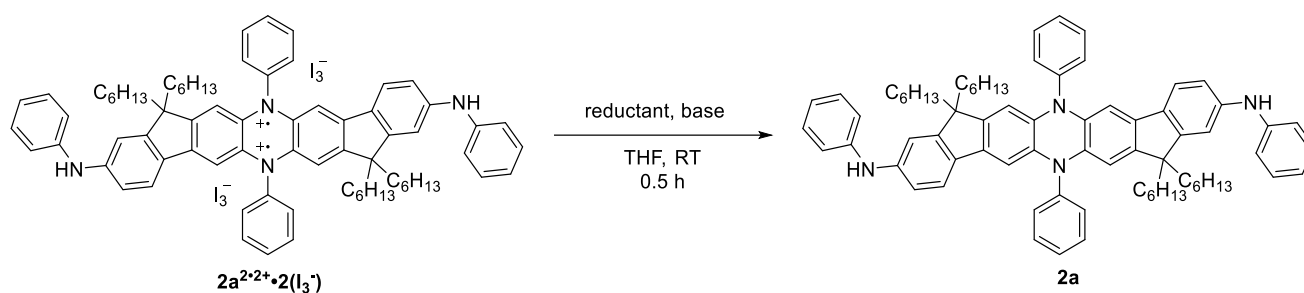


Fig S21. (a) UV-Vis and (b) RT EPR of $2\text{e}^{2\cdot 2+} \cdot 2(\text{I}_3^-)$.

Synthesis & Characterization of *N, N'*-Disubstituted Diphenyl Dihydrophenazines

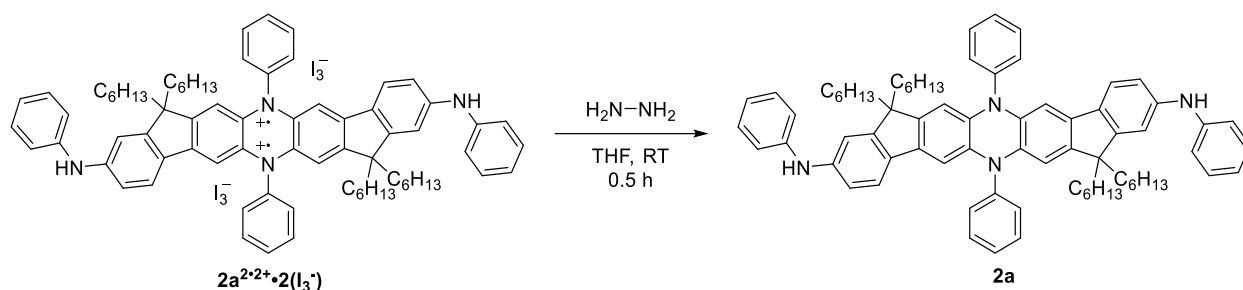
General Procedure: To an oven dried 20 mL scintillation vial with septa screw cap was added **2a**²⁺²⁺·2(I₃⁻) (0.10 g, 0.056 mmol, 1.0 eq). The vial was then evacuated and purged with N₂. Next, THF (2.0 mL) was added and mixed to form a dark green/brown solution. Next, reductant (80.0 mol eq) and (where applicable) base (10 mol eq) were added and mixed at ambient temperature. After 0.5 h, the vial was purged with a flow of N₂ until no solvent remained. The remaining yellow residue was redissolved into a minimum amount of THF and precipitated into water. The solids were collected by filtration, washed with water, and dried.

Table S1. Diradical Dication Triiodide Reduction Optimization.^a



entry	Reductant	Additive	Isolated Yield(%)
1	NaBH ₄	-	0
2	LiAlH ₄	-	0
3	NaBH ₄	pyr.	0
4	LiAlH ₄	pyr.	0
5	NaBH ₄	NEt ₃	79
6	LiAlH ₄	NEt ₃	63
7	NH ₂ NH ₂	-	90

^aReaction conditions: 0.056 mmol, 27.9 mM, 80 mol eq reductant, 10 mol eq base.



8,8,16,16-tetrahexyl- N^2, N^{10} ,6,14-tetraphenyl-6,8,14,16-tetrahydroindeno[1,2-*b*:1',2'-*i*]phenazine-2,10-diamine 2a was synthesized by the following procedure: To an oven dried 20 mL scintillation vial with septa screw cap was added **2a**²⁺·2(I₃⁻) (0.10 g, 0.056 mmol, 1.0 eq). The vial was then evacuated and purged with N₂. Next, THF (2.0 mL) was added and mixed to form a dark green/brown solution. Next, anhydrous hydrazine (100 μL, 4.5 mmol, 80.0 eq) was added. The reaction solution instantly changes to yellow. After 0.5 h, the vial was purged with a flow of N₂ until no solvent remained. The remaining yellow residue was redissolved into a minimum amount of THF and precipitated into water. The solids were collected by filtration, washed with water, and dried as a yellow solid (52 mg, 90%). ¹H NMR (400 MHz, THF-*d*₈) δ (ppm) 7.66 (t, *J* = 7.8 Hz, 4H) 7.51-7.44 (m, 6H), 7.30 (s, 2H), 7.06 (t, *J* = 8.3 Hz, 4H), 6.94-6.88 (m, 8H), 6.79 (dd, *J* = 8.2, 1.8 Hz, 2H), 6.66 (t, *J* = 7.30 Hz, 2H), 5.94 (s, 2H), 5.64 (s, 2H), 1.17-0.95 (m, 32H), 0.78 (t, *J* = 7.2 Hz, 12H), 0.68-0.58 (m, 8H); ¹³C NMR (201 MHz, THF-*d*₈) δ (ppm) 152.8, 145.8, 143.6, 142.5, 136.9, 136.8, 135.6, 135.1, 132.2, 132.1, 129.9, 126.1, 120.0, 119.5, 117.7, 117.1, 113.5, 108.7, 104.4, 50.0, 41.0, 35.3, 32.6, 23.6, 21.6, 14.6; HRMS (ESI⁺) [*M*]⁺ calcd. for C₇₄H₈₄N₄: *m/z* = 1028.6696, found *m/z* = 1028.6720.

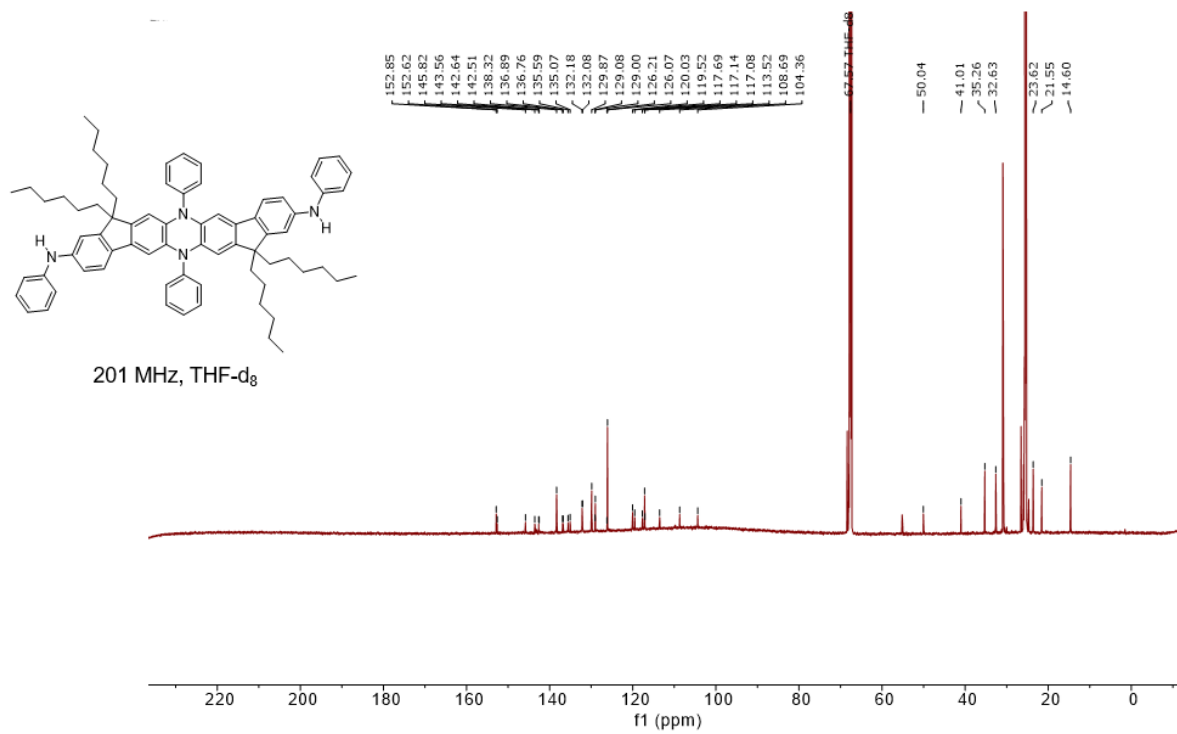
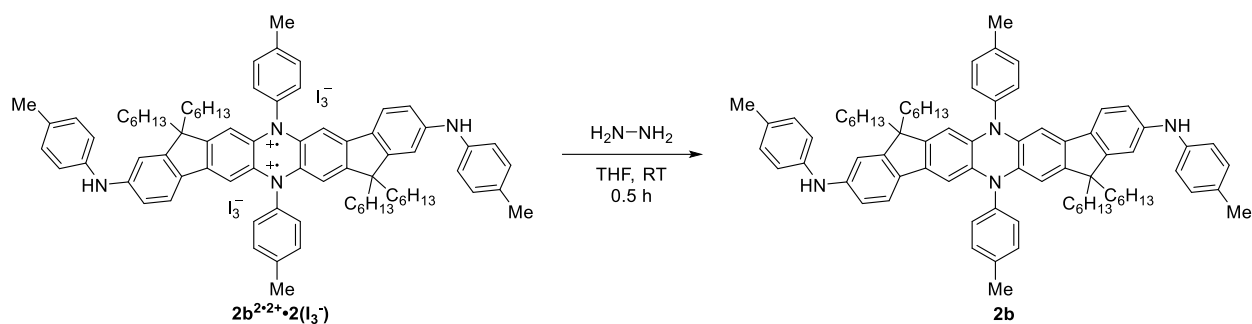


Fig S23. ¹³C NMR of **2a**.



8,8,16,16-tetrahexyl- N^2, N^{10} ,6,14-tetra-*p*-tolyl-6,8,14,16-tetrahydrodiindeno[1,2-*b*:1',2'-*i*]phenazine-2,10-diamine **2b** was synthesized from $2b^{2+} \cdot 2(I_3^-)$ following the same procedure for the synthesis of **2a**. Compound **2b** obtained as a brown solid (47 mg, 80%). ^1H NMR (800 MHz, THF-d_8) δ (ppm); 7.50 (d, $J = 7.8$ Hz, 2H), 7.37 (d, $J = 7.9$ Hz, 4H), 7.11 (s, 2H), 7.0-6.86 (m, 16H), 6.76 (d, $J = 8.2$ Hz, 2H), 5.94 (s, 1H), 5.67 (s, 1H), 2.50 (s, 6H), 2.21 (s, 6H), 1.19-1.00 (m, 32H), 0.83 (t, $J = 7.3$ Hz, 12H), 0.72-0.58 (m, 8H); ^{13}C NMR (201 MHz, THF-d_8) δ (ppm) 152.6, 143.22, 143.2, 143.1, 139.9, 138.7, 137.0, 136.8, 135.0, 135.0, 132.8, 131.9, 130.4, 129.4, 119.4, 118.0, 116.8, 112.5, 108.4, 104.0, 55.1, 41.0, 32.6, 30.8, 24.7, 23.6, 21.6, 20.8, 14.6; HRMS (ESI+) $[M]^+$ calcd. for $\text{C}_{78}\text{H}_{92}\text{N}_4$: $m/z = 1084.7322$, found $m/z = 1084.7305$.

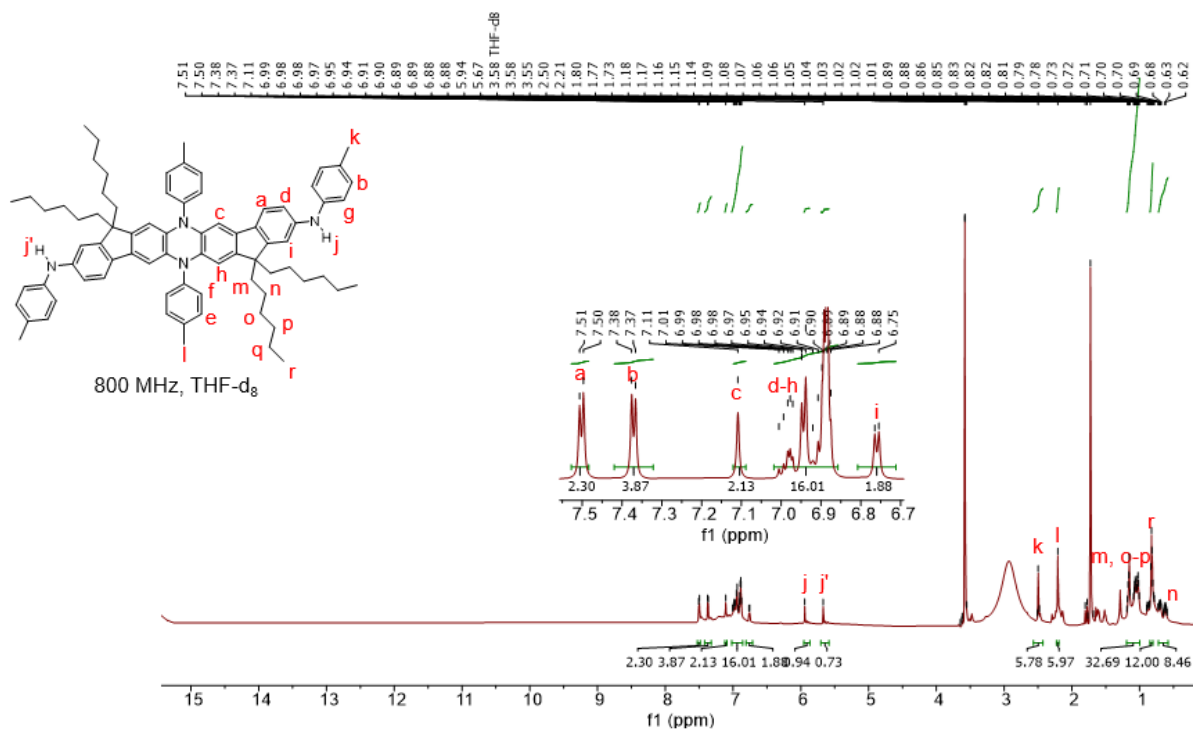


Fig S24. ^1H NMR of **2b**.

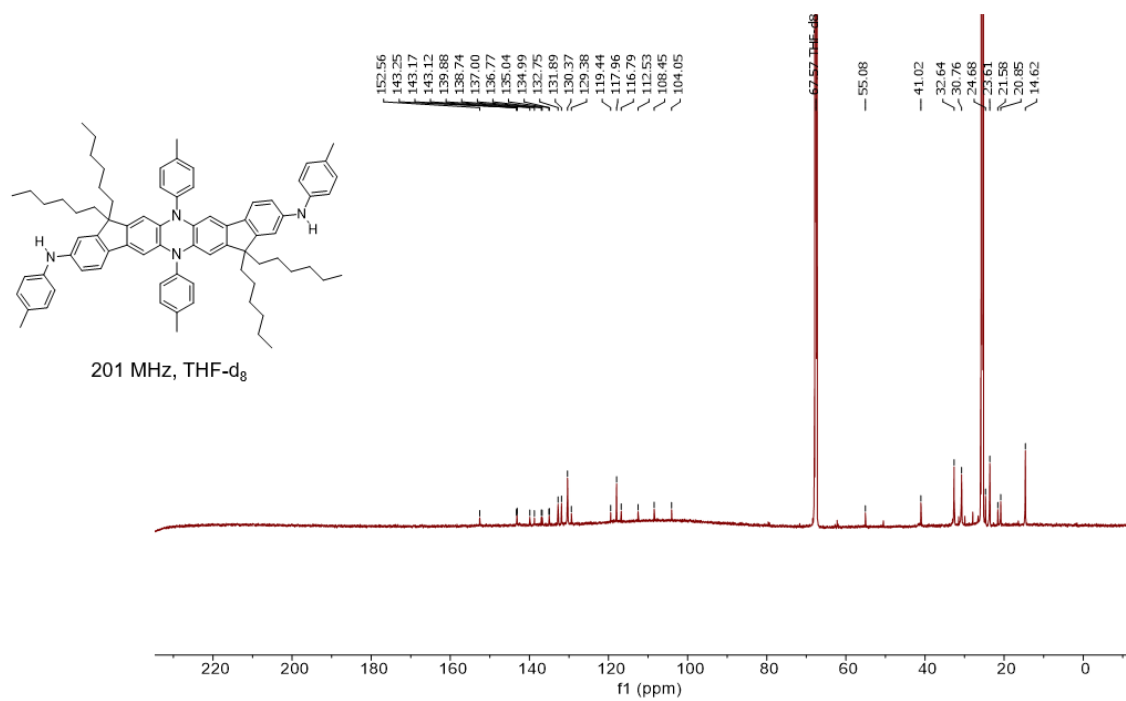
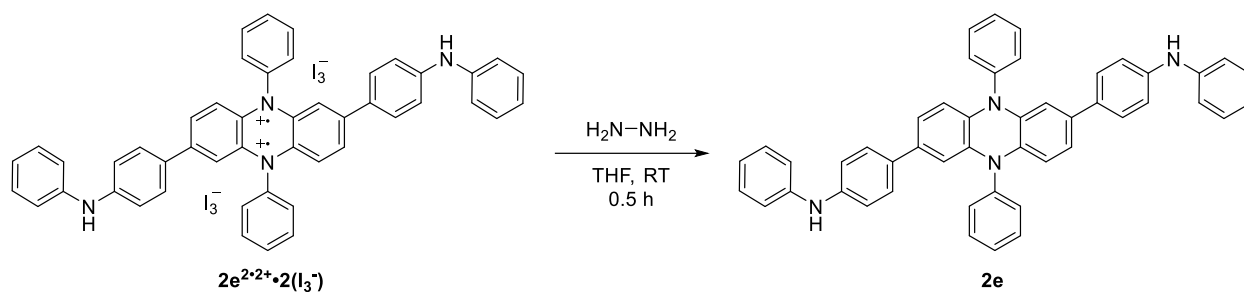


Fig S25. ^{13}C NMR of **2b**.



4,4'-(5,10-diphenyl-5,10-dihydrophenazine-2,8-diyl)bis(*N*-phenylaniline) 2e was synthesized from $2e^{2+} \cdot 2(I_3^-)$ following the same procedure for the synthesis of **2a**. Compound **2e** obtained as an off-white solid (41 mg, 87%). ^1H NMR (400 MHz, THF- d_8) δ (ppm); 7.46 (td, J = 6.8, 1.9 Hz, 8H), 7.35 (d, J = 9.2 Hz, 2H), 7.22-7.14 (m, 4H), 7.13-7.05 (m, 10H), 6.96 (t, J = 7.9 Hz, 4H), 6.88 (d, J = 8.6 Hz, 2H), 6.83-6.76 (m, 2H), 6.53 (d, 7.8 Hz, 2H), 6.49 (t, J = 7.3 Hz, 2H); ^{13}C NMR (201 MHz, THF- d_8) δ (ppm) δ 145.3, 145.0, 143.8, 143.6, 142.6, 138.9, 134.9, 134.0, 133.7, 129.96, 127.8, 127.7, 120.9, 120.8, 119.6, 119.4, 118.6, 118.5, 118.2, 118.1; HRMS (ESI $^+$) $[M]^+$ calcd. for $C_{48}H_{36}N_4$: m/z = 668.2940, found m/z = 668.2908.

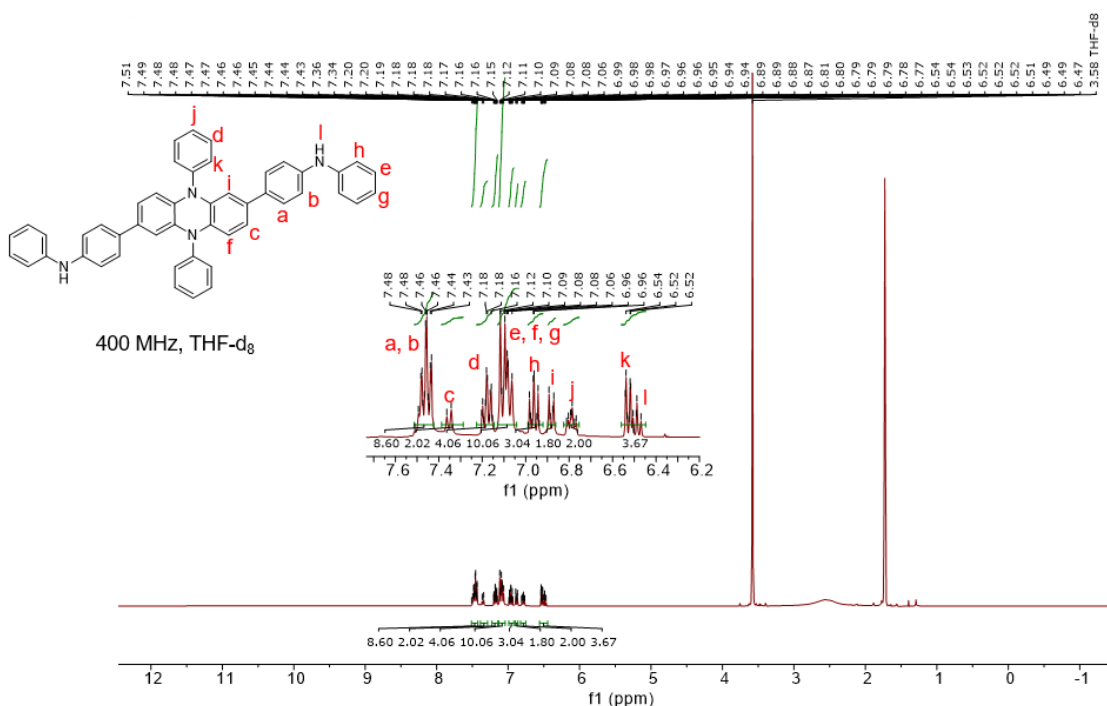


Fig S26. ^1H NMR of **2e**.

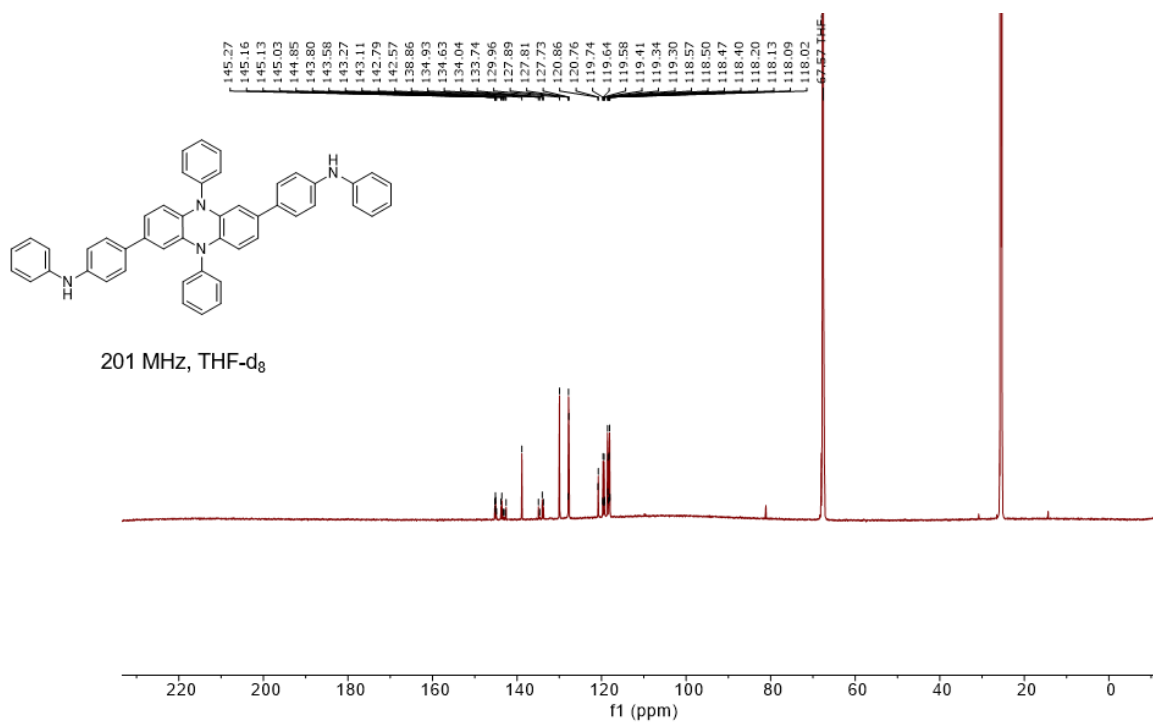


Fig S27. ^{13}C NMR of **2e**.

Spectroelectrochemistry Experiments

The spectroelectrochemical experiments were measured using a Biologic SP-150 potentiostat in combination with the Agilent Technologies Cary 6000i UV-Vis-NIR Spectrophotometer. Solutions were prepared in THF at a concentration of 1.5×10^{-4} mM with 0.2 M TBAPF₆ in THF as the supportive electrolyte, a platinum wire as the counter electrode, and a leakless Ag/AgCl electrode as reference electrode.

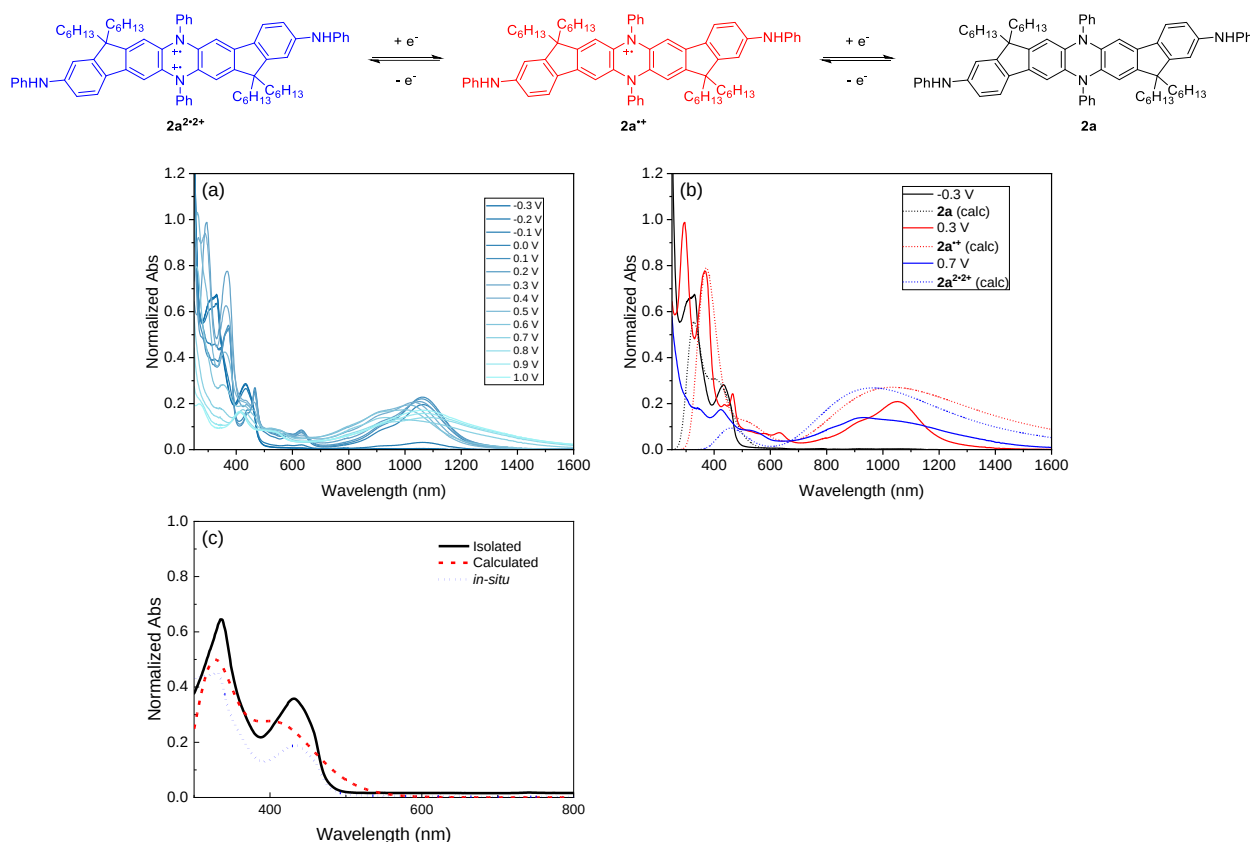


Fig S28. (a) Full range spectroelectrochemistry of **2a²⁺²⁺·2(I₃⁻)**; (b) selected spectroelectrochemistry of **2a²⁺²⁺·2(I₃⁻)** and simulated absorption spectra of **2a²⁺²⁺·2(I₃⁻)** (dotted blue line), **2a^{•+}·I₃⁻** (dotted red line), and **2a** (dotted black line); and (c) UV-Vis absorption comparison of **2a** isolated (solid black line), simulated (dashed red line), and *in-situ* from spectroelectrochemistry (dotted blue line).

X-Ray Diffraction Data

The single crystals of $2\mathbf{a}^{2+} \cdot 2(\mathbf{I}_3^-)$ were grown by vapor diffusion using chloroform/hexanes. A single crystal of $2\mathbf{a}^{2+} \cdot 2(\mathbf{I}_3^-)$ was coated with a trace of Fomblin oil and transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a Mo $K\alpha$ wavelength ($\lambda = 0.71073 \text{ \AA}$) sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, and a Photon II area detector. The instrument is equipped with an Oxford Cryosystems low temperature device and examination and data collection were performed at 150 K. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3¹⁵ and SADABS¹⁶. The space groups were assigned using XPREP within the SHELXTL suite of programs^{17,18} and solved by direct methods using ShelXS [4] or dual methods using ShelXT¹⁹ and refined by full matrix least squares against F^2 with all reflections using ShelXL2018²⁰ using the graphical interface ShelXL.²¹ H atoms attached to carbon were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for aromatic and alkene C-H moieties, and to 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH₂ and CH₃ moieties, respectively. The amine H atom position was refined, and the N-H distance was restrained to 0.88(2) Å. $U_{\text{iso}}(\text{H})$ values were set to a multiple of $U_{\text{eq}}(\text{C})$ with 1.5 for CH₃, and 1.2 for C-H, CH₂ and N-H units, respectively.

One of the two hexyl chains is disordered over two orientations. The two disordered moieties were restrained to have similar geometries as the other not disordered hexyl chain. U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.491(10) to 0.509(10).

Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2236746 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

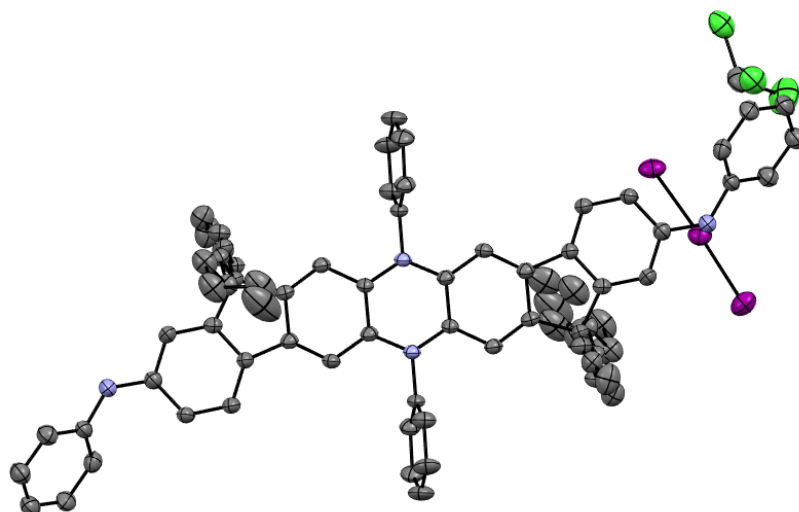


Fig S29. Displacement ellipsoid view of $2\mathbf{a}^{2+} \cdot 2(\mathbf{I}_3^-)$. 50% probability displacement ellipsoids. H atoms omitted for clarity.

Table S2. Crystal Data for $2\mathbf{a}^{2+} \cdot 2(\mathbf{I}_3^-)$

Crystal Data	
Chemical Formula	$\text{C}_{78}\text{H}_{84}\text{N}_4\text{I}_6$
Moiety Formula	$\text{C}_{78}\text{H}_{84}\text{N}_4^{2+} \times 2(\mathbf{I}_3^-)$
M_r	1790.94
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
a, b, c (Å)	10.5664(6), 12.5295(8), 16.6641(10)
α, β, γ (°)	79.906(4), 78.017(4), 70.671(3)
V (Å ³)	2020.4(2)
Z	1
Radiation Type	Mo $K\alpha$
μ (mm ⁻¹)	2.547
Crystal Size (mm)	$0.28 \times 0.09 \times 0.02$
Data Collection	
Diffractometer	Bruker AXS D8 Quest three circle diffractometer
Absorption Correction	multi-scan
T_{min}, T_{max}	0.536, 0.951
No. of measured, independent, and observed $[I > 2\sigma(I)]$ reflections	44030, 10055, 7124
R_{int}	0.0647
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.0764, 0.1416, 1.023
No. of reflections	10055
No. of parameters	467
No. of restraints	184
H-atom treatment	H-atom parameters mixed
	$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 8.5991P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	1.704, -1.325
CCDC	2236746

General Procedure for O-ATRP of MMA

The general procedure for polymerization was adapted from previous work.^{22,23} To an oven dried 20 mL scintillation vial with a septa screw cap was added 0.1 eq of **2a**. The vial was then evacuated and purged with N₂. Next, anhydrous DMAC (1.0 mL) and degassed, inhibitor free MMA (1.0 mL, 100 eq) was added. The mixture was stirred until full dissolution. The vial was then placed into the light well photoreactor approximately 2.5 cm away from the light source on all sides (Fig S30). Degassed initiator, ethyl α -bromoisobutyrate (EBiB, 1.0 eq) or ethyl α -bromophenylacetate (EBP, 1.0 eq), was added to initiate the polymerization. The vials were stirred at RT for 8 h. An aliquot was pulled after 8 h from the reactor to measure the conversion via ¹H NMR in CDCl₃. The reaction mass was precipitated into methanol (200 mL). The solids were collected, washed, and dried. Control reactions were performed with the same procedure, omitting the addition of **2a**.

O-ATRP LED Light Well Photoreactor

The LED light well was prepared by lining a 600 mL glass beaker with aluminum foil. To this foil, rows of LED light strips (MONSTER Model MLB7-1027) were adhered. The outside of the beaker was masked off with black vinyl tape. Atop the photoreactor a fan was placed to cool the LED light strip and maintain ambient temperature.

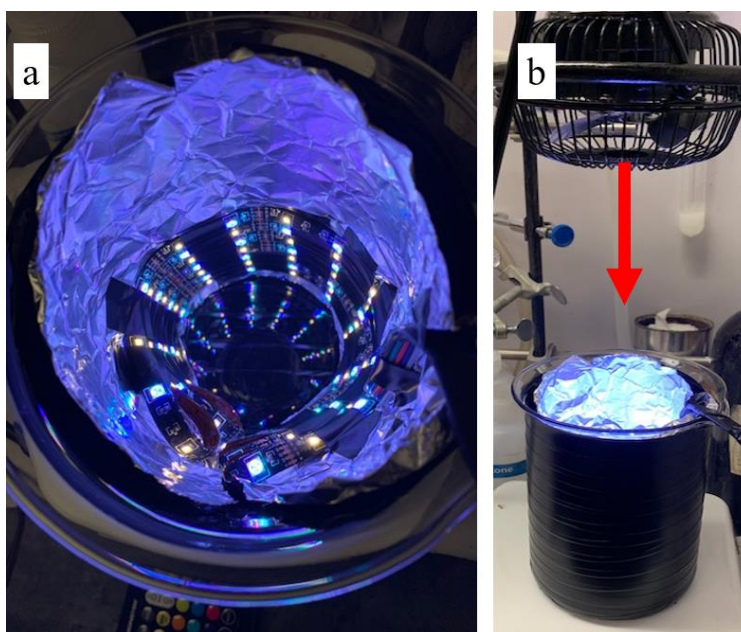
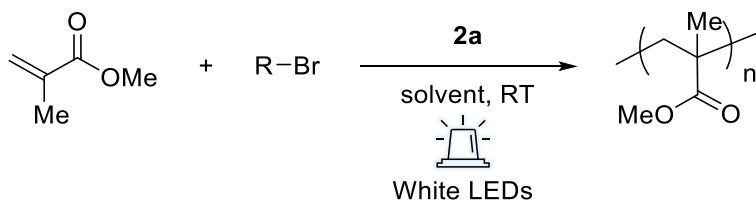


Fig S30. LED light well photoreactor; (a) topside view inside well and (b) side profile of well; during the reaction, the fan is lowered, and the entire photoreactor is covered with aluminum foil.

Table S3. Polymerization data of MMA using **2a**. Polymerizations were performed according to the above procedure using a ratio of [MMA]:[initiator]:[**2a**] = [100]:[1]:[0.1]. *Indicates no **2a**.



entry	Initiator (R-Br)	Solvent	Conv. (%)	M_n (kDa)	M_w (kDa)	$\bar{D}$	I^* (%)
S1	EBiB	THF	70.3	27.8	48.9	1.76	36.0
S2	EBP	THF	-	-	-	-	-
S3	EBP	DMAC	69.2	14.9	19.2	1.29	67.1
S4*	EBiB	DMAC	-	-	-	-	-
S5*	EBP	DMAC	-	-	-	-	-
S6	EBP	DMAC	88.5	20.2	28.2	1.40	49.5
S7	EBP	DMAC	87.8	22.8	30.1	1.41	43.9
S8	EBP	DMAC	80.6	24.1	37.0	1.53	41.1
S9	EBP	DMAC	82.6	19.2	28.5	1.48	52.1

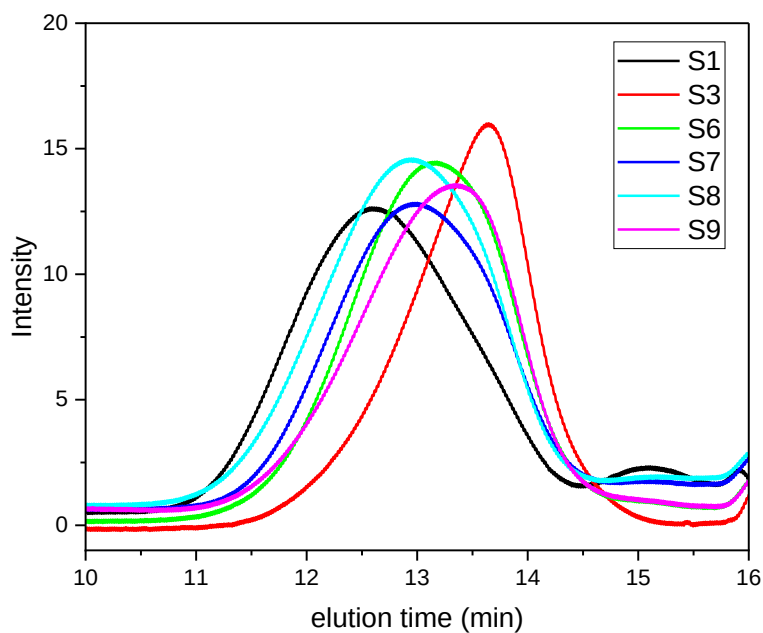


Fig S31. GPC traces of **S1**, **S3**, **S6–S9**.

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