Supplementary Material (ESI) for Green Chemistry

Supporting Information

Experimental

General Remarks. Starting materials that were bought from Sigma-Aldrich were used without further purification. The ^{1}H NMR spectra were recorded on a Varian Inova 500 at 500 MHz or a Varian Gemini 200 at 200 MHz. ^{13}C NMR spectra were recorded at 125.7 MHz on a Varian Inova 500. MS data were obtained at San Diego State University using HP1100 Finnnigan LCQ. Column chromatography was performed on 230-400 mesh 32-74 μm 60 Å silica gel from Fisher Scientific. Elemental analyses were performed at NuMega Resonance Labs in San Diego, CA.

Synthesis of 2-[bis-(3-dimethylamino-propyl)-amino]-ethanesulfonic acid, sodium salt (1): 3,3'-Iminiobis(*N, N*-dimethylpropylamine) (5.00 g, 0.0267 mol) was added to vinylsulfonic acid sodium salt (6.81 g, 0.535 mol) as a 25 wt. % solution in water, and the mixture was heated at reflux for five days. The solvent was removed using a rotary evaporator to yield a crude brown-colored product which was further purified on a short silica gel column using MeOH /NH_4OH (98:2). After purification by column, the excess methanol was removed *in vacuo*, and the remaining yellow gum was dissolved in a minimal amount of deionized water and filtered, and pure product **1** was isolated as a golden oil after removing the water *in vacuo* (6.632 g, 0.02091 mol, 78.3% yield). ^{1}H NMR (D_2O, 500 MHz): δ 1.77 (4H, m, $NCH_2CH_2CH_2N$), 2.48 (12H, s, $N(CH_3)$), 2.56 (4H, t, J = 7.4 Hz, $NCH_2CH_2CH_2N(CH_3)_2$), 2.69 (4H, t, , J = 7.2 Hz, $NCH_2CH_2CH_2N(CH_3)_2$), 2.96 (2H, t, , J = 6.8 Hz, $NCH_2CH_2SO_3^-$), 3.08 (2H, t, J = 6.8 Hz, $NCH_2CH_2SO_3^-$),). $^{13}C\{^{1}H\}$ NMR (D_2O, 125.7 MHz): δ 25.1 ($NCH_2CH_2CH_2N$), 46.2 ($N(CH_3)$), 49.5 ($NCH_2CH_2SO_3^-$), 50.3 ($NCH_2CH_2SO_3^-$), 53.4 ($NCH_2CH_2CH_2N(CH_3)_2$), 59.2 ($NCH_2CH_2CH_2N(CH_3)_2$). MS (m/z): 318 ($M+Na^+$), 296 (M+1). IR (KBr, cm^{-1}): 1182($\nu_{S=O, asym}$), 1039($\nu_{S=O, sym}$). Anal. calcd for $C_{12}H_{28}N_3NaO_3S$: C, 45.41; H, 8.89; N, 13.24. Found: C, 44.80 H, 9.23 N, 13.59.

Synthesis of 2-(bis-pyridin-2-yl-methyl-amino)-ethanesulfonic acid, sodium salt (2): Bis-pyridin-2-yl-methyl-amine (0.500 g, 2.51 mmol) was added to vinylsulfonic acid sodium salt (1.96 g, 3.76 mmol) as a 25 wt. % solution in water, and the mixture was heated at reflux for three days while monitoring the reaction progress by tlc, whereupon the solution turned from yellow to green. The solvent was removed using a rotary evaporator to yield a crude green-colored product which was further purified on a short silica gel column using MeOH /NH_4OH (99:1), leaving behind the green-colored impurities. After purification by column, the excess methanol was removed *in vacuo*, and the remaining yellow gum was dissolved in a minimal amount of deionized water and filtered, and pure product **2** was isolated as a golden oil after removing the water *in vacuo* (0.612 g, 1.86 mmol, 74.1 % yield). ^{1}H NMR (D_2O, 500 MHz): δ 3.01 (2H, m, $NCH_2CH_2SO_3^-$), 3.18 (2H, m, $NCH_2CH_2SO_3^-$), 3.68 (4H, s, $NCH_2(NC_5H_4)$), 7.26 (2H, m, py-5), 7.38 (2H, m, py-3), 7.75 (2H, m, py-4), 8.40 (2H, d, , J = 5.2 Hz, py-6). $^{13}C\{^{1}H\}$ NMR (D_2O, 125.7 MHz): δ 50.3 ($NCH_2CH_2SO_3^-$), 52.1 ($NCH_2CH_2SO_3^-$), 62.0 ($NCH_2(NC_5H_4)$, 126.0 (py-5), 127.1 (py-3), 140.8 (py-4), 151.0 (py-6), 160.0 (py-2). MS (m/z): 330 ($M + Na^+$), 308 (M+1). IR (KBr, cm^{-1}): 1194($\nu_{S=O, asym}$), 1040($\nu_{S=O, sym}$). Anal.

calcd for $C_{14}H_{16}N_3NaO_3S$: C, 51.06; H, 4.90; N, 12.76. Found: C, 50.63 H, 5.26 N, 13.17.

Synthesis of 2-[bis-(2-pyridin-2-yl-ethyl)-amino]-ethanesulfonic acid, sodium salt (3): Bis-(2-pyridin-2-yl-ethyl)-amine[1] [2](0.300 g, 0.872 mmol) was added to vinylsulfonic acid sodium salt (0.907 g, 1.74 mmol) as a 25 wt. % solution in water, and the mixture was heated at reflux for four days while monitoring the reaction progress by tlc, whereupon the solution turned from yellow to brown. The solvent was removed using a rotary evaporator to yield a crude brown-colored product which was further purified on a short silica gel column using MeOH /NH_4OH (99:1). After purification by column, the excess methanol was removed *in vacuo*, and the remaining yellow gum was dissolved in a minimal amount of deionized water and filtered, and pure product **3** was isolated as a golden oil after removing the water *in vacuo* (0.182 g, 0.509 mmol, 58.4 % yield). ^{1}H NMR (D_2O, 500 MHz): δ 2.95 (8H, m, $NCH_2CH_2(NC_5H_4)$), 3.09 (4H, m, $NCH_2CH_2SO_3^-$), 7.28 (4H, m, py-5 and py-3), 7.77 (2H, m, py-4), 8.42 (2H, m, py-6). $^{13}C\{^1H\}$ NMR (D_2O, 125.7 MHz): δ 36.5 ($NCH_2CH_2(NC_5H_4)$), 49.7 ($NCH_2CH_2SO_3^-$), 50.7 ($NCH_2CH_2SO_3^-$), 55.5 ($NCH_2CH_2(NC_5H_4)$, 125.0 (py-5), 126.8 (py-3), 140.9 (py-4), 151.1 (py-6), 161.6 (py-2). MS (m/z): 358 ($M + Na^+$), 336 (M+1). IR (KBr, cm^{-1}): 1202($\nu_{S=O, asym}$), 1044 ($\nu_{S=O, sym}$). Anal. calcd for $C_{16}H_{20}N_3NaO_3S$: C, 53.77; H, 5.64; N, 11.76. Found: C, 53.36 H, 6.01 N, 12.11.

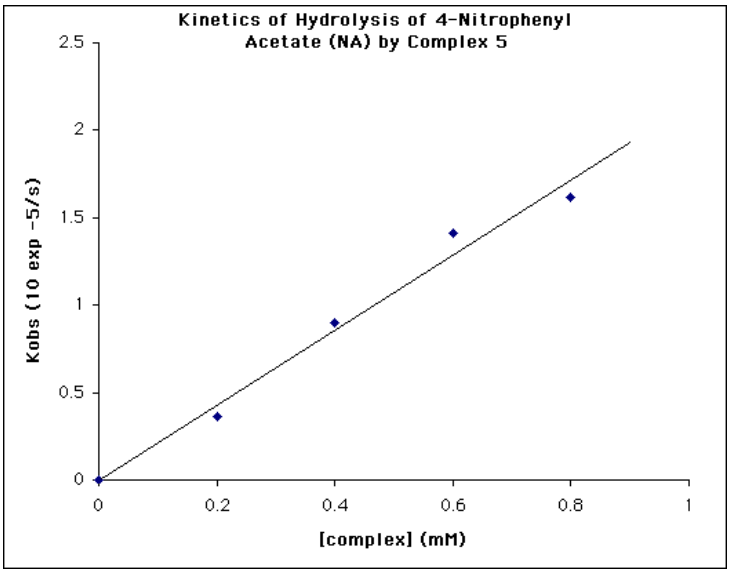
Synthesis of 2-(2-pyridin-2-yl-ethylamino)-ethanesulfonic acid, sodium salt (4): 2-pyridin-2-yl-ethylamine (0.329 g, 2.69 mmol) was added to vinylsulfonic acid sodium salt (1.413 g, 2.69 mmol) as a 25 wt. % solution in water, and the mixture was heated at reflux for one day while monitoring the reaction progress by tlc, whereupon the solution turned from yellow to brown. After 24 hrs, the solvent was removed using a rotary evaporator to yield a crude brown-colored product which was further purified on a short silica gel column using MeOH /NH_4OH (99:1). After purification by column, the excess methanol was removed *in vacuo*, and the remaining yellow gum was dissolved in a minimal amount of deionized water and filtered, and pure product **3** was isolated as a white solid after removing the water *in vacuo* (0.182 g, 0.509 mmol, 58.4 % yield). ^{1}H NMR (D_2O, 500 MHz): δ 3.18 (2H, m, $NCH_2CH_2(NC_5H_4)$), 3.24 (2H, m, $NCH_2CH_2(NC_5H_4)$), 3.41 (4H, m, $NCH_2CH_2SO_3^-$), 7.39 (2H, m, py-5 and py-3), 7.84 (1H, m, py-4), 8.48 (1H, m, py-6). $^{13}C\{^1H\}$ NMR (D_2O, 125.7 MHz): δ 35.4 (($NCH_2CH_2(NC_5H_4)$), 46.0 ($NCH_2CH_2SO_3^-$), 49.4 ($NCH_2CH_2SO_3^-$), 49.9 ($NCH_2CH_2(NC_5H_4)$, 125.8 (py-5), 126.9 (py-3), 141.3 (py-4), 151.6 (py-6), 158.9 (py-2). MS (m/z): 253 ($M + Na^+$), 231 (M+1). IR (KBr, cm^{-1}): 1226($\nu_{S=O, asym}$), 1036($\nu_{S=O, sym}$). Anal. calcd for $C_9H_{13}N_2NaO_3S$: C, 42.85; H, 5.19; N, 11.10. Found: C, 42.97 H, 5.46 N, 11.48.

Preparation of Zinc dichloride 2-(2-pyridin-2-yl-ethylamino)-ethanesulfonate, sodium salt, trihydrate (5): 2-(2-pyridin-2-yl-ethylamino)-ethanesulfonic acid, sodium salt, **4** (0.100 mg, 0.396 mmol) was dissolved in ~5 mL of deioinized H_2O in a glass vial, and one equiv. of $ZnCl_2$ (0.054 g, 0.40 mmol) was added and the solution stirred at r.t. After 1 hr, the light yellow solution was filtered through a Celite-plugged pipet, and the filtrate was dried *in vacuo* to yield a yellow solid. The yellow solid was washed several

times with cold MeOH and redissolved in ~1 mL of hot deionized H_2O, and the solvent was allowed to evaporate slowly at r.t. After 1 week, white crystals of **5** formed (0.119 g, 0.270 mmol, 68.1 %). ^{1}H NMR (D_2O, 500 MHz): δ 3.21 (2H, m, NC*H*$_2$CH$_2$(NC$_5$H$_4$)), 3.25 (2H, m, NCH$_2$C*H*$_2$(NC$_5$H$_4$)), 3.43 (4H, m, NC*H*$_2$C*H*$_2$SO$_3^-$), 7.41 (2H, m, py-5 and py-3), 7.87 (1H, m, py-4), 8.61 (1H, m, py-6). IR (KBr, cm^{-1}): 1267($\nu_{S=O, asym}$), 1043($\nu_{S=O, sym}$). Anal. calcd for $C_{18}H_{38}N_4Na_2O_{12}S_2Zn_2Cl_4$: C, 24.42; H, 4.33; N, 6.33. Found: C, 24.95 H, 4.09 N, 6.61.

X-ray Crystal Structure Determination. Diffraction intensity data were collected with a Bruker Smart Apex CCD diffractometer at 150(2) K using MoKα - radiation (0.71073 Å). The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2. Hydrogen atoms at the N(1) atom and in water molecules were found on the residual density map and refined with isotropic thermal parameters, other H atoms were taken in calculated positions. All software and sources scattering factors are contained in the SHELXTL (5.10) program package (G.Sheldrick, Bruker XRD, Madison, WI). Crystal data: plate, colorless, 0.38 x 0.31 x 0.06 mm^3, $C_9H_{19}Cl_2N_2NaO_6SZn$, FW 442.58, monoclinic, space group $P2_1/c$, a = 18.3353(10), b = 7.6965(4), c = 12.7734(7) Å, β = 104.148(1)°, V = 1747.9(2) Å^3, Z = 4, D_c = 1.682 g cm^3, T = 150(2) K, μ = 4.10 cm^{-1}, F(000) = 904, max./min. transmission 0.896/0.535, 10766 measured reflections, 4038 independent reflections [R_{int} = 0.0220], 227 parameters, $R1$ = 0.0348, $wR2$ = 0.0745 (all data), $R1$ = 0.0302, $wR2$ = 0.0723 ($I > 2\sigma(I)$), max./min. residual density 0.610/-0.296 e·Å^3, goodness-of-fit (F^2) = 1.031. CCDC 268563. See http://www.rsc.org/suppdata/gc/b5/b500264h/ for crystallographic data in .cif or other electronic format.

Kinetics Studies. The hydrolysis of 4-nitrophenyl acetate (NA) was followed using an Agilent 8453 UV-vis spectrophotometer with kinetics software and temperature regulator by following the release of 4-nitrophenolate at 400 nm and using an initial slope method. The studies were conducted at 25 ^{0}C, pH 7.4, I = 0.10 ($NaNO_3$) in 10% v/v CH_3CN.



1. Brady, L. E.; Freifelder, M.; Stone, G. R. *J. Org. Chem.,* **1961**, *26*, 4757-4758.