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Novel thiophosphorylated calix[4]resorcinol Mannich bases and their electrochemical behavior in hydrogen evolution reaction

Irina R. Knyazeva, Victoria I. Matveeva, Vera V. Khrizanforova,
Yulia H. Budnikova and Alexander R. Burilov

Experimental Section

General. NMR experiments were performed on a Bruker AVANCE-600 spectrometer at 303K equipped by 5 mm broadband probehead working at 600.1 MHz in ^{1}H and 242.9 in ^{31}P experiments. Chemical shifts were reported relative to residual signal of deuterated solvent for ^{1}H and 85% H_3PO_4 (0 ppm) as external reference for ^{31}P. IR spectra were recorded on a Bruker Vector 22 Fourier spectrometer (Karlsruhe, Germany) in the range from 400 to 3800 cm^{-1}. Samples were studied as emulsion in Nujol. MALDI-TOF mass spectra were obtained on a ULTRAFLEX III mass spectrometer (Bruker Daltonik, Bremen, Germany). Recording was performed with the use of plastic and metal plates. 2,5-Dihydroxy-benzoic acid (2,5-DHB) was used as a matrix.

Calix[4]resorcinol 2a. A mixture of calix[4]resorcinol **1** (0.15 g, 0.10 mmol), diethylamine (0.06 g, 0.80 mmol), and paraformaldehyde (0.02 g, 0.80 mmol) in ethanol (6 ml) was refluxed for 44 h. The precipitate was filtered, washed with ethanol and dried in vacuum up to a constant weight. The pure compound **2a** was obtained as slightly pink powder (0.14 g, yield 78%), mp > 210 ºC (dec). ^{31}P NMR (242.9 MHz, DMSO-*d*$_6$) δ 54.2 ppm. ^{1}H NMR (600.1 MHz, DMSO-*d*$_6$) δ 0.91 (s, 12H, H12), 0.93 (s, 12H, $-NCH_2-C\underline{H}_3$), 0.95 (s, 12H, $-NCH_2-C\underline{H}_3$), 1.24 (s, 12H, H12), 2.46 (m, 16H, $-NC\underline{H}_2-CH_3$), 3.66 (c, 8H, H13), 4.08 (m, 8H, H10), 4.39 (m, 8H, H10), 5.72 (s, 4H, H5), 6.20 (s, 4H, H4), 6.71 (d, $^3J_{HH}$ = 8.4 Hz, 8H, H7), 6.97 (d, $^3J_{HH}$ = 8.4 Hz, 8H, H8) ppm. IR ν_{max}: 829 (P = S); 972, 1005 (P-O-C); 3100–3600 (OH) cm^{-1}. MALDI–MS: m/z = 1853.0 [M+H]$^+$ (calcd M = 1852.0). Anal. calcd. for $C_{92}H_{120}N_4O_{20}P_4S_4$: C, C 59.61; H 6.48; N 3.02; P 6.69; S 6.91. Found: C, 59.91; H, 6.08; N, 3.21; P, 6.39; S, 6.99.

Calix[4]resorcinol 2b was obtained as a slightly pink powder analogously from calix[4]resorcinol **1** (0.15 g, 0.10 mmol), piperidine (0.07 g, 0.80 mmol) and paraformaldehyde (0.02 g, 0.80 mmol) in ethanol (6 ml). Yield 0.16 g (84 %), mp > 190 ºC (dec). ^{31}P NMR (242.9 MHz, DMSO-*d*$_6$) δ 54.2 ppm. ^{1}H NMR (600.1 MHz, DMSO-*d*$_6$) δ 0.91 (s, 12H, H12), 1.24 (s, 12H, H12), 1.43 (m, 24H, $-CH_2-$), 2.36 (m, 16H, $-NCH_2-$), 3.58 (s, 8H, H13), 4.08 (m, 8H, H10), 4.39 (m, 8H, H10), 5.69 (s, 4H, H5), 6.14 (s, 4H, H4), 6.71 (d, $^3J_{HH}$ = 8.1 Hz, 8H, H7), 6.96 (d, $^3J_{HH}$ = 8.1 Hz, 8H, H8). IR ν_{max}: 828 (P = S); 972, 1004 (P-O-C); 3200–3600 (OH) cm^{-1}. MALDI–MS: m/z = 1901.0 [M+H]$^+$ (calcd M = 1900.0). Anal. calcd. for $C_{96}H_{120}N_4O_{20}P_4S_4$: C, 60.63; H, 6.32; N, 2.95; P, 6.53; S, 6.74. Found: C, 60.37; H, 6.33; N, 2.97; P, 6.63; S, 6.52.

Calix[4]resorcinol 2c, 4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20-tetrakis[4-(5,5-dimethyl-2-sulfido-1,3,2-dioxaphosphinan-2-yl)oxyphenyl]-5,11,17,23-tetrakis(*N*-morpholinomethyl)pentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene, was obtained as a slightly pink powder analogously by heating calix[4]resorcinol **1** (0.15 g, 0.10 mmol) and paraformaldehyde (0.02 g, 0.80 mmol) in morpholine (5 ml) at 75 ºC for 12 h. Yield 0.17 g (90%), mp > 200 ºC (dec). ^{31}P NMR (242.9 MHz, DMSO-*d*$_6$) δ 54.2 ppm. ^{1}H NMR (600.1 MHz, DMSO-*d*$_6$) δ 1.44 (s, 12H, H12), 1.77 (s, 12H, H12), 2.97 (br.m, 16H, -NCH$_2$-), 4.10 (br.m., 16H, -OCH$_2$-), 4.25 (s, 8H, H13), 4.57 (m, 8H, H10), 4.95 (m, 8H, H10), 6.29 (s, 4H, H5), 6.91 (s, 4H, H4), 7.43 (d, $^{3}J_{HH}$ = 8.17 Hz, 8H, H7), 7.59 (d, $^{3}J_{HH}$ = 8.17 Hz, 8H, H8). IR ν_{max}: 828 (P = S); 970, 1004 (P-O-C); 3100–3600 (OH) cm^{-1}. MALDI–MS: m/z = 1909.0 [M+H]$^{+}$ (calcd M = 1908.0). Anal. calcd. for $C_{92}H_{112}N_4O_{24}P_4S_4$: C, 57.86; H, 5.87; N, 2.94; P, 6.50; S, 6.71. Found: C, 57.82; H, 5.74; N, 2.94; P, 6.51; S, 6.42.

Electrochemical studies

The supporting electrolyte, Bu_4NBF_4, used for electrochemical studies was purchased from Sigma-Aldrich and dried overnight at 100 °C under vacuum prior to use. Anhydrous DMF used for electrochemistry was purchased from Sigma-Aldrich. Cyclic voltammetry measurements were performed with E2P potentiostat of BASi Epsilon (USA) composed of measuring block, Dell Optiplex 320 computer with installed EpsilonES-USB-V200 program, and C3 electrochemical cell. Stationary glassy-carbon electrode (3.0 mm diameter) was used as working electrode. Platinum wire of 0.5 mm diameter was used as an auxiliary electrode. Measurements were performed under argon.