Supporting Information

Synthesis, Spectral Property and Dyeing Assessment of Azo Disperse Dyes Containing Carbonyl and Dicyanovinyl Groups

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Received November 19, 2012, Accepted December 19, 2012

Synthesis of 4-Aminobenzaldehyde (2a). A mixture of 4-nitrobenzaldehyde (2.50 g, 16.54 mmol) and $SnCl_2 \cdot 2H_2O$ (18.66 g, 82.70 mmol) in ethanol was stirred for 1 h at 70 °C under argon atmosphere. After completion of reaction, the solution was cooled down to room temperature and then poured into ice. The solution was basified to pH 78 by addition of 5% aqueous sodium bicarbonate solution. After that, the solution was extracted by using ethyl acetate. The organic phase was treated with charcoal and dried over sodium sulfate. A crude product was used without further purification. Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.77 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 29.1 Hz, 2H), 4.11 (bs, 2H).

General Procedure of Diazo-Coupling Reaction. To 1 N aqueous HCl solution (20 mL) was added 4-aminobenzaldehyde (1.25 g, 10.31 mmol) in acetone dropwise at 0 °C under argon atmosphere. After adding, sodium nitrite (0.71 g, 10.31 mmol) in water was added dropwise to the solution maintaing 0 °C. The solution was stirred for another 30 min. After that, corresponding coupling components (10.31 mmol) in acetic acid and acetone was added dropwise to the solution and stirred for 4-7 h until the reaction was finished. After completion of reaction, the pH value of diazo liquor was adjusted to pH 5-6 by adding sodium acetate saturated aqueous solution and stirred for another 20 min. The solution was separated to two phase by using ethyl acetate and water, and the organic phase was dried over sodium sulphate and concentrated. The resulting mixture was purified by flash column chromatography on silica gel and/or recrystallization.

Synthesis of 1-(4-((4-(dimethylamino)phenyl)diazenyl)-phenyl)ethanone (4a). Compound **4a** was synthesized from commercial compound **2b** according to the similar procedure by the diazo-coupling reaction described above (yield 78%): Brown-scarlet solid; mp 180-181 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, *J* = 5.2 Hz, 2H), 7.90 (t, *J* = 7.1 Hz, 4H), 6.76 (d, *J* = 6.9 Hz, 2H), 3.12 (s, 6H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 197.6, 156.0, 153.0, 143.8, 137.0, 129.4, 125.6, 122.2, 111.5, 40.3, 26.8.

Synthesis of 4-((4-(bis(2-hydroxyethyl)amino)-2-chlorophenyl)diazenyl)benzaldehyde (3c). Compound **3c** was synthesized from compound **2a** according to the similar procedure by the diazo-coupling reaction described above (yield 41%): Red solid; mp 123-124 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.04 (s, 1H), 7.98 (s, 4H), 7.79 (d, *J* = 9.2 Hz, 1H), 6.82 (d, *J* = 2.6 Hz, 1H), 6.64 (dd, *J* = 2.6 and 9.3 Hz, 1H), 3.95 (t, *J* = 4.5 Hz, 4H), 3.71 (t, *J* = 4.8 Hz, 4H), 3.12 (bs, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 191.8, 156.7, 151.6, 139.7, 136.6, 130.8, 123.2, 118.7, 112.7, 111.2, 60.5, 55.1.

Synthesis of 1-(4-((4-(bis(2-hydroxyethyl)amino)-2-chlorophenyl)diazenyl)phenyl)ethanone (4c). Compound **4c** was synthesized from commercial compound 2b according to the similar procedure by the diazo-coupling reaction described above (yield 72%): Red solid; mp 120-121 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 9.3 Hz, 1H), 6.82 (d, *J* = 2.7 Hz, 1H), 6.64 (dd, *J* = 2.7 and 9.3 Hz, 1H), 3.96 (t, *J* = 4.5 Hz, 4H), 3.72 (t, *J* = 4.8 Hz, 4H), 2.97 (bs, 2H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 197.7, 155.8, 151.5, 139.7, 139.4, 137.5, 129.4, 122.8, 118.6, 112.7, 111.2, 77.2, 60.6, 55.1, 26.8.

Synthesis of *N*-(5-(diallylamino)-2-((4-formylphenyl)-diazenyl)-4-methoxyphenyl)acetamide (3d). Compound 3d was synthesized from compound **2a** according to the similar procedure by the diazo-coupling reaction described above (yield 43%): Scarlet-red solid; mp 117-118 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.07 (bs, 2H), 8.28 (s, 1H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 7.88 Hz, 2H), 7.36 (s, 1H), 5.86-5.99 (m, 2H), 5.25 (t, *J* = 9.2 Hz, 4H), 4.01 (d, *J* = 5.8 Hz, 4H), 3.89 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.5, 168.4, 156.6, 147.1, 146.7, 136.2, 134.1, 133.4, 132.9, 130.9, 122.4, 117.8, 107.8, 103.1, 55.8, 54.2, 25.5.

Synthesis of *N*-(2-((4-acetylphenyl)diazenyl)-5-(diallyl-amino)-4-methoxyphenyl)acetamide (4d). Compound **4d** was synthesized from commercial compound **2b** according to the similar procedure by the diazo-coupling reaction described above (yield 58%): Blood-red solid; mp 102-103

°C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.07 (bs, 1H), 8.27 (s, 1H), 8.08 (d, J = 6.9 Hz, 2H), 7.81 (d, J = 6.8 Hz, 2H), 7.36 (s, 1H), 5.85-5.98 (m, 2H), 5.23 (t, J = 9.4 Hz, 4H), 3.99 (d, J = 5.9 Hz, 4H), 3.89 (s, 1H), 2.66 (s, 3H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.3, 168.4, 155.6, 147.1, 146.3, 137.1, 134.2, 133.1, 132.9, 129.5, 122.0, 117.8, 108.0, 102.9, 55.8, 54.2, 26.8, 25.4.

Synthesis of 4-((1-methyl-2-phenyl-1*H*-indol-3-yl)diazenyl)benzaldehyde (3e). Compound **3e** was synthesized from compound **2a** according to the similar procedure by the diazo-coupling reaction described above (yield 56%): Orange solid; mp 179-180 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.02 (s, 1H), 8.67 (t, J = 4.5 Hz, 1H), 7.90 (q, J = 8.8 Hz, 4H), 7.69-7.66 (m, 2H), 7.60-7.56 (m, 3H), 7.46-7.43 (m, 3H) 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 191.8, 158.1, 137.7, 135.5, 133.7, 131.6, 130.7, 129.4, 129.3, 128.2, 124.6, 124.1, 123.5, 122.3, 118.6, 109.8, 31.8.

Synthesis of 1-(4-((1-methyl-2-phenyl-1*H*-indol-3-yl)diazenyl)phenyl)ethanone (4e). Compound **4e** was synthesized from commercial compound **2b** according to the similar procedure by the diazo-coupling reaction described above (yield 57%): Orange-red solid; mp 172-173 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.64 (t, J = 3.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 5.1 Hz, 2H), 7.51 (d, J = 4.5 Hz, 3H), 7.36 (d, J = 9.5Hz, 3H), 3.72 (s, 3H), 2.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.7, 157.2, 147.8, 137.7, 136.3, 133.5, 131.7, 129.3, 128.2, 124.5, 123.9, 123.5, 121.9, 118.7, 109.8, 31.8, 26.8.

Synthesis of 1-ethyl-5-((4-formylphenyl)diazenyl)-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (3f). Compound **3f** was synthesized from compound **2a** according to the similar procedure by the diazo-coupling reaction described above (yield 94%): Orange-yellow solid; mp 271-272 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 14.97 (bs, 1H), 10.01 (s, 1H), 7.99 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H), 4.06 (q, J = 7.1 Hz, 2H), 2.65 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 190.5, 161.4, 159.4, 158.3, 145.3, 134.4, 131.7, 124.7, 117.1, 114.0, 103.9, 35.4, 16.7, 13.0.

Synthesis of 5-((4-acetylphenyl)diazenyl)-1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonit rile (4f). Compound **4f** was synthesized from commercial compound **2b** according to the similar procedure by the diazo-coupling reaction described above (yield 96%): Yellow solid; mp 229-231 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 14.97 (s, 1H), 8.07 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 8.7 Hz, 2H), 4.05 (q, J = 7.1 Hz, 2H), 2.64 (s, 3H), 2.63 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.4, 161.4, 159.5, 158.4, 144.2, 135.2, 130.4, 124.3, 116.7, 114.1, 103.4, 35.3, 26.6, 16.7, 13.0.

General Procedure for Knoevenagel Condensation. A solution of ketone or aldehyde (0.17-0.42 mmol) and an excess of malononitrile (0.85-2.10 mmol) in pyridine was heated at 95 °C (ketone) or room temperature (aldehyde) and stirred for 3-24 h until the reaction was finished. After cooling down to room temperature, pyridine was removed in vacuum. The desired product was isolated and purified by filtration, washed by methylene chloride, followed by recrystallization.

Synthesis of 2-(1-(4-((4-(dimethylamino)phenyl)diazenyl)phenyl)ethylidene)malononitrile (6a). Compound **6a** was synthesized from compound **4a** according to the similar procedure by the Knoevenagel condensation described above (yield 12%): Dark brown-red solid; mp 185-186 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89 (dd, J = 2.7, 5.6 Hz, 4H), 7.67 (d, J = 8.4 Hz, 2H), 6.74 (d, J = 9.0 Hz), 3.01 (s, 6H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.2, 155.5, 153.1, 143.7, 135.7, 128.6, 125.7, 122.7, 113.0, 111.5, 84.1, 40.3, 24.1.

Synthesis of 2-(4-((4-(bis(2-hydroxyethyl)amino)-2-chlorophenyl)diazenyl)benzylidene)malononitrile (5c). Compound **5c** was synthesized from compound **3c** according to the similar procedure by the Knoevenagel condensation described above (yield 93%): Dark reddish brown solid; mp 222-223 °C; ^{1}H NMR (acetone-d_6, 300 MHz) δ 8.38 (s, 1H), 8.21 (d, J = 8.6 Hz, 2H), 8.04 (d, J = 8.7 Hz, 2H), 7.86 (d, J = 9.4 Hz, 1H), 7.04 (d, J = 2.8 Hz, 1H), 6.92 (dd, J = 2.9 and 9.5 Hz, 1H), 4.24 (t, J = 5.4 Hz, 2H), 3.86 (t, J = 5.3 Hz, 4H), 3.77 (t, J = 5.4 Hz, 4H); ^{13}C NMR (acetone-d_6, 75 MHz) δ 159.5, 156.3, 153.2, 139.8, 138.7, 132.1, 132.1, 123.0, 118.4, 114.1, 113.2, 112.0, 111.4, 81.7, 59.1, 59.0, 54.0.

Synthesis of 2-(1-(4-((4-(bis(2-hydroxyethyl)amino)-2-chlorophenyl)diazenyl)phenyl)ethylidene)malononitrile (6c). Compound **6c** was synthesized from compound **4c** according to the similar procedure by the Knoevenagel condensation described above (yield 60%): Reddish brown solid; mp 157-158 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.96 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 9.3 Hz, 1H), 7.69 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 2.5 Hz, 1H), 6.65 (dd, J = 2.6 and 9.3 Hz, 1H), 3.96 (t, J = 4.7 Hz, 4H), 3.72 (t, J = 4.7 Hz, 4H), 3.04 (bs, 2H), 2.67 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.2, 155.2, 151.7, 139.7, 136.4, 128.6, 123.2, 118.7, 112.9, 112.7, 111.3, 84.4, 60.5, 55.1, 24.1.

Synthesis of *N*-(5-(diallylamino)-2-((4-(2,2-dicyanovinyl)phenyl)diazenyl)-4-methoxyphenyl)acetamide (5d). Compound **5d** was synthesized from compound 3d according to the similar procedure by the Knoevenagel condensation described above (yield 76%): Dark navy solid; mp 179-180 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.04 (bs, 2H), 8.26 (s, 1H), 8.04 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.77 (s, 1H) 7.34 (s, 1H), 5.86-5.99 (m, 2H), 5.25 (t, J = 8.2 Hz, 4H), 4.04 (d, J = 5.7Hz, 4H), 3.89 (s, 1H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.4, 158.5, 156.5, 147.4, 147.0, 134.2, 133.9, 133.1, 132.2, 130.9, 122.8, 117.9, 114.0, 113.0, 107.1, 81.6, 55.8, 54.3, 25.5.

Synthesis of *N*-(5-(diallylamino)-2-((4-(1,1-dicyanoprop-1-en-2-yl)phenyl)diazenyl)-4-methoxyphenyl)acetamide (6d). Compound **6d** was synthesized from compound **4d** according to the similar procedure by the Knoevenagel condensation described above (yield 40%): Dark violet solid; mp 61-63 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.07 (bs, 1H), 8.27 (s, 1H), 8.09 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.36 (s, 1H), 5.85-5.98 (m, 2H), 5.24 (t, J = 9.2

Hz, 4H), 3.99 (d, J = 5.7 Hz, 4H), 3.89 (s, 3H), 2.66 (s, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.9, 168.4, 155.2, 147.1, 146.7, 135.9, 134.1, 133.5, 132.9, 128.8, 122.4, 117.9, 112.9, 107.7, 102.8, 55.9, 54.2, 25.5, 24.1.

Synthesis of 2-(4-((1-methyl-2-phenyl-1*H*-indol-3-yl)diazenyl)benzylidene)malononitrile (5e). Compound **5e** was synthesized from compound **3e** according to the similar procedure by the Knoevenagel condensation described above (yield 53%): Dark reddish brown solid; mp 225-226 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.64 (t, J = 5.0 Hz, 1H), 7.96 (d, J = 8.6 Hz, 2H), 7.83 (d, J = 8.6 Hz, 2H), 7.70-7.44 (m, 6H), 7.42 (d, J = 2.1 Hz, 3H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.9, 158.1, 149.2, 137.9, 134.2, 132.1, 131.6, 130.2, 129.6, 129.0, 128.3, 124.9, 124.4, 123.6, 122.8, 118.6, 114.3, 113.2, 110.0, 80.6, 31.9.

Synthesis of 2-(1-(4-((1-methyl-2-phenyl-1*H*-indol-3-yl)diazenyl)phenyl)ethylidene)malononitrile (6e). Compound **6e** was synthesized from compound **4e** according to the similar procedure by the Knoevenagel condensation described above (yield 76%): Scarlet-red solid; mp 219-220 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.67-8.63 (m, 1H), 7.84 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.9 Hz, 4H), 7.59-7.57 (m, 3H), 7.45-7.39 (m, 3H), 3.85 (s, 3H), 2.66 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.3, 156.8, 137.7, 134.8, 131.6, 129.4, 129.2, 128.7, 128.3, 124.7, 124.1, 123.5, 122.3, 118.6, 113.3, 109.8, 83.4, 31.8, 24.0.

Synthesis of 2-(1-(4-((5-cyano-1-ethyl-2-hydroxy-4-methyl-6-oxo-1,6-dihydropyridin-3-yl)diazenyl)phenyl)-ethylidene)malononitrile (6f). Compound **6f** was synthesized from compound **4f** according to the similar procedure by the Knoevenagel condensation described above (yield 43%): Light orange solid; 285-286 °C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 14.48 (bs, 1H), 7.86 (q, J = 8.5 Hz, 4H), 3.89 (q, J = 7.1 Hz, 2H), 2.64 (s, 3H), 2.55 (s, 3H), 1.14 (t, J = 6.9 Hz, 3H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 175.9, 160.6, 160.2, 159.6, 144.7, 133.8, 130.2, 125.0, 117.8, 115.3, 114.1, 113.9, 102.5, 83.0, 35.0, 31.2, 24.5, 16.9, 13.1.

UV/Vis Absorption Spectra of the Synthesized Dyes in DCM and MeOH.