Supporting Information for

Post-Polymerisation Diversification of Conjugated Polymer by Inverse Electron Demand Diels-Alder Reaction

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Materials and Methods

General Experimental Procedure

Commercial reagents were used as supplied from Sigma Aldrich, Alfa Aesar, or Combi blocks without further purification. Tetrazine 1 was prepared by modification of previously reported procedures.1

Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol 500 MHz using CDCl₃ as the solvent. Data are reported as follows: chemical shift (integration, splitting (s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, sxt = sextet, spt = septet, m = multiplet), coupling constant, assignment).

Infrared spectra (FT-IR) were recorded using a Perkin-Elmer Paragon 1000 Fourier transform Spectrometer and with samples pelletized with KBr, and absorption maxima (λ_max) being quoted in wavenumbers (cm⁻¹). UV spectra were recorded on a Shimadzu UV3101PC UV-vis-NIR spectrophotometer with chloroform as the solvent and at a monomer concentration of about 2.5 x 10⁻⁵ M. High Resolution Mass Spectrometry (HRMS) was carried out by the National University of Singapore Mass Spectrometry Service using a Bruker MicrOTOF-QII positive ion nano-electrospray.

Proportion of protonated polymer was estimated using the following equation:

\[
\frac{[HP^+]}{[P]} \approx \frac{\varepsilon_f - \varepsilon_x}{\varepsilon_f}
\]

Whereby εᵢ = ε of polymer at local maxima between 538 nm to 574 nm when amount of TFA added is 20 µL, and εₓ = ε of polymer at local maxima between 538 to 574 nm when the amount of TFA added is x µL.

Emission ratio was calculated by the following equation:

\[
\text{Emission ratio} = \frac{Emission_x}{Initial\ emission}
\]

Whereby “initial emission” refers to the average measured emission (between 460 to 700 nm) of the polymer when no metal ions is added, and emissionₓ refers to the measured emission of the polymer (between 460 to 700 nm) when x amount of metal ions is added.

General method A for small molecule iEDDA reaction

\[
\text{Chlorobenzene, 160 °C, 16 hrs}
\]

To a red solution of tetrazine 1 (404 mg, 1 mmol, 1 eq) in chlorobenzene (5 mL) was added the corresponding aryl alkyne (5 eq). The solution was stirred at 160 °C for 16 hours, with the solution turning from red to yellowish brown, then cooled to RT, and concentrated in vacuo to remove excess chlorobenzene. The solid was then re-dissolved in minimum chloroform and reprecipitated in methanol, and filtered to obtain a yellowish-brown powder, which was dried and used without further purification.
3,6-bis(5-bromothiophen-2-yl)-4-phenylpyridazine (3a)

General procedure A was applied to tetrazine 1 with phenylacetylene (548 µL, 5 mmol). A yellowish-brown powder was obtained (444 mg, 92%). IR (λ<sub>max</sub>/cm<sup>-1</sup>) 3058, 1578, 1492, 1484, 1380, 1237, 1077. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>) 7.51-7.49 (4H, m), 7.37 – 7.35 (3H, m), 7.10 (1H, d, J = 4.2 Hz), 6.78 (1H, d, J = 3.8 Hz), 6.35 (1H, d, J = 4.2 Hz). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) 152.0, 151.6, 141.4, 141.3, 138.4, 136.3, 131.3, 130.6, 129.7, 129.4, 128.4, 128.3, 123.8, 117.7, 117.6. HRMS (FTMS +p NSI) m/z: [M + H]<sup>+</sup> calculated for C<sub>18</sub>H<sub>11</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>2</sub> 476.8725, found = 476.8723, Δ = 0.42 ppm.

3,6-bis(5-bromothiophen-2-yl)-4-(p-tolyl)pyridazine (3b)

General procedure A was applied to tetrazine 1 with p-tolylacetylene (633 µL, 5 mmol). A yellowish-brown powder was obtained (442 mg, 90%). IR (λ<sub>max</sub>/cm<sup>-1</sup>). 3031, 2917, 1610, 1578, 1509, 1484, 1374, 1236, 1212, 1178, 1073. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>) 7.61 (1H, d, J = 3.6 Hz), 7.54 (1H, s), 7.32 – 7.25 (4H, m), 7.13 (1H, d, J = 3.6 Hz), 6.84 (1H, d, J = 3.7 Hz), 6.65 (1H, d, J = 3.7 Hz), 2.46 (3H, s). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) 151.7, 151.6, 140.6, 140.3, 140.2, 139.5, 132.9, 131.5, 130.7, 130.5, 130.1, 128.4, 129.3, 127.7, 124.3, 118.2, 118.0, 21.6. HRMS (FTMS +p NSI) m/z: [M + H]<sup>+</sup> calculated for C<sub>19</sub>H<sub>13</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>2</sub> 490.8880 found = 490.8881, Δ = 0.20 ppm.

3,6-bis(5-bromothiophen-2-yl)-4-(4-methoxyphenyl)pyridazine (3c)

General procedure A was applied to tetrazine 1 with 4-ethynylanisole (647 µL, 5 mmol). A yellowish-brown powder was obtained (447 mg, 88%). IR (λ<sub>max</sub>/cm<sup>-1</sup>) 2963, 1607, 1581, 1578, 1509, 1484, 1374, 1236, 1212, 1178, 1073. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>) 7.48 (1H, s), 7.38 (1H, d, J = 3.6 Hz), 7.29 (2H, d, J = 8.2 Hz), 7.10 (1H, d, J = 3.6 Hz), 7.01 (2H, d, J = 8.2 Hz), 6.81 (1H, d, J = 4.2 Hz), 6.51 (1H, d, J = 4.2 Hz). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) 160.8, 152.0, 151.9, 141.3, 141.1, 138.5, 131.3, 130.7, 130.0, 129.9, 128.1, 127.0, 123.6, 117.8, 117.5, 114.8, 55.6. HRMS (FTMS +p NSI) m/z: [M + H]<sup>+</sup> calculated for C<sub>19</sub>H<sub>13</sub>Br<sub>2</sub>N<sub>2</sub>OS<sub>2</sub> 506.8831 found = 506.8829, Δ = 0.39 ppm.

3,6-bis(5-bromothiophen-2-yl)-4-(4-fluorophenyl)pyridazine (3d)
General procedure A was applied to tetrazine 1 with 1-ethynyl-4-fluorobenzene (572 µL, 5 mmol). A brown powder was obtained (430 mg, 87%). IR (λ_{max}/cm^{-1}) 3047, 1606, 1509, 1435, 1380, 1236, 1162, 1078. $^1$H NMR (500.1 MHz, CDCl$_3$) 7.47 (1H, s), 7.37 – 7.34 (3H, m), 7.20 (2H, t, J = 8.3 Hz), 7.10 (1H, d, J = 4.7 Hz), 6.82 (1H, d, J = 4.1 Hz), 6.41 (1H, d, J = 4.1 Hz). $^{19}$F NMR (470.6 MHz, CDCl$_3$) -110.6 $^{13}$C NMR (100.6 MHz, CDCl$_3$) 163.5 (d, J = 247.9 Hz), 152.1, 151.7, 141.2, 137.3, 132.2, 131.3, 130.7, 130.5, 130.4, 129.9, 126.8, 123.3, 117.7, 116.8, 116.6. HRMS (FTMS +p NSI) m/z: [M + H]$^+$ calculated for C$_{19}$H$_{10}$Br$_2$F$_3$N$_2$S$_2$ 544.8599 found = 544.8596, Δ = 0.55 ppm.

3,6-bis(5-bromo thiophen-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridazine (3e)

Stille Coupling of P1

To a 100 mL round-bottomed flask with a large oval stirrer bar was added tetrazine 1 (404 mg, 1 mmol), (4,4'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (828 mg, 1 mmol), and tetrakis(triphenylphosphine)palladium(0) (57.8 mg, 0.05 mmol). The flask was sealed with a septum and evacuated / backfilled with nitrogen three times. Degassed toluene (10 mL) was then added via syringe. The mixture was heated at 120°C for 24 hours. The solution was allowed to cool, then precipitated in methanol (100 mL). Filtration gave the crude polymer as a purple powder. The polymer was purified by Soxhlet extraction by acetone (3 hours), hexane (3 hours), and finally chloroform (3 hours). Chloroform was then removed in vacuo and the polymer was re-dissolved in a minimum amount of chloroform. The polymer was then re-precipitated in methanol, filtered, and dried under vacuum to yield a purple solid (475 mg, 63%, M$_n$ = 5.0 kDa, PDI = 1.42). IR (λ_{max}/cm^{-1}) 2922, 2851, 2344, 1444, 1388,1080, 1063, 1001. $^1$H NMR (500.1 MHz, CDCl$_3$) 8.20 (br), 7.03 (br), 6.82 (br), 6.80 (br), 6.77 (br). $^{13}$C NMR (100.6 MHz, CDCl$_3$) 163.5 (d, J = 247.9 Hz), 152.1, 151.1, 141.0, 140.9, 140.8, 140.0, 136.8, 132.1, 131.3, 130.8, 129.9, 129.0, 127.0, 126.5, 124.9, 123.1, 118.1, 118.0. HRMS (FTMS +p NSI) m/z: [M + H]$^+$ calculated for C$_{19}$H$_{10}$Br$_2$F$_3$N$_2$S$_2$ 544.8599 found = 544.8596, Δ = 0.55 ppm.

3a

Stille Coupling of P2a (ii)

To a 100 mL round-bottomed flask with a large oval stirrer bar was added 3,6-bis(5-bromo thiophen-2-yl)-4-phenyl pyridazine 3a (93 mg, 0.2 mmol), (4,4'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (165 mg, 0.2 mmol), and tetrakis(triphenylphosphine)palladium(0) (11.5 mg, 0.01 mmol). The flask was sealed with a septum and evacuated / backfilled with nitrogen three times. Degassed toluene (2 mL) was then added via syringe. The mixture was heated at 120°C for 24 hours. The solution was allowed to cool, then precipitated in methanol (100 mL). Filtration gave the crude polymer as an orange-red powder. The polymer was purified by Soxhlet extraction by acetone (3 hours), hexane (3 hours), and finally chloroform (3 hours). Chloroform was then removed in vacuo and the polymer was re-
dissolved in a minimum amount of chloroform. The polymer was then re-precipitated in methanol, filtered, and dried under vacuum to yield a yellow solid (110 mg, 67 %, M_n = 8.9 kDa, PDI = 1.69). IR (λ_max/cm⁻¹) 2921, 2850, 1442, 1380, 1078, 792. ^1H NMR (500.1 MHz, CDCl₃) 7.60 – 7.48 (br), 7.47 – 7.38 (br), 7.20 – 7.14 (br), 7.05 – 7.14 (br), 6.90 – 6.84 (br), 6.60 – 6.58 (br), 2.87 – 2.71 (br), 1.75 – 1.08 (m, alkyl peaks), 0.93 – 0.78 (br).

General method B for polymer iEDDA reaction

To a dark purple solution of polymer P₁ (37.8 mg, 0.05 mmol) in chlorobenzene (3 mL) was added the corresponding aryl alkyne (2 mmol, 10 eq). The solution was stirred at 160 °C for 16 hours, cooled to RT, then precipitated in methanol and filtered. The filtrate was then re-dissolved in minimum chloroform (~ 1 mL) and re-precipitated in methanol a second time to obtain an orange-red solid, which was dried in vacuo.

P2a(i)

General procedure B was applied to polymer P₁ with phenylacetylene (219 µL, 2 mmol). An orange powder was obtained (35.6 mg, 87%, M_n = 5.3 kDa, PDI = 1.47). IR (λ_max/cm⁻¹) 2922, 2851, 1446, 1384, 1073, 758. ^1H NMR (500.1 MHz, CDCl₃) 7.63 – 7.48 (br), 7.47 – 7.38 (br), 7.20 – 7.15 (br), 7.06 – 6.95 (br), 6.90 – 6.84 (br), 6.61 – 6.48 (br), 2.94 – 2.47 (br), 1.75 – 1.08 (m, alkyl peaks), 0.91 – 0.78 (br).

P2b(i)

General procedure B was applied to polymer P₁ with p-tolylacetylene (253 µL, 2 mmol). An orange powder was obtained (32.1 mg, 77%, M_n = 6.0 kDa, PDI = 1.42). IR (λ_max/cm⁻¹) 2920, 2849, 1437, 1377, 1076, 794. ^1H NMR (500.1 MHz, CDCl₃) 7.60 – 7.51 (br), 7.38 – 7.24 (br), 7.20 – 7.15 (br), 7.06 – 6.95 (br), 6.90 – 6.84 (br), 6.61 – 6.48 (br), 2.90 – 2.47 (br), 2.50 – 2.41 (br, phenyl CH₃), 1.75 – 1.03 (m, alkyl peaks), 0.90 – 0.78 (br).

P2c(i)

General procedure B was applied to polymer P₁ with 4-ethynylanisole (258 µL, 2 mmol). An orange powder was obtained (37.2 mg, 88%, M_n = 5.9 kDa, PDI = 1.43). IR (λ_max/cm⁻¹) 2920, 2850, 1607, 1438, 1378, 1290, 1248, 1174, 1030, 830, 793. ^1H NMR (500.1 MHz, CDCl₃) 7.60 – 7.50 (br), 7.38 – 7.24 (br), 7.20 – 7.15 (br), 7.07 – 6.97 (br), 6.62 – 6.61 (br), 6.55 (br), 2.90 – 2.72 (br), 2.50 – 2.41 (br, phenyl CH₃), 1.75 – 1.03 (m, alkyl peaks), 0.89 – 0.77 (br).
General procedure B was applied to polymer P1 with 1-ethynyl-4-fluorobenzene (228 µL, 2 mmol). An orange powder was obtained (25.9 mg, 62%, $M_n = 6.2$ kDa, PDI = 1.38). IR ($\lambda_{\text{max}}$/cm$^{-1}$) 2921, 2850, 1437, 1379, 1231, 1158, 1077, 835, 790. $^1$H NMR (500.1 MHz, CDCl$_3$) 7.62 – 7.50 (br), 7.45 – 7.38 (br), 7.30 – 7.20 (br), 7.05 – 6.96 (br), 6.92 – 6.88 (br), 6.62 (s), 6.54 (s), 2.87 – 2.48 (br), 2.26 (s), 1.78 (s), 1.73 – 0.95 (m, alkyl peaks), 0.92 – 0.76 (br). $^{19}$F NMR (470.6 MHz, CDCl$_3$) 111.1.

General procedure B was applied to polymer P1 with 4-ethynyl-α,α,α-trifluorotoluene (327 µL, 2 mmol). An orange powder was obtained (28.9 mg, 65%, $M_n = 5.4$ kDa, PDI = 1.43). IR ($\lambda_{\text{max}}$/cm$^{-1}$) 2922, 2851, 1578, 1441, 1380, 1322, 1167, 1129, 1068, 843, 791. $^1$H NMR (500.1 MHz, CDCl$_3$) 7.82 – 7.79 (br), 7.62 – 7.50 (br), 7.45 – 7.38 (br), 7.30 – 7.20 (br), 7.05 – 7.15 (br), 7.06 – 6.95 (br), 6.92 – 6.85 (br), 6.62 (s), 6.54 – 6.50 (br), 2.87 – 2.48 (br), 2.26 (s), 1.77 (s), 1.74 – 1.03 (m, alkyl peaks), 0.91 – 0.77 (br). $^{19}$F NMR (470.6 MHz, CDCl$_3$) 62.5.
Figure S1: UV Spectra of P1 reacted with 1 eq of arylalkyne (P2e(i) partial) and 10 eq of aryl alkyne (P2e(i)).
Figure S2: UV Spectra of polymers with iterative addition of TFA. (a) P2a(i). (b) P2b(i). (c) P2c(i). (d) P2d(i). (e) P2e(i).
Fluorescence quenching of polymers with metal ions

![Graphs](image)

**Figure S3:** Emission spectra of polymers with iterative addition of metal ions. Left: P2c(i), right: P2e(i). (a) Addition of CuCl₂, (b) FeCl₃, (c) AgNO₃, (d) NiCl₂. All metal concentrations were 100 mg mL⁻¹ in water. Measurements were conducted in THF with a concentration of ~2.5 × 10⁻⁵ M.
References

Appendix A: $^1$H, $^{13}$C and $^{19}$F NMR spectra