

# Supporting Information

## Electrochemical Behavior of Thiocarbonylthio Chain Transfer Agents for RAFT Polymerization

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### Experimental Details

#### Materials

RAFT agents TC-6,<sup>1</sup> TC-8, TC-9, TC-11,<sup>2</sup> TC-12, TC17,<sup>3</sup> DC-2,<sup>4</sup> DC-3,<sup>4</sup> DC-6,<sup>1</sup> X-1,<sup>1</sup> and X-3<sup>1</sup> were kindly provided by current and former researchers at CSIRO. *tert*-Butyl dithiobenzoate (DB-6) was synthesized following the procedure described by Chernikova et al.<sup>5</sup> TC-4,<sup>6</sup> TC-5,<sup>7</sup> TC-7,<sup>8</sup> TC-13,<sup>8</sup> and X-2<sup>9</sup> were synthesized as previously described. RAFT agents DB-1, DB-2, DB-3, DB-4, DB-5, DB-7, TC-14, TC-18, TC-19, DC-4, and DC-7 were purchased from Aldrich; TC-1, TC-2, TC-10, TC-15, TC-16, DC-1, and DC-5 were purchased from Boron Molecular, and TC-3 was purchased from STREM. The structure and purity of RAFT agents was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR. TBAPF<sub>6</sub>, KPF<sub>6</sub>, and decamethylferrocene (Me<sub>10</sub>Fc) were used without further purification. Solvents (anhydrous or HPLC grade) were used as received. *N,N*-dimethylacrylamide (DMA), purchased from Aldrich, was distilled under reduced pressure prior to polymerization.

NMR data for RAFT agents:

4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (DB-1): <sup>1</sup>H NMR,  $\delta$ , ppm: 1.95 (s, 3H, CH<sub>3</sub>), 2.43-2.77 (m, 4H, 2  $\times$  CH<sub>2</sub>), 7.38-7.58 (m, 5H, ArH). <sup>13</sup>C NMR,  $\delta$ , ppm: 24.5, 29.8, 33.4, 46.0, 118.7, 127.1, 129.0, 133.5, 144.9, 176.8, 222.5

2-cyano-2-propyl benzodithioate (DB-2): <sup>1</sup>H NMR,  $\delta$ , ppm: 1.95 (s, 6H, 2  $\times$  CH<sub>3</sub>), 7.38-7.93 (m, 5H, ArH). <sup>13</sup>C NMR,  $\delta$ , ppm: 26.8, 42.1, 120.3, 127.0, 128.9, 144.9, 223.5

cyanomethyl benzodithioate (DB-3): <sup>1</sup>H NMR,  $\delta$ , ppm: 4.19 (s, 2H, CH<sub>2</sub>), 7.42-8.01 (m, 5H, ArH). <sup>13</sup>C NMR,  $\delta$ , ppm: 22.4, 114.9, 127.4, 129.1, 133.9, 143.8, 222.7

cumyl dithiobenzoate (DB-4): <sup>1</sup>H NMR,  $\delta$ , ppm: 2.01 (s, 6H, 2  $\times$  CH<sub>3</sub>), 7.22-7.87 (m, 10H, ArH). <sup>13</sup>C NMR,  $\delta$ , ppm: 28.7, 56.9, 127.0, 127.1, 128.4, 128.5, 132.1, 144.6, 146.7, 227.5

benzyl benzodithioate (DB-5): <sup>1</sup>H NMR,  $\delta$ , ppm: 4.60 (s, 2H, CH<sub>2</sub>), 7.26-7.40 (m, 10H, ArH). <sup>13</sup>C NMR,  $\delta$ , ppm: 42.7, 127.3, 128.1, 128.7, 129.1, 129.7, 132.8, 135.3, 145.1, 228.1

*tert*-butyl dithiobenzoate (DB-6): <sup>1</sup>H NMR,  $\delta$ , ppm: 1.68 (s, 9H, 3  $\times$  CH<sub>3</sub>), 7.32-7.87 (m, 5H, ArH). <sup>13</sup>C NMR,  $\delta$ , ppm: 28.6, 52.6, 127.0, 128.5, 132.0, 147.6, 230.7

2-(phenylcarbonothioylthio)propanoic acid (DB-7): <sup>1</sup>H NMR,  $\delta$ , ppm: 1.72 (d, 3H, CH<sub>3</sub>), 4.80-1.84 (q, 1H, CH), 7.38-8.01 (m, 5H, ArH). <sup>13</sup>C NMR,  $\delta$ , ppm: 16.7, 48.4, 127.4, 128.8, 133.3, 144.5, 176.6, 226.1

4-cyano-4-(((dodecylthio)carbonothioyl)thio)pentanoic acid (TC-1):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.88 (t, 3H,  $\text{CH}_3$ ), 1.26 (m, 16H,  $8 \times \text{CH}_2$ ), 1.32-1.41 (m, 2H,  $\text{CH}_2$ ), 1.66-1.73 (m, 2H,  $\text{CH}_2$ ), 1.89 (s, 3H,  $\text{CH}_3$ ), 2.35-2.71 (m, 4H,  $2 \times \text{CH}_2$ ), 3.33 (t, 2H,  $\text{SCH}_2$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.5, 23.1, 25.2, 28.0, 29.3, 29.4, 29.7, 29.8, 29.9, 30.0, 32.3, 33.9, 37.5, 46.6, 119.3, 176.7, 217.2

2-cyanobutan-2-yl dodecyl carbonotrithioate (TC-2):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.88 (t, 3H,  $\text{CH}_3$ ), 1.17 (t, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.22 (s, 16H,  $8 \times \text{CH}_2$ ), 1.38-1.41 (m, 2H,  $\text{CH}_2$ ), 1.89 (s, 2H,  $\text{CH}_2$ ), 2.00-2.05 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 3.33 (t, 2H,  $\text{SCH}_2$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 9.56, 14.5, 23.1, 24.7, 28.1, 29.3, 29.4, 29.7, 29.8, 29.9, 30.0, 32.3, 33.0, 37.3, 42.3, 119.9, 218.1

2-cyano-2-propyl dodecyl trithiocarbonate (TC-3):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.88 (t, 3H,  $\text{CH}_3$ ), 1.26 (m, 16H,  $8 \times \text{CH}_2$ ), 1.30-1.41 (m, 2H,  $\text{CH}_2$ ), 1.65-1.77 (m, 2H,  $\text{CH}_2$ ), 1.88 (s, 6H,  $2 \times \text{CH}_3$ ), 3.33 (t, 2H,  $\text{SCH}_2$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.5, 23.1, 23.8, 27.4, 28.1, 29.3, 29.4, 29.7, 29.8, 29.9, 30.0, 32.3, 33.9, 37.3, 42.7, 119.3, 120.8, 218.2

butyl (2-cyanopropan-2-yl) carbonotrithioate (TC-4):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.94 (t, 3H,  $\text{CH}_3$ ), 1.41-1.47 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 1.67-1.70 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 1.88 (s, 6H,  $2 \times \text{CH}_3$ ), 3.35 (t, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 13.9, 22.5, 27.4, 30.1, 37.0, 42.7, 120.8, 218.2

2-cyanopropan-2-yl methyl carbonotrithioate (TC-5):  $^1\text{H}$  NMR,  $\delta$ , ppm: 1.88 (s, 6H,  $2 \times \text{CH}_3$ ), 2.73 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 20.3, 23.8, 27.4, 42.8, 120.8, 218.6

cyanomethyl dodecyl trithiocarbonate (TC-6):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.88 (t, 3H,  $\text{CH}_3$ ), 1.28 (m, 16H,  $8 \times \text{CH}_2$ ), 1.30-1.43 (m, 2H,  $\text{CH}_2$ ), 1.69-1.73 (m, 2H,  $\text{CH}_2$ ), 3.37 (t, 2H,  $\text{SCH}_2$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.5, 21.7, 23.1, 28.1, 29.2, 29.4, 29.7, 29.8, 29.9, 30.0, 32.3, 38.3, 115.1, 219.1

phthalimidomethyl butyl trithiocarbonate (TC-7):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.93 (t, 3H,  $\text{CH}_3$ ), 1.39-1.47 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 1.65-1.72 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 3.38 (t, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 5.66 (s, 2H,  $\text{SCH}_2\text{N}$ ), 7.74-7.88 (m, 4H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 13.9, 22.4, 30.3, 37.4, 42.4, 124.1, 132.3, 134.8, 167.0, 221.2

ethyl 2-(((butylthio)carbonothioyl)thio)propanoate (TC-8):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.93 (t, 3H,  $\text{CH}_3$ ), 1.27 (t, 3H,  $\text{OCH}_2\text{CH}_3$ ), 1.39-1.48 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 1.59 (d, 3H,  $\text{CH}_3$ ), 1.65-1.72 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 3.37 (t, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 4.17-4.23 (m, 2H,  $\text{OCH}_2\text{CH}_3$ ), 4.78-4.84 (q, 1H, CH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 13.9, 14.4, 17.3, 22.4, 30.3, 37.3, 48.4, 62.2, 171.5, 222.5

ethyl 2-(((butylthio)carbonothioyl)thio)acetate (TC-9):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.93 (t, 3H,  $\text{CH}_3$ ), 1.28 (t, 3H,  $\text{OCH}_2\text{CH}_3$ ), 1.40-1.46 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 1.67-1.71 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 3.38 (t, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 4.17 (s, 2H,  $\text{CH}_2$ ), 4.18-4.24 (m, 2H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.0, 14.5, 22.4, 30.3, 37.6, 38.8, 62.4, 167.9, 222.8

S,S-dibenzyl trithiocarbonate (TC-10):  $^1\text{H}$  NMR,  $\delta$ , ppm: 4.63 (s, 4H,  $2 \times \text{CH}_2$ ), 7.28-7.36 (m, 10H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 41.9, 128.2, 129.1, 129.6, 135.3, 223.1

benzyl dodecyl carbonotrithioate (TC-11):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.88 (t, 3H,  $\text{CH}_3$ ), 1.26 (s, 16H,  $8 \times \text{CH}_2$ ), 1.38-1.42 (m, 2H,  $\text{CH}_2$ ), 1.67-1.72 (m, 2H,  $\text{CH}_2$ ), 3.37 (m, 2H,  $\text{CH}_2$ ), 4.61 (s, 2H,  $\text{CH}_2$ ), 7.27-7.35 (m, 5H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.5, 23.1, 28.3, 29.3, 29.5, 29.7, 29.8, 29.9, 30.0, 32.3, 37.4, 41.7, 128.1, 129.0, 129.6, 135.5, 224.2

methyl (1-phenylethyl) carbonotrithioate (TC-12):  $^1\text{H}$  NMR,  $\delta$ , ppm: 1.76 (d, 3H,  $\text{CH}_3$ ), 2.72 (s, 3H,  $\text{SCH}_3$ ), 5.33 (m, 1H, CH), 7.26-7.41 (m, 5H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 20.3, 21.3, 50.7, 128.0, 128.1, 129.0, 141.5, 224.0

dibutyl carbonotrithioate (TC-13):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.93 (t, 6H,  $2 \times \text{CH}_3$ ), 1.41-1.47 (m, 4H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 1.67-1.70 (m, 4H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 3.37 (t, 4H,  $\text{SCH}_2\text{CH}_2\text{CH}_2$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.0, 22.4, 30.4, 36.9, 225.2

dimethyl trithiocarbonate (TC-14):  $^1\text{H}$  NMR,  $\delta$ , ppm: 2.76 (s, 6H,  $2 \times \text{CH}_3$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 20.5, 226.2

4-(((2-carboxyethyl)thio)carbonothioyl)thio-4-cyanopentanoic acid (TC-15):  $^1\text{H}$  NMR,  $\delta$ , ppm: 1.88 (s, 3H,  $\text{CH}_3$ ), 2.42-2.86 (m, 6H,  $3 \times \text{CH}_2$ ), 3.56-3.65 (m, 2H,  $\text{SCH}_2\text{CH}_2$ ).

2-(2-carboxyethylsulfanylthiocarbonylsulfanyl)propionic acid (TC-16):  $^1\text{H}$  NMR,  $\delta$ , ppm: 1.45 (d, 3H,  $\text{CH}_3$ ), 2.61 (t, 2H,  $\text{SCH}_2\text{CH}_2$ ), 3.45 (t, 2H,  $\text{SCH}_2\text{CH}_2$ ), 4.47 (q, 1H, CH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 17.0, 31.6, 32.6, 48.0, 172.0, 172.6, 221.8

2,2'-(carbonothioylbis(thio))bis(2-methylpropanoic acid) (TC-17):  $^1\text{H}$  NMR,  $\delta$ , ppm: 1.44 (s, 12H,  $4 \times \text{CH}_3$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 25.0, 55.7, 174.4, 218.1

2-(((dodecylthio)carbonothioyl)thio)propanoic acid (TC-18):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.88 (t, 3H,  $\text{CH}_3$ ), 1.26 (m, 16H,  $8 \times \text{CH}_2$ ), 1.32-1.41 (m, 2H,  $\text{CH}_2$ ), 1.63 (d, 3H,  $\text{CH}_3$ ), 1.66-1.73 (m, 2H,  $\text{CH}_2$ ), 1.89 (s, 3H,  $\text{CH}_3$ ), 2.35-2.71 (m, 4H,  $2 \times \text{CH}_2$ ), 3.33 (t, 2H,  $\text{SCH}_2$ ), 4.85-4.90 (q, 1H, CH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.5, 16.9, 23.0, 28.2, 29.3, 29.4, 29.7, 29.8, 29.9, 30.0, 32.3, 37.9, 47.6, 17.4, 222.7

2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (TC-19):  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.88 (t, 3H,  $\text{CH}_3$ ), 1.25-1.71 (m, 20H,  $10 \times \text{CH}_2$ ), 1.73 (s, 6H,  $2 \times \text{CH}_3$ ), 3.28 (t, 2H,  $\text{SCH}_2$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.5, 23.1, 25.6, 28.2, 29.3, 29.5, 29.7, 29.8, 29.9, 30.0, 32.3, 37.4, 55.8, 178.2, 221.2

2-cyanobutan-2-yl 3,5-dimethyl-1H-pyrazole-1-carbodithioate (DC-1):  $^1\text{H}$  NMR,  $\delta$ , ppm: 1.22 (t, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.89 (s, 3H,  $\text{CH}_3$ ), 2.00-2.33 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 2.26 (s, 3H,  $\text{ArCH}_3$ ), 2.69 (s, 3H,  $\text{ArCH}_3$ ), 6.01 (s, 1H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 9.6, 14.0, 17.7, 24.2, 32.5, 46.6, 114.1, 120.2, 146.1, 152.2, 194.8

cyanomethyl (3,5-dimethyl-1H-pyrazole)-carbodithioate (DC-2):  $^1\text{H}$  NMR,  $\delta$ , ppm: 2.28 (s, 3H,  $\text{ArCH}_3$ ), 2.70 (s, 3H,  $\text{ArCH}_3$ ), 3.97 (s, 2H,  $\text{CH}_2$ ), 6.14 (s, 1H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.0, 17.3, 21.9, 114.4, 115.7, 146.5, 153.2, 195.7

benzyl 3,5-dimethyl-1H-pyrazole-1-carbodithioate (DC-3):  $^1\text{H}$  NMR,  $\delta$ , ppm: 2.25 (s, 3H,  $\text{ArCH}_3$ ), 2.70 (s, 3H,  $\text{ArCH}_3$ ), 4.41 (s, 2H,  $\text{CH}_2$ ), 6.08 (s, 1H, ArH), 7.27-7.41 (m, 5H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.0, 17.7, 41.8, 113.7, 127.9, 128.9, 130.0, 135.2, 145.9, 152.2, 200.6

2-cyanopropan-2-yl *N*-methyl-*N*-(pyridin-4-yl)carbamodithioate (DC-4):  $^1\text{H}$  NMR,  $\delta$ , ppm: 1.82 (s, 6H,  $2 \times \text{CH}_3$ ), 3.70 (s, 3H,  $\text{CH}_3$ ), 7.22-8.77 (m, 4H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 23.8, 27.6, 43.0, 45.0, 121.6, 122.1, 151.6, 152.3, 192.6

2-cyanobutan-2-yl methyl(pyridin-4-yl)carbamodithioate (DC-5):  $^1\text{H}$  NMR,  $\delta$ , ppm: 1.08 (t, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.81 (s, 3H,  $\text{CH}_3$ ), 1.91-2.24 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 3.69 (s, 3H,  $\text{CH}_3$ ), 7.23-8.76 (m, 4H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 9.5, 24.8, 32.8, 45.0, 48.5, 120.6, 122.1, 151.8, 152.3, 192.6

cyanomethyl methyl(pyridin-4-yl)carbamodithioate (DC-6):  $^1\text{H}$  NMR,  $\delta$ , ppm: 3.78 (s, 3H,  $\text{CH}_3$ ), 4.08 (s, 2H,  $\text{CH}_2$ ), 7.25-8.80 (m, 4H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 23.7, 46.3, 115.9, 122.0, 152.4, 193.7

cyanomethyl methyl(phenyl)carbamodithioate (DC-7):  $^1\text{H}$  NMR,  $\delta$ , ppm: 3.79 (s, 3H,  $\text{CH}_3$ ), 4.05 (s, 2H,  $\text{CH}_2$ ), 7.26-7.50 (m, 5H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 23.7, 116.4, 127.3, 130.2, 130.4, 194.3

*S*-(cyanomethyl) *O*-ethyl carbonodithioate (X-1):  $^1\text{H}$  NMR,  $\delta$ , ppm: 1.47 (t, 3H,  $\text{OCH}_2\text{CH}_3$ ), 3.89 (s, 2H,  $\text{CH}_2$ ), 4.69-4.75 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.0, 21.7, 71.9, 115.6, 209.3

*S*-((1,3-dioxoisindolin-2-yl)methyl) *O*-ethyl carbonodithioate (X-2):  $^1\text{H}$  NMR,  $\delta$ , ppm: 1.47 (t, 3H,  $\text{OCH}_2\text{CH}_3$ ), 4.68-4.72 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ), 5.35 (s, 2H,  $\text{SCH}_2\text{N}$ ), 7.74-7.89 (m, 4H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.1, 41.6, 70.9, 124.0, 132.3, 134.8, 167.0, 210.6

*O*-ethyl *S*-(1-phenylethyl) carbonodithioate (X-3):  $^1\text{H}$  NMR,  $\delta$ , ppm: 1.38 (t, 3H,  $\text{OCH}_2\text{CH}_3$ ), 1.71 (d, 3H,  $\text{CH}_3$ ), 4.60-4.64 (q, 2H,  $\text{OCH}_2\text{CH}_3$ ), 4.88-4.92 (q, 1H, CH), 7.24-7.38 (m, 5H, ArH).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.1, 22.1, 49.6, 70.1, 127.8, 128.9, 141.2, 167.0, 213.8

#### MacroRAFT agent synthesis

TC-15-PDMA (poly(*N,N*-dimethylacrylamide)) was prepared by conventionally initiated RAFT polymerization with TC-15 as the RAFT agent) as follows. DMA (1.00 g, 10.0 mmol, 10 equiv.), TC-15 (0.31 g, 1.0 mmol, 1 equiv.) and 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (8.20 mg, 0.025 mmol, 0.025 equiv.) were dissolved in pH 4 citric acid buffer (1.5 mL). Polymerization was carried out in a water bath at 70 °C after degassing with nitrogen for 15 minutes. The crude product was first freeze-dried to remove all citric acid buffer solution. The freeze-dried sample was then dissolved in a minimum amount of chloroform. Filtration was carried out by 0.3  $\mu\text{m}$  membrane filter to remove all citric acid buffer salts. The filtrate was then added dropwise to cold hexane for polymer extraction. Suction filtration was then carried out. The precipitation procedure was repeated three times. The final product was then dried under vacuum at 70 °C for 30 minutes (Yield = 0.89 g, 68 %).  $M_n$  was determined as 1310 (PEO equivalents) and dispersity as 1.23 by GPC.

#### Cyclic voltammetry

All cyclic voltammetry (CV) was conducted with an Autolab PGSTAT 302N potentiostat, in a 3-electrode cell with a glassy carbon (GC) rod counter electrode, 1 mM disk working electrode (GC, Au, or Pt), and Ag or Pt wire pseudo-reference electrode. Working electrodes were polished with 0.5  $\mu\text{M}$  alumina slurry and thoroughly rinsed before each CV experiment. The electrochemical cell was purged with argon or nitrogen prior to recording CVs and potentials were determined with reference to a decamethylferrocene ( $\text{Me}_{10}\text{Fc}$ ) internal standard. The half-wave potential of  $\text{Me}_{10}\text{Fc}$  was measured in 0.1 M TBAPF<sub>6</sub> in ACN and in DMF against a non-aqueous Ag/AgNO<sub>3</sub> (0.01 M) reference electrode, filled with the same electrolyte as used in the electrochemical cell, and determined as  $E_{1/2}(\text{Me}_{10}\text{Fc}) = -0.42 \text{ V vs. Ag/AgNO}_3$  in ACN, and  $-0.45 \text{ V vs. Ag/AgNO}_3$  in DMF. Literature values for  $E_{1/2}(\text{Me}_{10}\text{Fc})$  are  $+1 \text{ mV vs. Ag/AgCl/KCl (Sat'd)} = -44 \text{ mV vs. SCE}$  in ACN, and  $+86 \text{ mV vs. Ag/AgCl/KCl (Sat'd)} = +41 \text{ mV vs. SCE}$  in DMF; some divergence from these values may be expected due to the effect of liquid junction potential.<sup>10</sup> Unless otherwise stated, CVs were conducted in ACN or DMF with 1 mM RAFT agent, and 0.1 M TBAPF<sub>6</sub> as supporting electrolyte, or 0.5 M TBAPF<sub>6</sub> for CVs to study the effect of concentration. Ohmic ( $iR$ ) compensation was not used as a standard procedure because with the instrument used this option precluded automatic current ranging.  $iR$  compensation was used without current ranging for some key experiments to test whether the cell setup was efficient. In all cases, ohmic losses were found to be insignificant. For CVs with  $iR$  compensation,  $R_u$  was determined by EIS as 520  $\Omega$ , however  $iR$  compensation was set to the maximum available  $R_u$  value of 200  $\Omega$ .

#### *Bulk electrolysis experiments*

Bulk electrolyses of 2-cyano-2-propyl benzodithioate (DB-2) and of 2-cyanopropan-2-yl methyl carbonotrithioate (TC-5) were conducted with an Autolab PGSTAT 302N potentiostat, in a 3-electrode cell with a GC rod counter electrode separated from the bulk solution by a fritted glass tube, GC rod working electrode, and an Ag/AgNO<sub>3</sub> (0.01 M in ACN) reference electrode. A solution of 0.1 M TEABF<sub>4</sub> and 2 mM CTA was purged with nitrogen, and the peak reduction potential of CTAs was determined by CV. Electrolysis was conducted at  $E_{\text{pc}} - 0.2 \text{ V vs. Ag/AgNO}_3$  for each CTA until the current plateaued.

#### *Characterization*

All NMR spectra were recorded with a Bruker AV 400 or 500 MHz spectrometer at room temperature with CDCl<sub>3</sub> or CD<sub>3</sub>CN as solvent. UV-vis spectra were recorded in ACN with an Agilent Technologies Cary 60 UV-visible spectrophotometer in a 1 mm quartz cuvette. The background spectrum was recorded with ACN. GPC was carried out on a Waters Alliance system equipped with an Alliance 2695 Separations Module (integrated quaternary solvent delivery, solvent degasser and autosampler system), a Waters column heater module, a Waters 2414 RDI refractive index detector, a Waters PDA 2996 photodiode array detector (210–400 nm at 1.2 nm) and 2  $\times$  Agilent PL-Aquagel columns (PL-Aquagel Mixed H (8  $\mu\text{m}$ )), each 300 mm  $\times$  7.8 mm<sup>2</sup>, providing an effective molar mass range of 6000 to  $6 \times 10^7$ . The anionic mobile phase was 0.2 M NaNO<sub>3</sub>, 0.01 M Na<sub>3</sub>PO<sub>4</sub> and 200 ppm NaN<sub>3</sub> in Milli-Q water (pH = 8.0). The eluent had a flow rate of 1 mL min<sup>-1</sup> at 25 °C. Number average ( $M_n$ ) and weight average ( $M_w$ ) molar masses were evaluated using Waters Empower-3 software. The GPC columns were calibrated with low dispersity PEO standards (Polymer Laboratories) ranging from 233 to 1 016 921 g mol<sup>-1</sup>, and molar masses are reported as PEO equivalents.

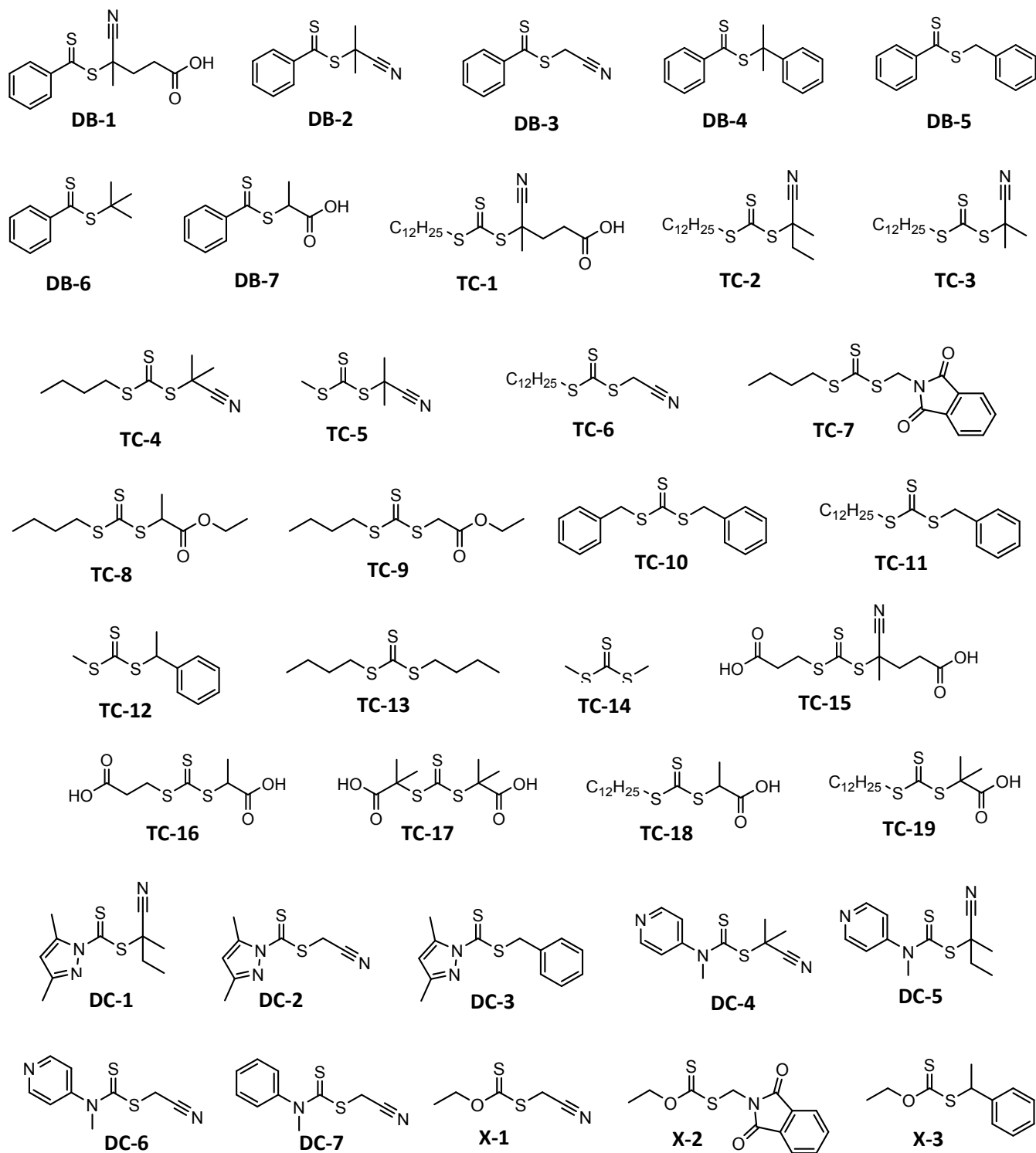
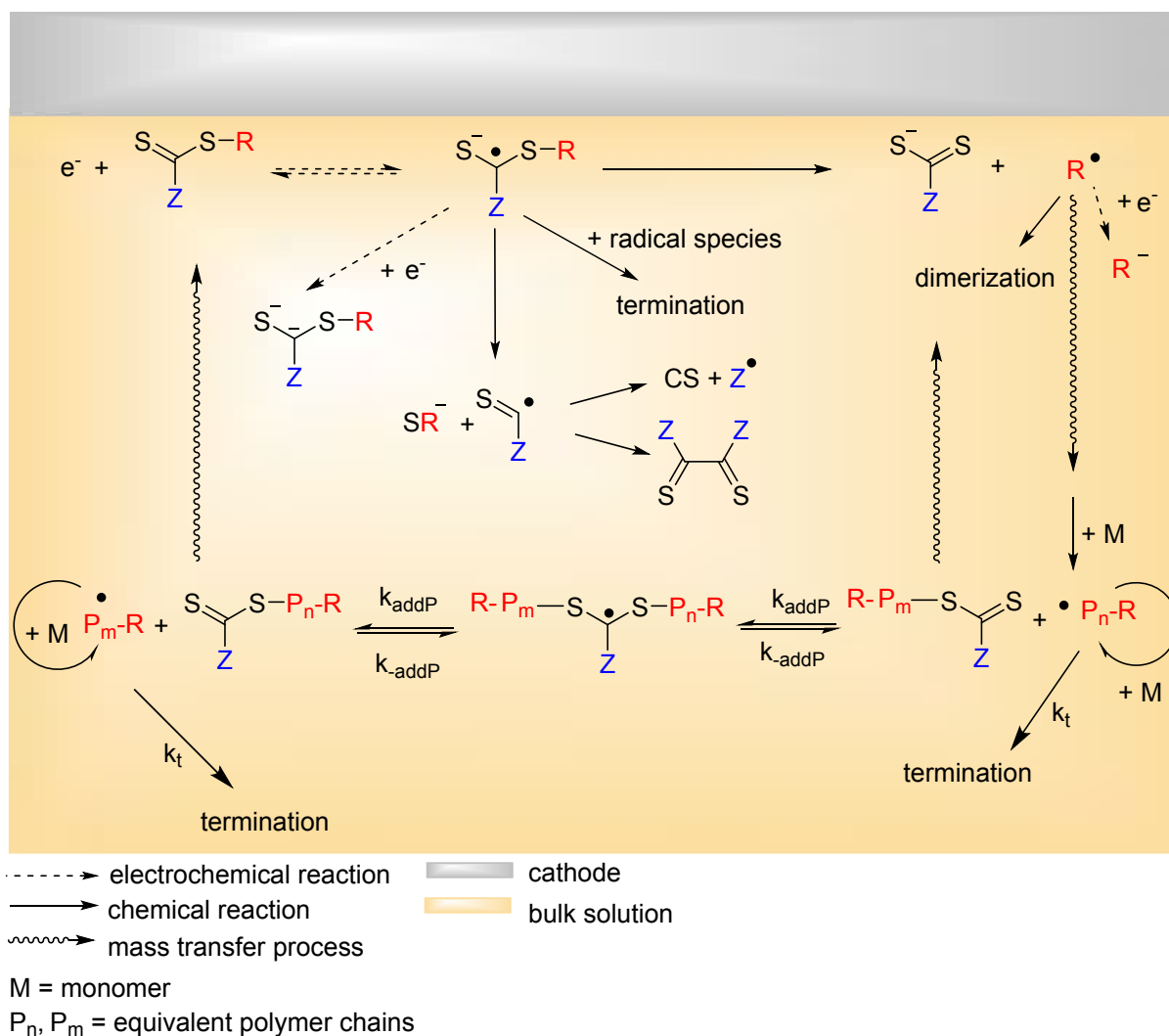


Chart S1. Structures of the RAFT agents studied.



Scheme S1. Postulated mechanisms for electrochemical reduction of RAFT agents ( $\text{S}=\text{C}(\text{Z})\text{S}-\text{R}$ ) by a one electron reduction at the electrode followed by a coupled chemical reaction (EC mechanism), and interaction with RAFT equilibrium in bulk solution. Electrogenenerated radicals ( $\text{R}^\bullet$ ) may diffuse into the bulk to react with monomers and initiate polymerization. MacroRAFT agents generated by the standard RAFT equilibrium may then diffuse back to the electrode where they can be reduced – at different potentials to that for the initial RAFT agent – to (re)generate initiating radicals which can compensate for termination reactions. Subsequent chemical reactions, and further electrochemical reductions at lower potentials, may also occur as indicated. The side reactions depicted here are indicative of possible reaction pathways described in the literature for electroreduction of similar compounds.<sup>11,12</sup>

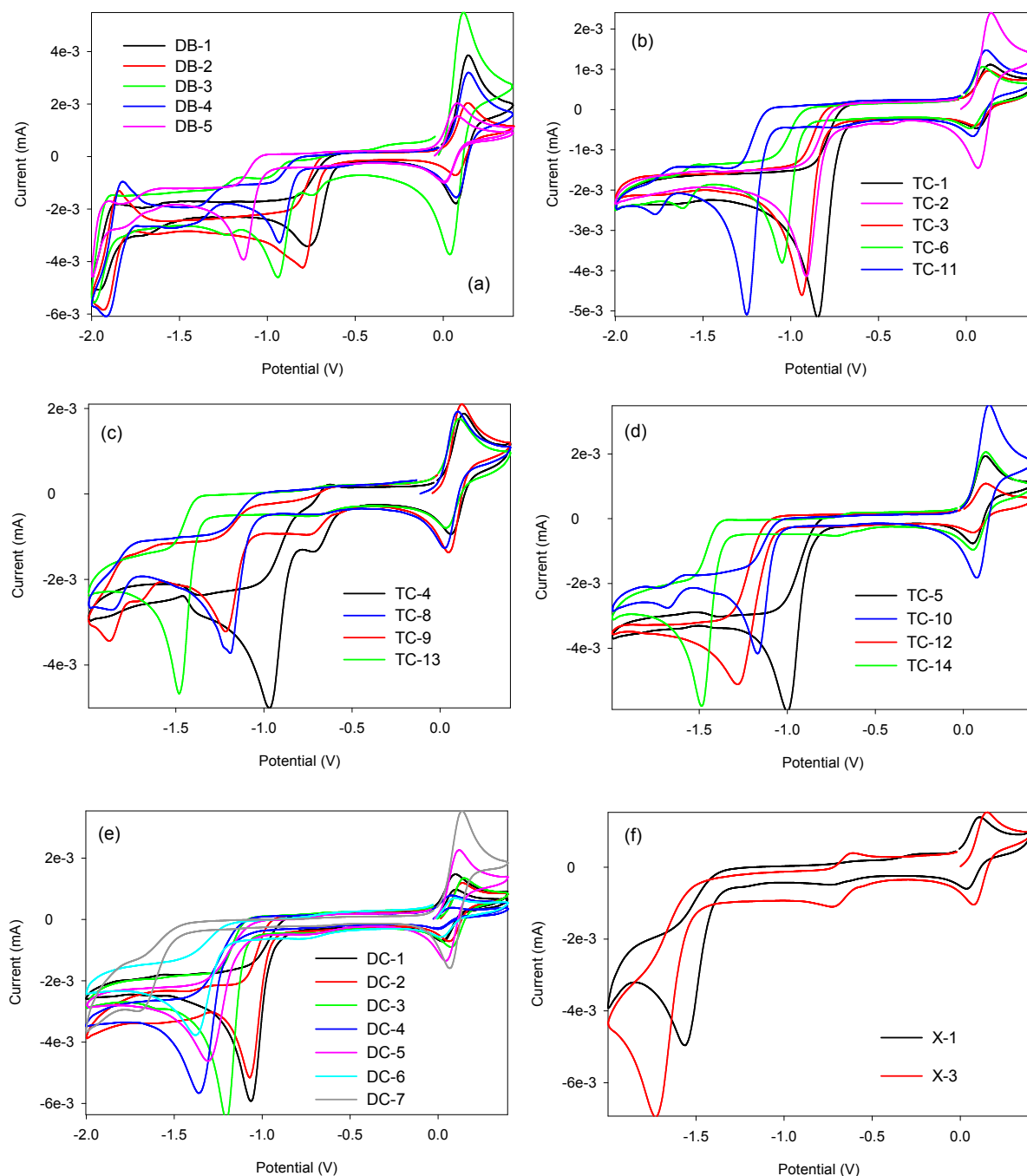


Figure S1. RAFT agent (1 mM) CVs in 0.1 M TBAPF<sub>6</sub>/ACN with Me<sub>10</sub>Fc internal standard,  $\nu = 100 \text{ mV s}^{-1}$ . (a) dithiobenzoates, (b) trithiocarbonates ( $Z = \text{S-C}_{12}\text{H}_{25}$ ), (c) trithiocarbonates ( $Z = \text{S-C}_4\text{H}_9$ ), (d) trithiocarbonates ( $Z = \text{S-CH}_3$  or S-benzyl), (e) dithiocarbamates, and (f) xanthates. W.E. = GC disk (1 mm), C.E. = GC rod, pseudo-R.E. = Pt wire. Peaks around 0 to +0.1 V originate from the Me<sub>10</sub>Fc internal standard, while those around -0.6 to -0.7 V are attributable to the reduction of small amounts of O<sub>2(g)</sub>.

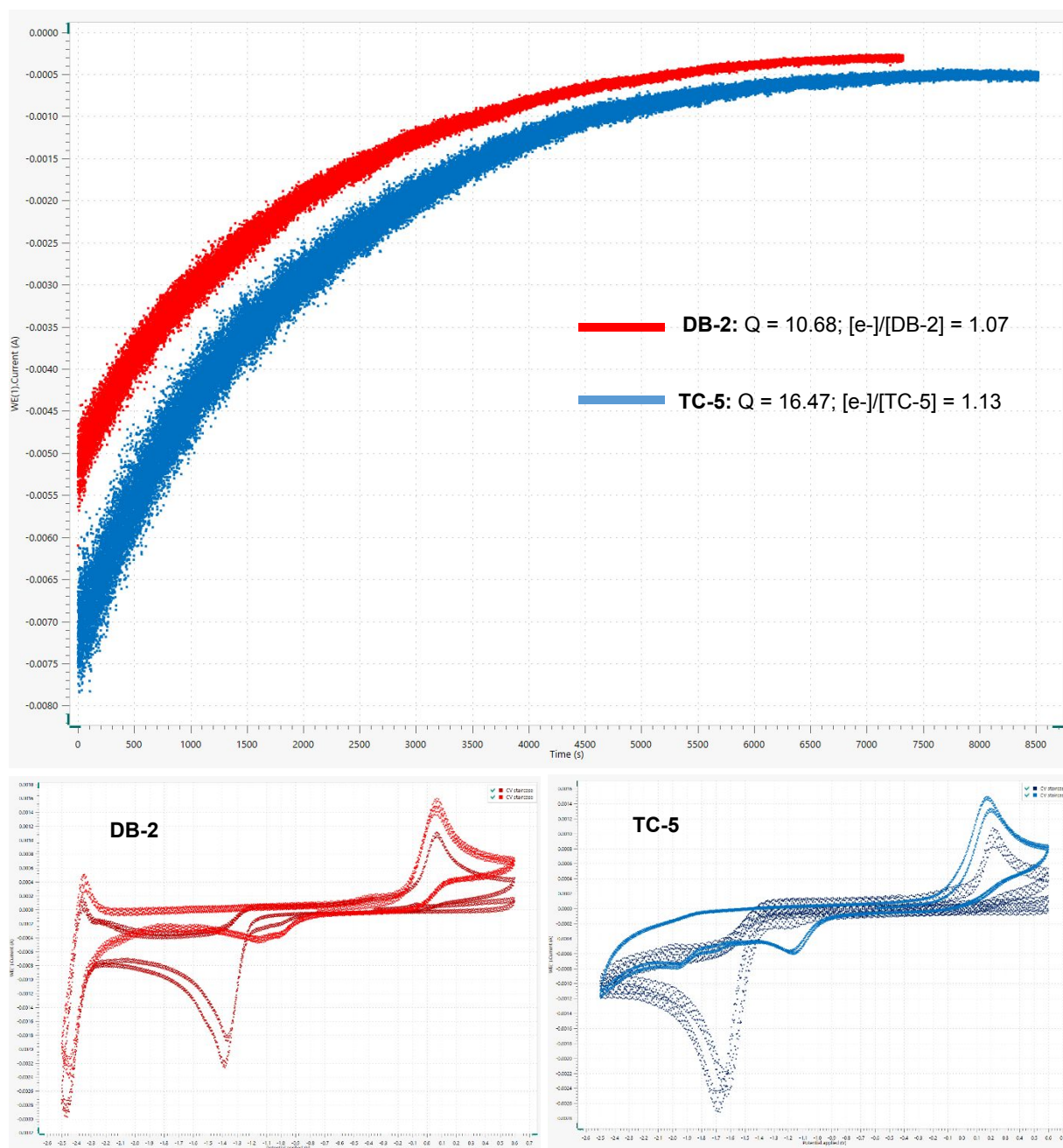


Figure S2. Electrolysis of DB-2 ( $n = 0.1039$  mmol) and of TC-5 ( $n = 0.1505$  mmol). *Top:* Current vs. time plots with  $E_{app} = -1.90$  V vs. R.E. for TC-5, and  $-1.60$  V vs. R.E. for DB-2. *Bottom:* CVs of DB-2 and TC-5 recorded before and after electrolysis. Electrolysis and CVs conducted in  $0.1$  M TEABF<sub>4</sub>/ACN. W.E. = GC rod, C.E. = GC rod, R.E. = Ag/Ag<sup>+</sup>.



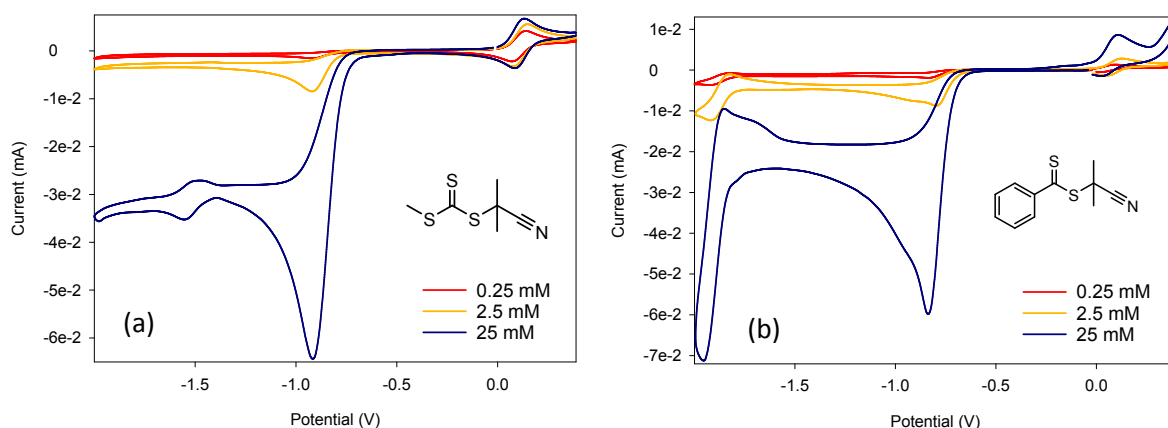


Figure S3. Concentration dependent CVs of (a) 2-cyanopropan-2-yl methyl carbonotrithioate (TC-5) and (b) 2-cyano-2-propyl benzodithioate (DB-2). CVs collected in 0.5 M TBAPF<sub>6</sub>/ACN with Me<sub>10</sub>Fc internal standard,  $\nu = 100 \text{ mV s}^{-1}$ . W.E. = GC disk (1 mm), C.E. = GC rod, pseudo-R.E. = Pt wire. The effect of initial substrate concentration ( $C^0$ ) on CVs can aid in distinguishing between an EC mechanism involving a first or second order chemical process; second order reactions (e.g. dimerization) will show an anodic shift of up to 19.7 mV per decade with increasing  $C^0$  as long as the chemical reaction has some influence on kinetics, as is the case in the KI kinetics zone.<sup>23</sup> CVs of DB-2 and TC-5 showed no significant concentration-dependent shift over two orders of magnitude (i.e.  $\leq \pm 5.5 \text{ mV}$ ). This is contrary to the conclusions of Falsig and Lund,<sup>20</sup> but in agreement with recent studies by Matyjaszewski *et al.*<sup>12</sup> Whilst this trend was also observed for some other RAFT agents under the same conditions, others showed an unexpected cathodic shift. Concentration dependence (or lack thereof) is therefore not sufficient to distinguish between follow-up chemical reaction mechanisms.

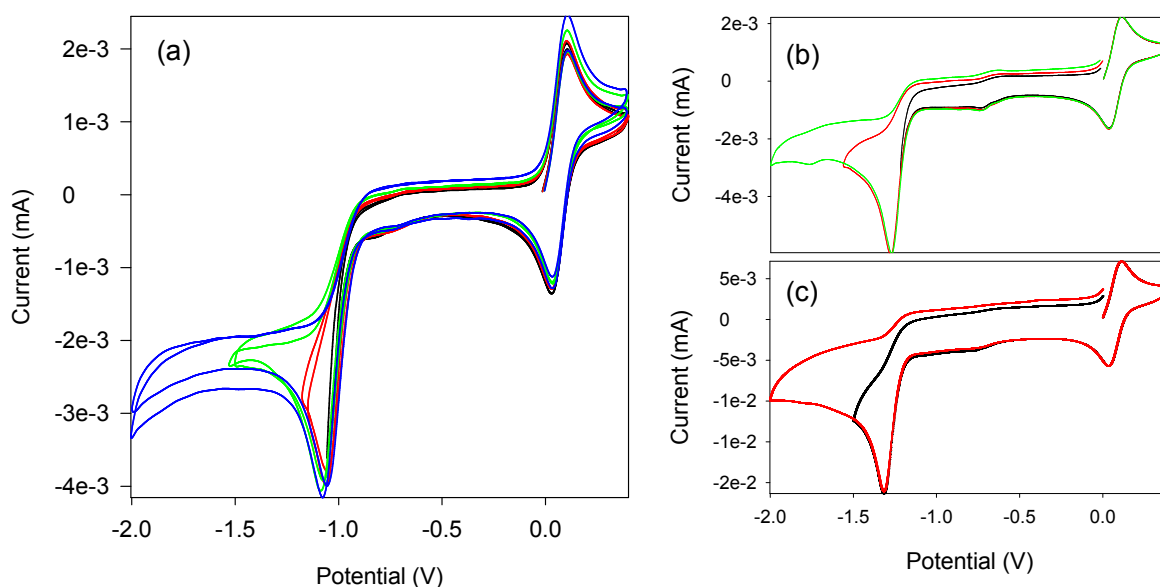


Figure S4. CVs of (a) 1 mM 2-cyanopropan-2-yl methyl carbonotrithioate (TC-5) at  $\nu = 100 \text{ mV s}^{-1}$ ; and of 1 mM benzyl dodecyl carbonotrithioate (TC-11) at (b)  $\nu = 100 \text{ mV s}^{-1}$  and at (c)  $\nu = 1 \text{ V s}^{-1}$  to successively lower reduction potentials, recorded in 0.1 M TBAPF<sub>6</sub>/ACN with Me<sub>10</sub>Fc internal standard. W.E. = 1 mm GC disk, C.E. = GC rod, pseudo-R.E. = Pt wire.

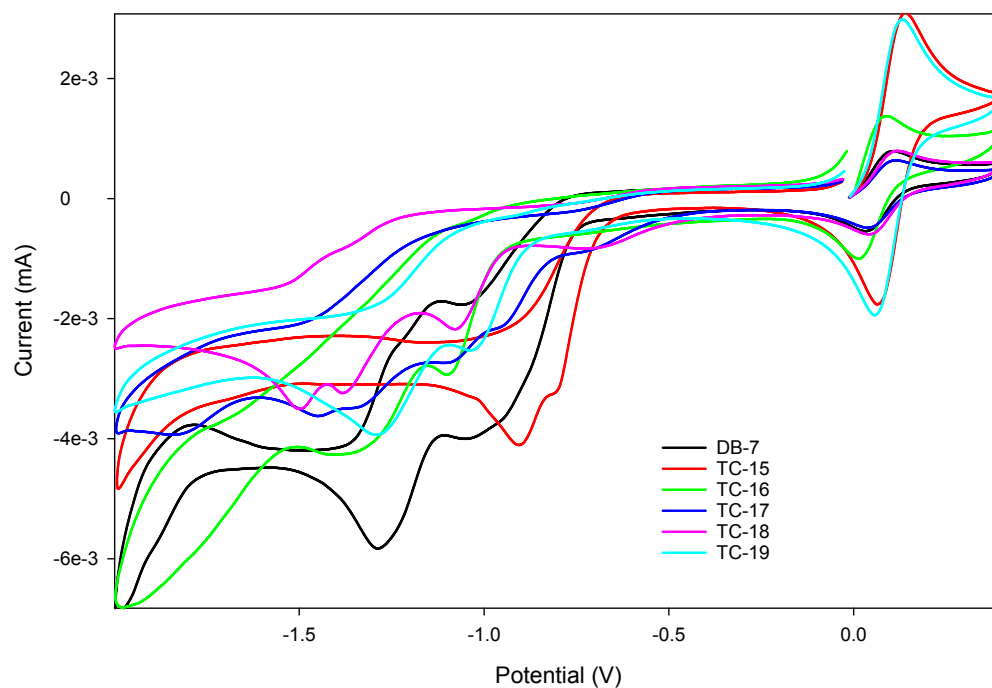


Figure S5. CVs of RAFT agents (1 mM) with  $-\text{COOH}$  functionality, recorded in 0.1 M  $\text{TBAPF}_6/\text{ACN}$  with  $\text{Me}_{10}\text{Fc}$  internal standard,  $\nu = 100 \text{ mV s}^{-1}$ . W.E. = 1 mm GC disk, C.E. = GC rod, pseudo-R.E. = Pt wire.

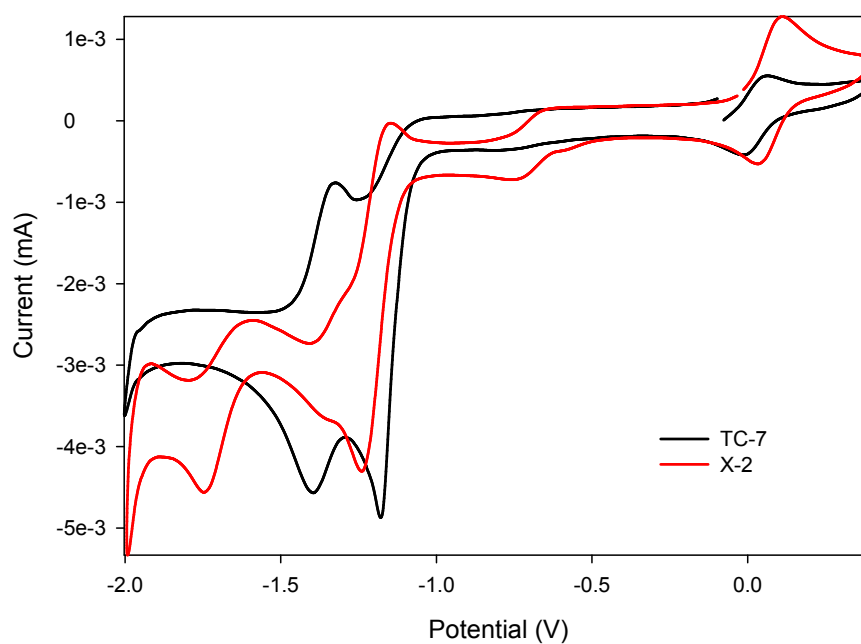


Figure S6. CVs of RAFT agents (1 mM) with phthalimide functionality, recorded in 0.1 M  $\text{TBAPF}_6/\text{ACN}$  with  $\text{Me}_{10}\text{Fc}$  internal standard,  $\nu = 100 \text{ mV s}^{-1}$ . W.E. = 1 mm GC disk, C.E. = GC rod, pseudo-R.E. = Pt wire.

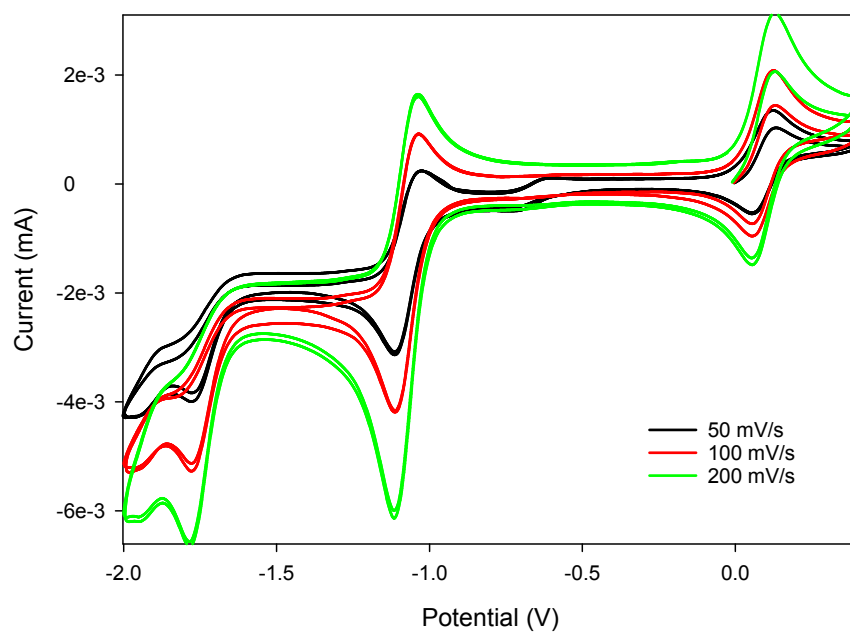


Figure S7. CVs of 1 mM *tert*-butyl dithiobenzoate (DB-6), recorded in 0.1 M TBAPF<sub>6</sub>/ACN with Me<sub>10</sub>Fc internal standard. W.E. = 1 mm GC disk, C.E. = GC rod, pseudo-R.E. = Pt wire.

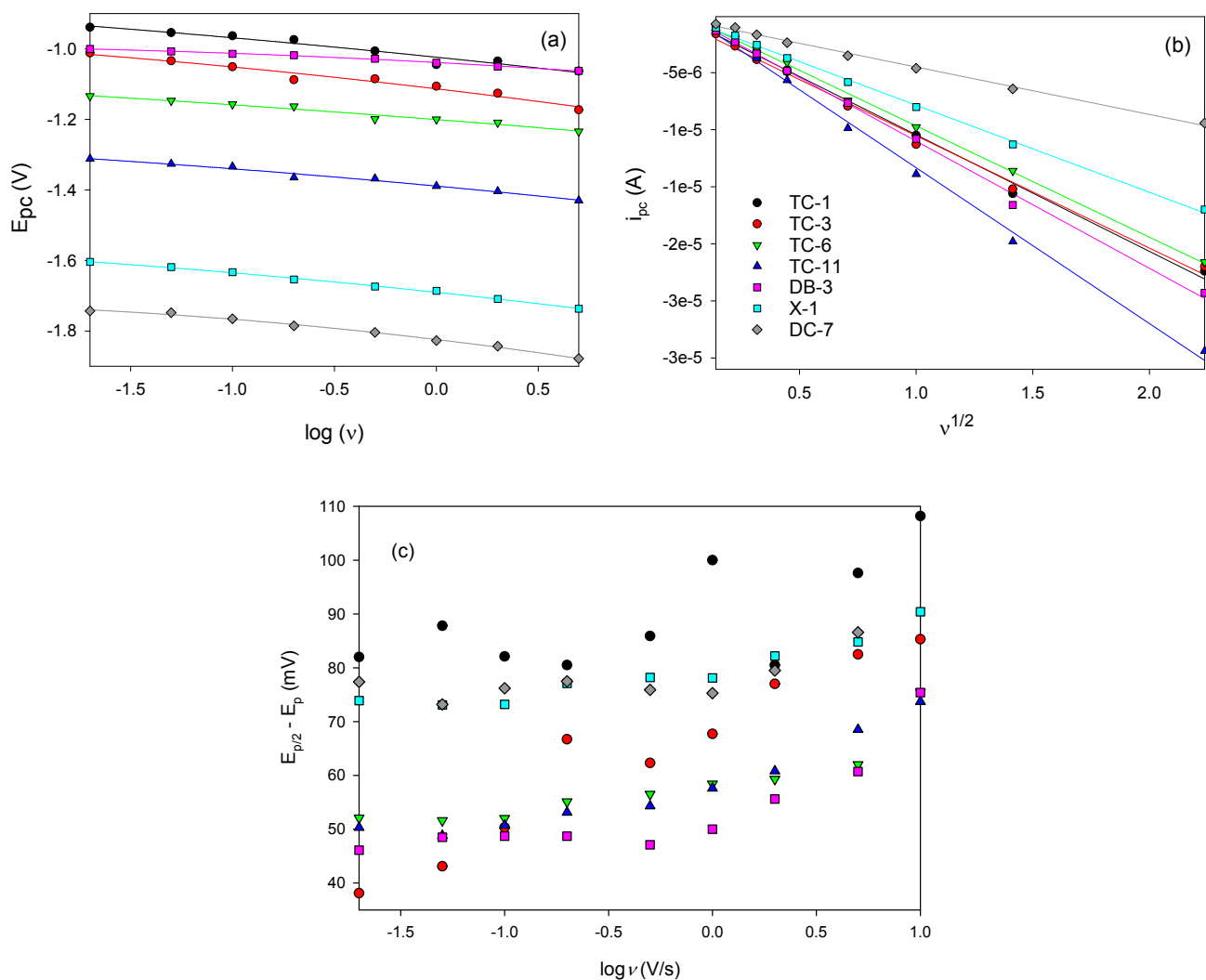


Figure S8. Plots of (a)  $E_{pc}$  (vs.  $\text{Me}_{10}\text{Fc}$ ) vs.  $\log v$ , (b)  $i_{pc}$  vs.  $v^{1/2}$ , and (c)  $E_{p/2} - E_p$  vs.  $\log v$  for RAFT agents with differing R- ( $Z = \text{S-C}_{12}\text{H}_{25}$ ) and Z-(R = cyanomethyl) groups. CVs recorded in 0.1 M TBAPF<sub>6</sub>/ACN with  $\text{Me}_{10}\text{Fc}$  internal standard at a range of scan rates. W.E. = 1 mm GC disk, C.E. = GC rod, pseudo-R.E. = Pt wire. This analysis is based on kinetic zone diagrams for EC reactions described by Nadjo and Sav  ant, where an expression related to the electron transfer rate constant is plotted against an expression related to the chemical reaction rate constant. These diagrams are divided into kinetic zones depending on the rate determining process; diffusion control (DO), kinetic control by the chemical reaction (KP), kinetic control by charge transfer (IR), or intermediate zones. Depending on the kinetic behavior of the system, peak reduction potential shifts by a characteristic amount with changing scan rate or with initial substrate concentration. It is noted that accuracy may be limited by the relatively small range of scan rates accessible with our experimental setup. The theoretical gradients in the KI zone for one-electron reduction followed by a first order chemical reaction should fall between 29.6 and 59.1 mV.

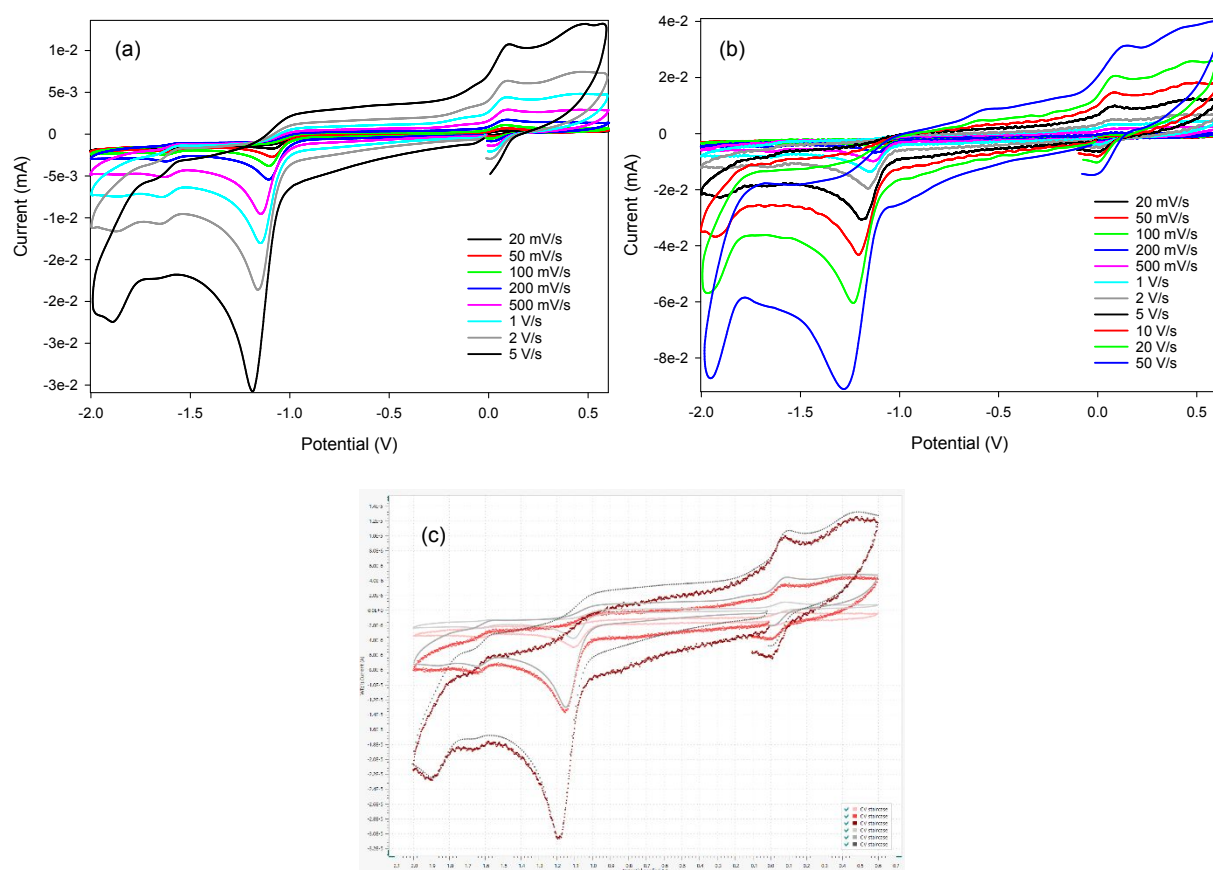


Figure S9. CVs of 1 mM cyanomethyl dodecyl trithiocarbonate (TC-6) recorded (a) without  $iR$  compensation across a range of scan rates, (b) with  $iR$  compensation ( $R_u = 200 \Omega$ ) across a range of scan rates, and (c) overlay of CVs with (red) and without (grey)  $iR$  compensation at  $\nu = 100 \text{ mV s}^{-1}$ ,  $1 \text{ V s}^{-1}$ , and  $5 \text{ V s}^{-1}$ . All CVs were recorded in  $0.1 \text{ M TBAPF}_6/\text{ACN}$  with  $\text{Me}_{10}\text{Fc}$  internal standard. W.E. =  $1 \text{ mm GC disk}$ , C.E. = GC rod, pseudo-R.E. = Pt wire.

Table S1. Peak reduction potentials (vs. SCE) of RAFT agents as determined <sup>a</sup>in this study (peak potentials determined against  $\text{Me}_{10}\text{Fc}$  and reported against SCE using literature values for reduction potentials  $\text{Me}_{10}\text{Fc}^{10}$ ; (+1 mV vs.  $\text{Ag}/\text{AgCl}/\text{KCl}$  (Sat'd) = -44 mV vs. SCE in ACN, and +86 mV vs.  $\text{Ag}/\text{AgCl}/\text{KCl}$  (Sat'd) = +41 mV vs. SCE in DMF), and <sup>b</sup>in recently published work by Matyjaszewski *et al.*<sup>13</sup> For both sets of data,  $\nu = 200 \text{ mV s}^{-1}$ . W.E. = GC. \*[RAFT agent] = 2 mM

RAFT agent	$E_{pc}$ (V vs. SCE)			
	0.1 M TBAPF <sub>6</sub> / ACN <sup>a</sup>	0.1 M TBAPF <sub>6</sub> / DMF <sup>a</sup>	0.1 M TEABF <sub>4</sub> / ACN <sup>b</sup>	0.1 M TEABF <sub>4</sub> / DMF <sup>b*</sup>
DB-1	-0.93	-0.90	-1.00	-0.94
DB-2	-0.96	-0.92	-1.04	-1.00
TC-1	-1.02			-1.05
DB-4	-1.10	-1.05	-1.17	-1.15
TC-3	-1.13		-1.28	-1.09
TC-6	-1.18		-1.29	-1.22
DC-4	-1.44			-1.46
DC-6	-1.47			-1.51
DC-7	-1.83	-1.85		-1.90

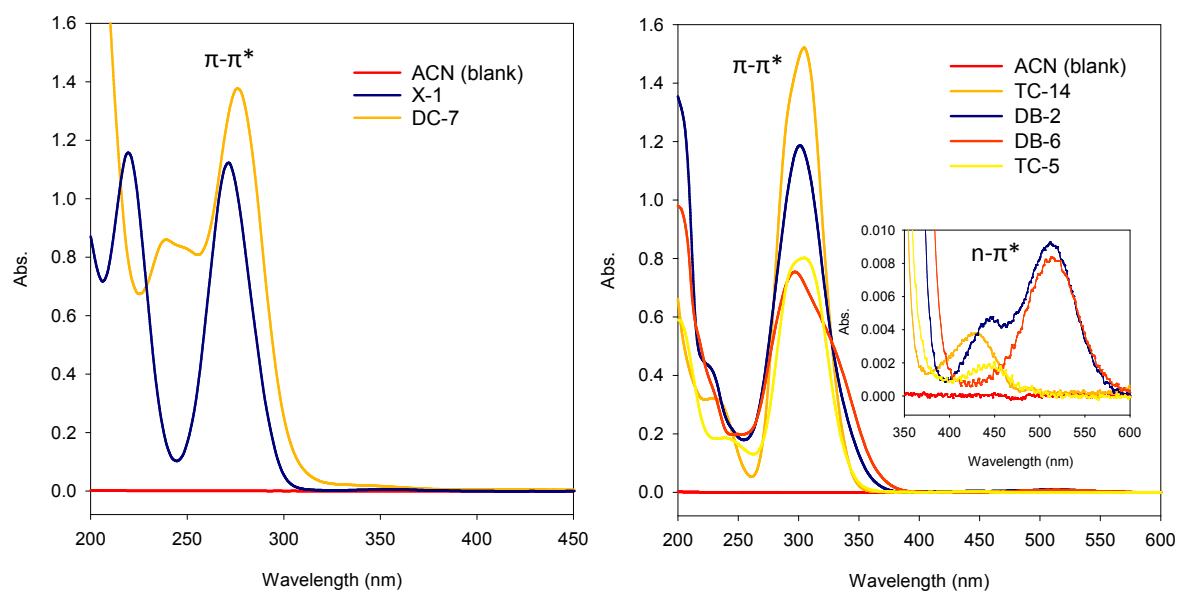


Figure S10. UV-vis spectra of RAFT agents in ACN.

Table S2. UV-vis absorption maxima wavelengths ( $\lambda$ , nm) for selected RAFT agents.

RAFT agent	Z-group	R-group	n- $\pi^*$	$\pi$ - $\pi^*$	n- $\sigma^*$
DB-1	Ph	C(CH <sub>3</sub> )(CN)(CH <sub>2</sub> ) <sub>2</sub> (COOH)	514	301	226
DB-2	Ph	C(CH <sub>3</sub> ) <sub>2</sub> CN	511	301	226
TC-1	S-C <sub>12</sub> H <sub>25</sub>	C(CH <sub>3</sub> )(CN)(CH <sub>2</sub> ) <sub>2</sub> (COOH)	449	309	345
TC-3	S-C <sub>12</sub> H <sub>25</sub>	C(CH <sub>3</sub> ) <sub>2</sub> CN	449	299	240
DB-4	Ph	C(CH <sub>3</sub> ) <sub>2</sub> Ph	519	302	-
TC-4	S-C <sub>4</sub> H <sub>9</sub>	C(CH <sub>3</sub> ) <sub>2</sub> CN	444	297	244
TC-5	S-CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>2</sub> CN	449	304	239
TC-6	S-C <sub>12</sub> H <sub>25</sub>	CH <sub>2</sub> CN	429	305	239
DB-6	Ph	C(CH <sub>3</sub> ) <sub>3</sub>	513	297	229
TC-10	S-Benzyl	CH <sub>2</sub> Ph	433	309	220
TC-11	S-C <sub>12</sub> H <sub>25</sub>	CH <sub>2</sub> Ph	429	309	218
TC-12	S-CH <sub>3</sub>	CH(CH <sub>3</sub> )Ph	431	309	-
TC-13	S-C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub>	431	309	229
TC-14	S-CH <sub>3</sub>	CH <sub>3</sub>	432	305	239
X-1	O- C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> CN	353	271	220
DC-7	N(Me)Ph	CH <sub>2</sub> CN	-	276	239

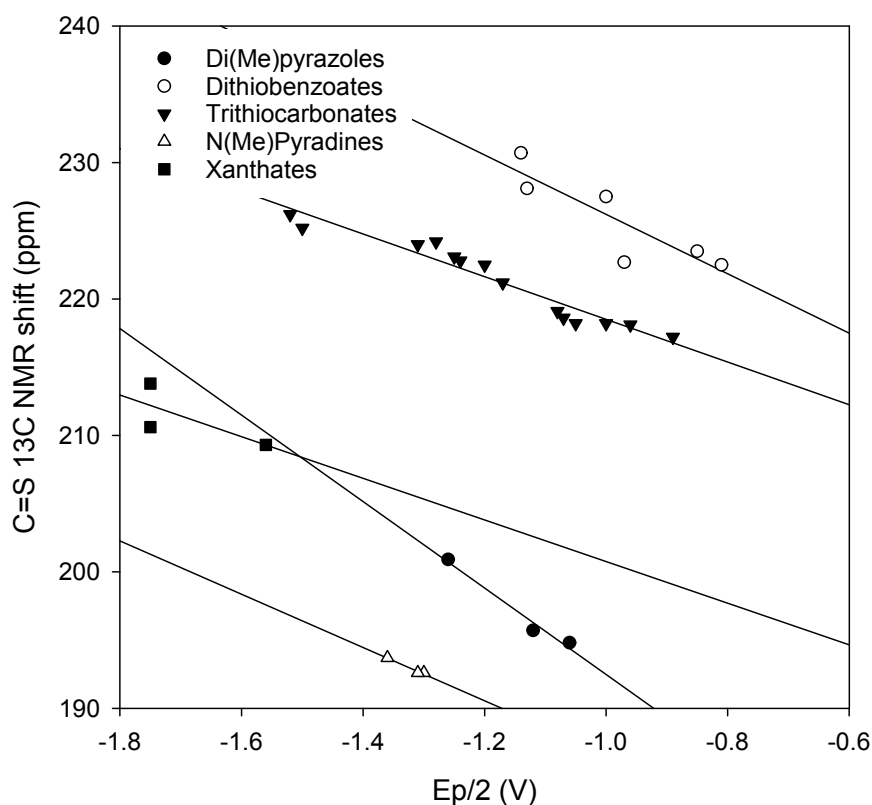


Figure S11. Plot of  $^{13}\text{C}$  NMR thiocarbonyl chemical shift vs.  $E_{p/2}$ . NMR spectra collected in  $\text{CDCl}_3$ ,  $E_{p/2}$  vs.  $\text{Me}_{10}\text{Fc}$  in 0.1 M  $\text{TBAPF}_6/\text{ACN}$ ,  $\nu = 100 \text{ mV s}^{-1}$ , W.E. = 1 mm GC disk.

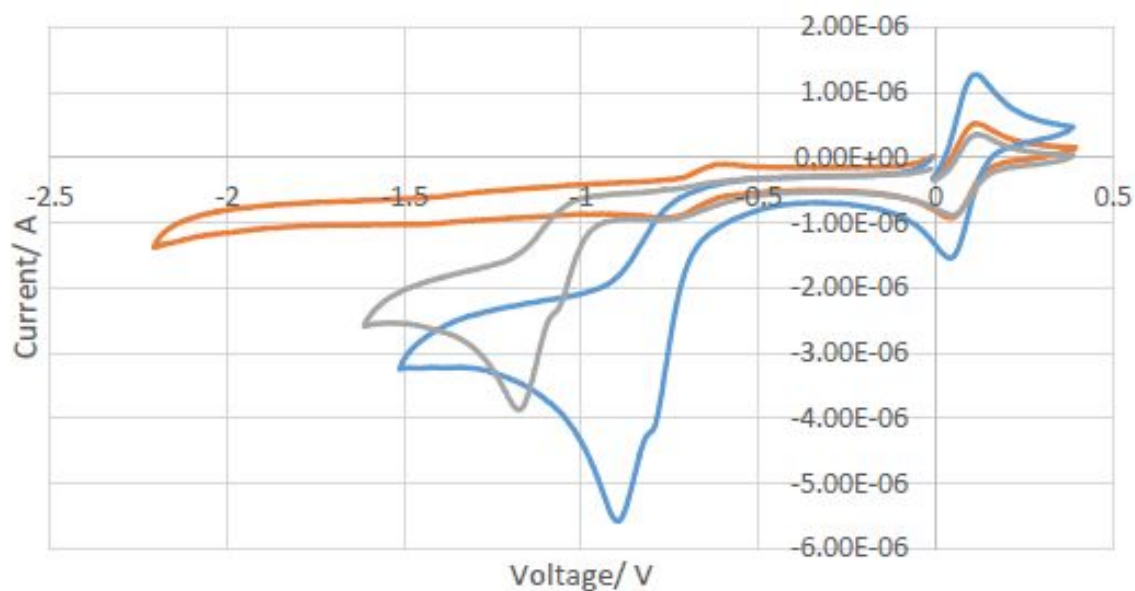


Figure S12. CVs of 1 mM (4-(((2-carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid (TC-15, blue line), and the macroRAFT agent TC-15-PDMA (poly(*N,N*-dimethylacrylamide)) prepared by conventionally initiated RAFT polymerization with TC-15 as the RAFT agent,  $M_n = 1310$ ,  $\bar{D} = 1.23$ , grey line) recorded in 0.1 M  $\text{TBAPF}_6/\text{ACN}$  with  $\text{Me}_{10}\text{Fc}$  internal standard (background scan of electrolyte shown, orange line). Pseudo-R.E. = Ag wire.

Table S3. Half-peak reduction potentials (vs. Me<sub>10</sub>Fc) of RAFT agents showing effect of solvent and working electrode material. CVs recorded in 0.1 M TBAPF<sub>6</sub> /ACN,  $\nu = 100 \text{ mV s}^{-1}$ . W.E. = 1 mm disk (GC, Au, or Pt), C.E. = GC rod, pseudo-R.E. = Ag or Pt wire.  $E_{1/2}(\text{Me}_{10}\text{Fc}) = -0.42 \text{ V vs. Ag/AgNO}_3$  in ACN, and  $-0.45 \text{ V vs. Ag/AgNO}_3$  in DMF.

RAFT agent	<i>Ep/2 (V vs. Me<sub>10</sub>Fc)</i>					
	Glassy Carbon (GC)		Gold (Au)		Platinum (Pt)	
	ACN	DMF	ACN	DMF	ACN	DMF
DB-1	-0.81	-0.86	-0.83	-0.90	-0.85	-0.90
DB-2	-0.85	-0.88	-0.88	-0.91	-0.98	-1.00
TC-15	-0.88	-0.98	-0.89	-1.05	-0.68	-0.92
DB-4	-1.00	-1.04	-1.03	-1.08	-1.13	-1.16
TC-19	-1.05	-1.16	-1.06	-1.16	-0.70	-0.80
TC-16	-1.08	-1.25	-0.81	-1.08	-0.59	-0.77
DB-6	-1.14	-1.19	-1.15	-1.19	-1.19	-1.20
TC-10	-1.25	-1.32	-1.28	-1.43	-1.40	-1.50
DC-7	-1.71	-1.80	-1.76	Out of range	Out of range	Out of range

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