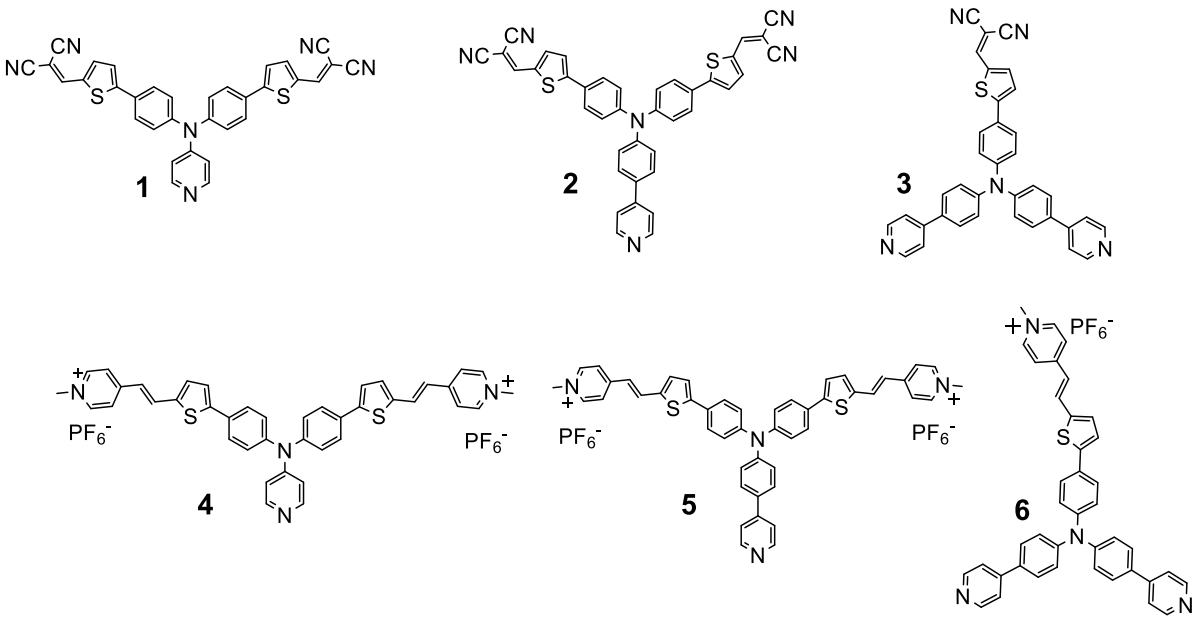
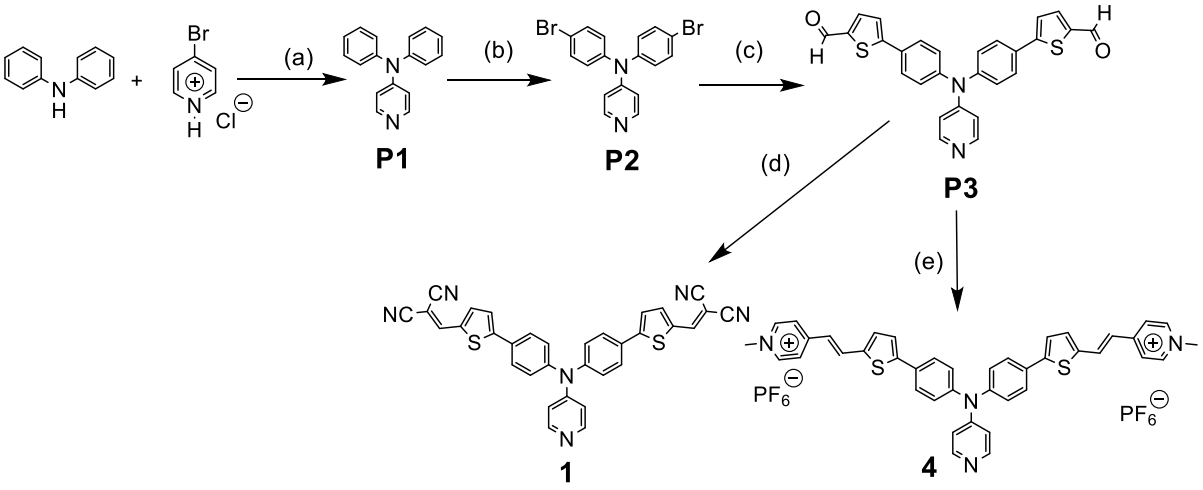
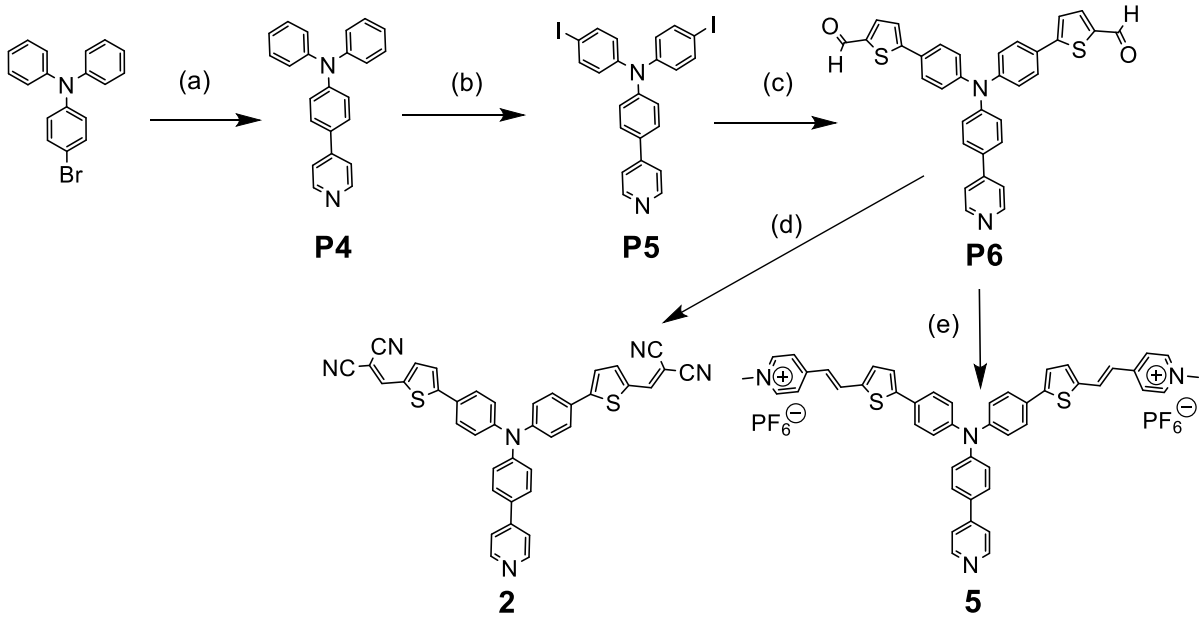
1. Structures of Dyes Studied



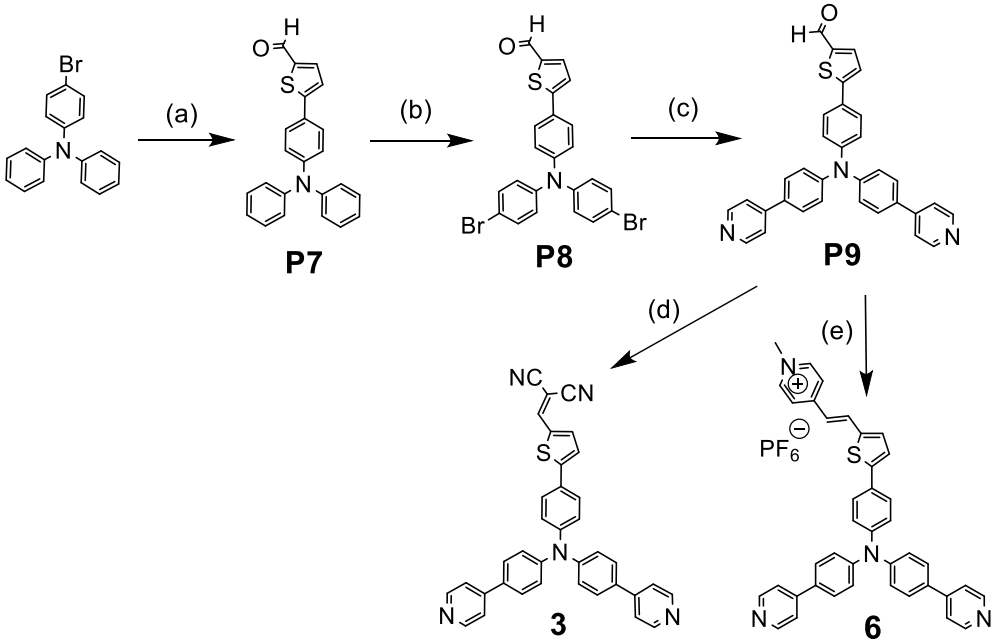
2. Synthetic Routes



Synthetic route to short pyridyl anchored dyes 1 and 4: (a) $Pd(OAc)_2$, (t-Bu)$_3$P, t-BuONa, toluene, 100 ^oC, 10h, 34%; (b) NBS, $CHCl_3$, reflux, overnight, 75%; (c) 5-formyl-2-thiophene boronic acid, $Pd(PPh_3)_4$, DME, 2M Na_2CO_3, reflux, 16h, 53%; (d) malononitrile, pyridine, toluene, 70 ^oC, 16h, 60%; (e) N-methyl picolinium iodide, piperidine, CH_3Cl/EtOH, 80 ^oC, 4 h, then NH_4PF_6, 25%.



Synthetic route to extended pyridyl anchored, *bis* acceptor dyes 2 and 5: (a) 4-pyridinylboronic acid, $Pd(PPh_3)_4$, DME, 2M Na_2CO_3, reflux, 16h, 77%; (b) ICl, $Zn(OAc)_2$, 1,4-dioxane, RT, 5h, 91%; (c) 5-formyl-2-thiophene boronic acid, $Pd(dppf)Cl_2$, toluene/methanol, K_2CO_3, reflux, 16h, 56%; (d) malononitrile, pyridine, toluene, 70 ^oC, 16h, 75%; (e) 4-methyl picolinium iodide, $CHCl_3$/EtOH, 80 ^oC, 4h, 45%.



Synthetic route to extended *bis*-pyridyl anchored, mono-acceptor dyes 3 and 6: (a) 5-formyl-2-thiophene boronic acid, $Pd(dppf)Cl_2$, toluene/methanol, K_2CO_3, reflux, 16 h, 89%; (b) NBS, rt, 2 h,

95%; (c) 4-pyridinylboronic acid, $Pd(PPh_3)_4$, DME, 2M Na_2CO_3, reflux, 16 h, 65%; (d) malononitrile, pyridine, toluene, 70 °C, 16h, 75%; (e) 4-methyl picolinium iodide, $CHCl_3$/ethanol, 80 °C, 4 h, 52%.

3. Synthetic Methods and Data

N,N-diphenylpyridin-4-amine (P1)

Diphenylamine (0.500 g, 2.954 mmol), 4-bromopyridine hydrochloride (0.690 g, 3.545 mmol), and $Pd(OAc)_2$ (0.045 g, 0.12 mmol), (*t*-Bu)$_3$P (0.04 g, 0.12 mmol), and *t*-BuONa (0.852 g, 8.86 mmol) were dissolved in toluene (40 mL) and stirred for 10 h at 100 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The residue was chromatographed on silica gel (hexane/ethylacetate = 3:7 as eluent) to give **P1** as colourless solid with 34 % yield. ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 8.23 (d, *J* = 6.6 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 4H), 7.17-7.20 (m, 6H), 6.73 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, δ): 153.70, 150.18, 145.25, 129.79, 126.69, 125.55, 112.78. ESI-MS: *m/z*: 247.12. Elemental analysis for $C_{17}H_{14}N_2$, Anal. (Calcd) %: C 82.78 (82.90); H 5.60 (5.73); N 11.25 (11.37).

N,N-bis(4-bromophenyl)pyridin-4-amine (P2)

Compound **P1** (0.300 g, 1.218 mmol) and N-bromosuccinimide (0.477 g, 2.68 mmol) were added to chloroform (30 mL) and several drops of acetic acid were then added. The mixture was stirred at room temperature for an hour and refluxed overnight, before cooling to room temperature and addition of water (50 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic layers dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography with hexane/ethylacetate (3:7) as the eluent. The product **P2** was obtained as a colourless solid with 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 8.27 (d, *J* = 6.8 Hz, 2H), 7.51 (d, *J* =8.8 Hz, 4H),

7.05 (d, *J* = 8.8 Hz, 4H), 6.77 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, δ): 153.01, 150.54, 144.08, 133.05, 127.88, 118.75, 113.53. ESI-MS (*m/z*): 404.94. Elemental analysis for $C_{17}H_{12}N_2Br_2$•$0.1C_6H_{14}$, Anal. (Calcd) %: C, 51.10 (51.22); H 3.31 (3.27); N 6.61 (6.78).

N,N-bis(5-formylthiophenyl)pyridin-4-amine (P3)

A 50 mL Schlenk tube was charged with 5-formylthiophene boronic acid (0.085 g, 0.544 mmol), $Pd(PPh_3)_4$ (0.006 g, 0.005 mmol), dimethoxyethane (6 mL) and 2 M aqueous sodium carbonate (1.5 mL), before purging with argon gas for 5 evacuate/refill cycles. Then compound **P2** (0.100 g, 0.247 mmol) was added. The tube was sealed and heated at 90 °C with very vigorous stirring for 16 h. Upon cooling to ambient temperature, the organics were removed by extracting three times with DCM. 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 silica gel column chromatography using hexane/ethylacetate (3/7, v/v) as eluent to give **P3** as a yellow powder in 52% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.89 (s, 2H), 8.36 (d, *J* = 7.0 Hz, 2H), 7.75 (d, *J* = 4.0 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 4H), 7.39 (d, *J* = 4.0 Hz, 2H), 7.24 (d, *J* = 9.0 Hz, 4H), 6.91 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 182.71, 153.09, 152.90, 150.60, 146.03, 142.53, 137.47, 130.13, 127.92, 126.43, 124.78, 124.08, 114.78. ESI-MS (*m/z*): 467.0872. Elemental analysis for $C_{27}H_{18}N_2O_2S_2$, Anal. (Calcd) %: C (69.62) 69.51; H 3.95 (3.89); N 5.91 (6.00).

N,N-diphenyl-4-(pyridin-4-yl)aniline (P4)

A 50 mL Schlenk tube was charged with 4-pyridyl boronic acid (0.568 g, 4.626 mmol), $Pd(PPh_3)_4$ (0.178 mg, 0.154 mmol), dimethoxyethane (10 mL) and 2 M aqueous sodium carbonate (2.5 mL), and was purged with argon gas for 5 evacuate/refill cycles. Then 4-bromotriphenylamine (0.500 g, 1.542 mmol) was added. The tube was sealed and heated at

90 °C with very vigorous stirring for 16 h. Upon cooling to ambient temperature, the mixture was extracted three times with DCM. 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 silica gel column chromatography using hexane/ethylacetate (7/3, v/v) as eluent to give **P4** (77%) as a pale yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.61 (d, *J* = 6.2 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 6.2 Hz, 2H), 7.29 (m, 4H), 7.16-7.12 (m, 6H), 7.08 (tt, *J* = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 150.14, 148.99, 147.71, 147.26, 130.92, 129.45, 127.66, 125.01, 123.63, 122.91, 120.89. ESI-MS (m/z): 323.1542. Elemental analysis for $C_{23}H_{18}N_2$, Anal. (Calcd) %: C 85.61 (85.68); H 5.58 (5.63); N 8.78 (8.69).

4-iodo-N-(4-iodophenyl)-N-(4-(pyridin-4-yl)phenyl)aniline (P5)

A 1 M solution of iodine monochloride in DCM (6.20 mL, 6.20 mmol) was added to 5 mL of dioxane. Zinc acetate was added to the above solution, which was stirred for 15 minutes at room temperature. Compound **P4** (0.500 g, 1.551 mmol) was dissolved in 5 mL of dioxane and added slowly, and stirring was continued at room temperature overnight. After the reaction completed (monitored by TLC), the reaction mixture was poured into sodium thiosulfate solution (1 M, 30 mL) and extracted twice with dichloromethane. The combined organic fractions were dried over $MgSO_4$, then filtered and the volume reduced *in vacuo*. The crude product was further purified by silica gel column chromatography using hexane/ethylacetate (7/3, v/v) as eluent to give compound **P5** (91%) as a pale yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.63 (d, *J* = 6.2 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 4H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 6.2 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 150.06, 147.81, 147.57, 146.62, 138.54, 132.41, 128.02, 126.44, 123.95, 121.04, 86.88. ESI-MS (m/z): 574.95. Elemental analysis for $C_{23}H_{16}N_2I_2$, Anal. (Calcd) %: C 48.19 (48.11); H 2.81 (2.81); N 4.94 (4.88).

4-{Bis-[4-(5-formyl-thiophen-2-yl)-phenyl]-amino}-N,N-diphenyl-4-(pyridin-4-yl)aniline (P6)

A 50 mL Schlenk tube was charged with 5-formylthiophene boronic acid (0.060 g, 0.383 mmol), $Pd(PPh_3)_4$ (0.040 mg, 0.035 mmol), dimethoxyethane (8 mL) and 2 M aqueous sodium carbonate (2.0 mL), and purged with argon gas for 5 evacuate/refill cycles. Then compound **P5** (0.100 g, 0.174 mmol) was added. The tube was sealed and heated at 90 °C with very vigorous stirring for 16 h. Upon cooling to ambient temperature, the mixture was extracted three times with DCM. 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 silica gel column chromatography using hexane/ethylacetate (3/7, v/v) as eluent to give compound **P6** (56%) as a yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.88 (s, 2H), 8.61-8.70 (br s, 2H), 7.73 (d, *J* = 3.9 Hz, 2H), 7.61 (m, 6H), 7.52 (d, *J* = 6.2 Hz, 2H), 7.35 (d, *J* = 3.9 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 4H). ^{13}C NMR (125 MHz, CDCl3, δ): 182.68, 153.73, 149.91, 147.76, 147.68, 147.55, 142.00, 137.62, 133.17, 128.28, 128.23, 127.65, 125.00, 124.53, 123.53, 121.19. ESI-MS (m/z): 543.12. Elemental analysis for $C_{33}H_{22}N_2O_2S_2$•$1.2H_2O$, Anal. (Calcd) %: C 70.18 (70.24); H 4.16 (4.36); N 5.03 (4.96).

5-{4-[bis(4-pyridin-4-yl)phenyl]aminophenyl}-thiophene-2-carbaldehyde (P9)

A 50 mL of Schlenk tube was charged with 4-pyridyl boronic acid (0.096 g, 0.78 mmol), $Pd(PPh_3)_4$ (0.045 g, 0.039 mmol), dimethoxyethane (8 mL) and 2 M aqueous sodium carbonate (2.0 mL), then the tube was purged with argon gas for 5 evacuate/refill cycles. Compound **P8** (0.100 g, 0.195 mmol) was and the tube was sealed and heated at 90 °C with very vigorous stirring for 16 h. Upon cooling to ambient temperature, the mixture was extracted three times with DCM. 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 silica gel column chromatography using hexane/ethylacetate (2/8, v/v) as eluent to give compound **P9** (65%) as a yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.88 (s, 1H), 8.66 (br s, 4H), 7.73 (d, *J* = 4.1 Hz, 1H), 7.59-7.62 (m, 6H), 7.50 (d, *J* = 5.2 Hz, 4H), 7.35 (d, *J* = 4.0 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 4H), 7.20 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 182.66, 153.84, 150.33, 148.04, 147.64, 147.32, 141.93, 137.62, 133.19, 128.14, 127.98, 127.59, 124.90, 124.28, 123.44, 121.12. ESI-MS (*m/z*): 510.16. Elemental analysis for $C_{33}H_{23}N_3OS$, Anal. (Calcd) %: C 77.65 (77.78); H 4.61 (4.55); N 8.13 (8.25).

4-(Bis-{4-[5-(2,2-dicyano-vinyl)-thiophene-2-yl]-phenyl}-amino)-pyridine (1)

A mixture of compound **P3** (0.050 g, 0.107 mmol), malononitrile (0.142 g, 2.14 mmol) and pyridine (0.2 mL) in anhydrous toluene (6 mL) was deoxygenated five times by placing under vacuum and backfilling with argon, and then heated at 70 ^{o}C for 16 h. After cooling to room temperature, the solvent was removed and the residue was purified by column chromatography over silica with a dichloromethane/methanol mixture (9:1) as the eluent to give **1** as a black solid (0.035 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$, δ) 8.40 (d, *J* = 6.3 Hz, 2H), 7.80 (s, 2H), 7.7 (d, *J* = 4.2 Hz, 2H), 7.7 (d, *J* = 8.7 Hz, 4H), 7.42 (d, *J* = 4.1 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 4H), 6.93 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 155.15, 152.62, 150.87, 150.44, 146.68, 140.09, 134.31, 129.15, 128.19, 126.26, 124.54, 115.46, 114.11, 113.33. ESI-MS (*m/z*): 563.11. Elemental analysis for $C_{33}H_{18}N_6S_2$, Anal. (Calcd) %: C 70.29 (70.44); H 3.31 (3.22); N 15.09 (14.94).

4-(Bis-{4-[5-(2,2-dicyano-vinyl)-thiophene-2-yl]-phenyl}-amino)-4-phenylpyridine (2)

A mixture of compound **P6** (0.060 g, 0.110 mmol), malononitrile (0.146 g, 2.21 mmol) and pyridine (0.2 mL) in anhydrous toluene (6 mL) was deoxygenated five times by placing under

vacuum and backfilling with argon, and then heated at 70 °C for 16 h. After cooling to room temperature, the solvent was removed and the residue was purified by column chromatography over silica gel by using dichloromethane/methanol mixture (9:1) as the eluent to give **2** (75%) as a red solid. ^{1}H NMR (500 MHz, $(CD_3)_2CO$, δ): 8.63 (d, *J* = 6.2 Hz, 2H), 8.41 (s, 2H), 7.97 (d, *J* = 4.2 Hz, 2H), 7.88 (m, 6H), 7.72 (d, *J* = 4.2 Hz, 2H), 7.68 (d, *J* = 6.2 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 4H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$, δ: 155.22, 151.65, 150.43, 148.40, 147.21, 146.63, 141.82, 134.05, 133.79, 128.29, 127.94, 127.43, 125.68, 124.59, 124.42, 120.80, 114.38, 113.74, 75.25. ESI-MS (*m/z*): 639.14. Elemental analysis for $C_{39}H_{22}N_6S_2 \bullet 0.6H_2O$, Anal. (Calcd): C 72.07 (72.11); H 3.74 (3.60); N 12.54 (12.94).

5-{4-[bis(4-pyridin-4-yl)phenyl]aminophenyl}-thiophene-2-vinyldinitrile (3)

A mixture of compound **P9** (0.100 g, 0.196 mmol), malononitrile (0.130 g, 1.962 mmol) and pyridine (0.2 mL) in anhydrous toluene (6 mL) was deoxygenated five times by placing under vacuum and backfilling with argon, and then heated at 70 °C for 16 h. After cooling to room temperature, the solvent was removed and the residue was purified by column chromatography over silica with a dichloromethane/methanol mixture (9:1) as the eluent to give compound **3** (75%) a brown solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.66 (d, *J* = 5.8 Hz, 4H), 7.77 (s, 1H), 7.70 (d, *J* = 4.2 Hz, 1H), 7.61-7.63 (m, 6H), 7.50 (d, *J* = 6.2 Hz, 4H), 7.38 (d, *J* = 4.2 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 4H), 7.19 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 156.23, 150.35, 148.82, 147.37, 147.29, 140.29, 133.66, 133.61, 128.23, 127.86, 126.71, 125.23, 123.82, 123.72, 121.12, 114.35, 113.54. ESI-MS (*m/z*): 558.1735. Elemental analysis for $C_{36}H_{23}N_5S \bullet H_2O$, Anal. (Calcd) %: C 75.16 (75.10); H 4.35 (4.38); N 12.18 (12.17).

4-(Bis-{4-[5-(2-[N-methyl-4-pyridiniumyl-vinyl)-thiophene-2-yl]-phenyl}-amino)-pyridine dihexafluorophosphate (4)

A 50 mL round bottom flask was charged with compound **P3** (0.050 g, 0.107 mmol) and N-methylpicolinium iodide (0.063 g, 0.268 mmol) and a 1:1 mixture of chloroform and ethanol was added (10 mL). A catalytic amount of piperidine was added and the mixture was refluxed at 80 ^{o}C for 4 hrs, before cooling to room temperature and addition of an excess of solid NH_4PF_6. The mixture was stirred until the product precipitated. Compound **4** (0.025 g, 25%, pale brown) was collected by vacuum filtration and washed several times with water and then diethyl ether. ^{1}H NMR (500 MHz, CD_3CN, δ): 8.41 (d, *J* = 7.0 Hz, 4H), 8.30 (dd, *J* = 4.8 Hz, 2H), 7.96 (d, *J* = 16.1 Hz, 1H), 7.93 (d, *J* = 7.1 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 4H), 7.47 (m, 2H), 7.27 (d, *J* = 8.7 Hz, 4H), 7.07 (d, *J* = 16.0 Hz, 2H), 6.89 (dd, *J* = 4.7 Hz, 2H), 4.17 (s, 3H). ^{13}C NMR (125 MHz, (CD_3CN, δ): 153.82, 149.80, 148.68, 148.59, 148.40, 147.86, 145.05 139.83, 134.70, 134.46, 132.76, 129.19, 128.88, 127.69, 125.39, 125.18, 125.09, 123.84, 121.69, 121.53, 47.67. ESI-MS (*m/z*): 323.11 $[M - 2PF_6]^{2+}$. Elemental analysis for $C_{41}H_{34}F_{12}N_4P_2S_2$, Anal. (Calcd) %: C 52.57 (52.49); H 3.66 (4.49); N 5.98 (5.37).

4-(Bis-{4-[5-(2-[N-methyl-4-pyridiniumyl-vinyl)-thiophene-2-yl]-phenyl}-amino)-4-phenylpyridine dihexafluorophosphate (5)

A 50 mL round bottom flask was charged with compound **P6** (0.060 mg, 0.110 mmol) and N-methyl picolinium iodide (0.057 g, 0.1841 mmol), which were then dissolved in 50:50 chloroform:ethanol (10 mL). A catalytic amount of piperidine was added and the mixture was refluxed at 80 ^{o}C for 4 h. After cooling to room temperature, excess solid NH_4PF_6 was added and the mixture was stirred until precipitation occurred. The precipitate was collected by vacuum filtration and washed several times with water and diethyl ether to yield **5** (45%) as a dark red solid. ^{1}H NMR (500 MHz, CD_3CN, δ): 8.61 (d, *J* = 6.2 Hz, 2H), 8.39 (d, *J* = 6.9 Hz, 4H), 7.96 (d, *J* = 16.1 Hz, 2H), 7.92 (d, *J* = 6.9 Hz, 4H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 4H), 7.61 (d, *J* = 6.2 Hz, 2H), 7.44 (m, 4H), 7.25 (d, *J* = 8.9 Hz, 2H), 7.18 (d, *J* = 8.7

Hz, 4H), 7.05 (d, *J* = 16.0 Hz, 2H), 4.16 (s, 6H). ^{13}C NMR (125 MHz, CD_3CN, δ): 150.45, 148.43, 145.05, 134.71, 134.47, 128.77, 127.67, 125.30, 125.20, 125.05, 123.84, 121.53, 47.67. ESI-MS(*m/z*): 361.13 $[M - 2PF_6]^{2+}$. Elemental analysis for $C_{47}H_{38}N_5F_{12}N_4P_2S_2$, Anal. (Calcd) %: C 55.73 (55.80); H 3.78 (3.92); N 5.53 (5.45).

5-{4-[bis(4-pyridin-4-yl)phenyl]aminophenyl}-thiophene-2-N-methylpyridinium hexafluorophosphate (6)

A 50 mL round bottom flask was charged with compound **P9** (0.050 g, 0.098 mmol) and N-methyl picolinium iodide (0.057 g, 0.245 mmol) and 1:1 chloroform:ethanol (10 mL) was added. A catalytic amount of piperidine was added to the above mixture, which was refluxed at 80 ^{o}C for 4 h. The mixture was cooled to room temperature and excess solidNH_4PF_6 was added, before stirring until precipitation occurred. The precipitate was collected by vacuum filtration and washed several times with water and ether to yield **6** as a red solid (52%). ^{1}H NMR (500 MHz, CD_3CN, δ): 8.60 (d, *J* = 6.1 Hz, 4H), 8.37 (d, *J* = 6.8 Hz, 2H), 7.93 (d, *J* = 16.1 Hz, 1H), 7.91 (d, *J* = 7.0 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 4H), 7.69-7.66 (m, 6H), 7.44 (m, 2H), 7.24 (d, *J* = 8.7 Hz, 4H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 15.9 Hz, 2H), 4.16 (s, 3H). ^{13}C NMR (125 MHz, (CD_3CN, δ): 153.82, 149.80, 148.68, 148.59, 148.40, 147.86, 145.05 139.83, 134.70, 134.46, 132.76, 129.19, 128.88, 127.69, 125.39, 125.18, 125.09, 123.84, 121.69, 121.53, 47.67. ESI-MS (*m/z*): 599.23 $[M - PF_6]^{+}$. Elemental analysis for $C_{40}H_{31}F_6N_4PS{\bullet}H_2O$, Anal. (Calcd) %: C 62.89 (62.99); H 4.32 (4.36); N 7.41 (7.34).