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Click reaction in the synthesis of novel thiophosphorylated ligands for electrochemical hydrogen evolution

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Experimental Section

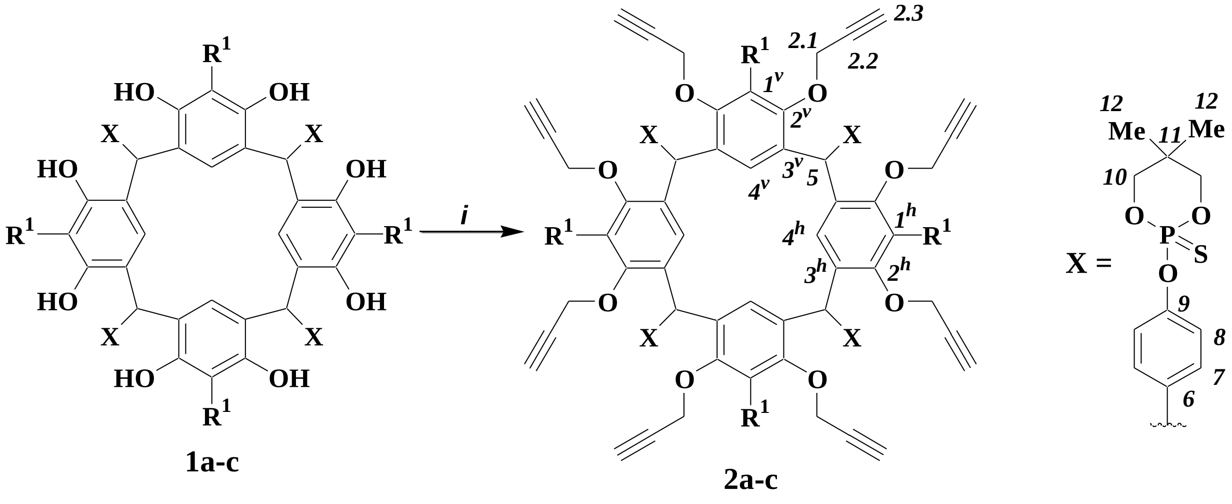
General

NMR experiments were performed on a Bruker AVANCE-600 spectrometer at 303 K equipped with 5 mm broadband probehead working at 600.1 MHz in ^{1}H, 150.9 MHz in ^{13}C and 242.9 in ^{31}P experiments. Chemical shifts were reported relative to residual signal of deuterated solvents for ^{1}H and 85% H_3PO_4 (0 ppm) as external reference for ^{31}P. IR spectra of solid compounds have been registered using Bruker Vector-27 FTIR spectrometer in the 400–4000 cm^{-1} range (optical resolution 4 cm^{-1}). The samples were prepared as KBr pellets. The MALDI mass spectra were recorded on an Ultraflex III TOF/TOF mass spectrometer (Bruker Daltonic GmbH, Bremen, Germany) operated in the linear mode with the registration of positively charged ions or negatively charged ions. A Nd:YAG laser (λ = 355 nm, repetition rate 100 Hz) was used. The mass spectrum was obtained with an accelerating voltage of 25 kV and an ion extraction delay time of 30 ns. The resulting mass spectrum was formed due to multiple laser irradiation of the crystal (50 shots). The metal target MTP AnchorChipTM was used. Portions (0.5 μl) of a 1% matrix solution in acetonitrile and of a 0.1% sample solution in methanol were consecutively applied onto the target and evaporated. 2,5-Dihydroxybenzoic acid (DHB) was used as a matrix. The polyethylene glycol was used to calibrate the mass scale of the device. The data were obtained using the FlexControl program (Bruker Daltonik GmbH, Germany) and processed using the FlexAnalysis 3.0 program (Bruker Daltonik GmbH, Germany). The elemental analysis was carried out on a CHNS analyzer EuroEA3028-HT-OM (Eurovector SpA, Italy). The samples were weighed on Sartorius CP2P (Germany) microbalances in tin capsules. Callidus 4.1 software was used to perform quantitative measurements and evaluate the data received.

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 dia.) was used as working electrode. Platinum wire of 0.5 mm diameter was used as auxiliary electrode. Measurements were performed under argon.

Experimental procedure for the preparation and spectroscopic data of 2a-c



1a-c

2a-c

a R^1=H, *rccc*-isomer, *cone*
b R^1=Me, *rccc*-isomer, *cone*
c R^1=Me, *rctt*-isomer, *chair*

a R^1=H, *rccc*-isomer, *boat*
b R^1=Me, *rccc*-isomer, *boat*
c R^1=Me, *rctt*-isomer, *chair*

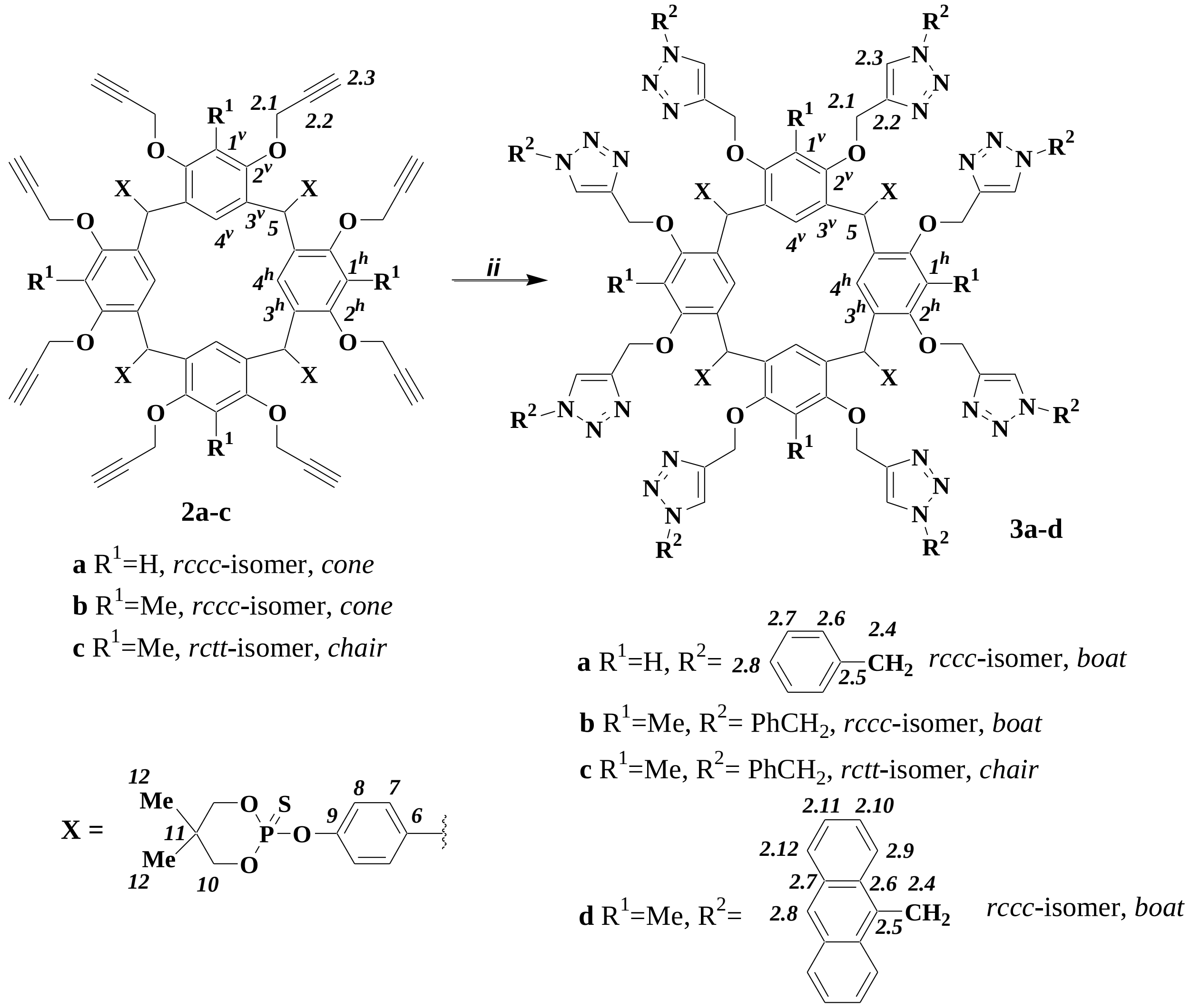
Scheme S1 *Reagents and conditions*: *i*, $BrCH_2C≡CH$, K_2CO_3, MeCN, reflux.

Calix[4]resorcinol 2a. To a suspension of calix[4]resorcinol **1a** (0.59 g, 0.39 mmol) and pre-dried anhydrous K_2CO_3 (0.86 g, 6.24 mmol) in dry MeCN (45 ml), propargyl bromide (0.74 g, 6.24 mmol) was added. The mixture was stirred and heated to 90 °C for 24 h under an inert atmosphere. The course of the reaction was controlled by MALDI-MS. The reaction was stopped when only peak of the fully substituted product could be observed. The precipitate formed was filtered, washed with acetonitrile; the filtrate was evaporated to dryness. The residue was reprecipitated from chloroform with hexane. After drying *in vacuo* (40 ºC, 0.06 Torr), pure **2a** as *rccc*-isomer in the *boat* conformation was obtained (0.69 g, 98%) as an orange powder. Mp > 120 ºC (dec). ^{31}P NMR (242.9 MHz, acetone-d_6, 30 ºC): δ = 54.2 ppm. ^{1}H NMR (600.1 MHz, acetone-d_6, 233 K): δ 1.00 (s, 12H, H12), 1.31 (s, 12H, H12), 3.22 (t, 4H, $^4J_{HH}$ 2.2 Hz, H2.3^h), 3.29 (t, $^4J_{HH}$ 2.2 Hz, 4H, H2.3^v), 4.13 (m, 8H, H10), 4.35 and 4.55 (dd, $^4J_{HH}$ 2.2 Hz, $^2J_{HH}$ 16.2 Hz, 8H, H2.1^h), 4.57 (m, 8H, H10), 4.64 and 4.74 (dd, $^4J_{HH}$ 2.2 Hz, $^2J_{HH}$ 16.2 Hz, 8H, H2.1^v), 5.80 (s, 4H, H5), 6.03 (s, 2H, H4^h), 6.30 (s, 2H, H4^v), 6.83 (s, 2H, H1^h), 6.86 (d, $^3J_{HH}$ 8.0 Hz, 8H, H7), 6.92 (s, 2H, H1^v), 7.13 (d, $^3J_{HH}$ 8.0 Hz, $^4J_{PH}$ 1.3 Hz, 8H, H8) ppm. ^{13}C NMR (150.9 MHz, acetone-d_6, 233 K): δ 21.4 (s, C12), 22.7 (s, C12), 33.6 (d, $^3J_{PC}$ 6.3 Hz, C11), 43.9 (s, C5), 58.6 (br.s, C2.1), 77.6 (br.s, C2.3), 79.4 (d, $^2J_{PC}$ 8.5 Hz, C10), 80.8 (br.s, C2.2), 102.6 (s, C1), 121.7 (d, $^3J_{PC}$ 4.5 Hz, C8), 127.5 (s, C3), 129.3 (s, C4), 131.6 (s, C7), 142.0 (s, C6), 150.4 (d, $^3J_{PC}$ 7.2 Hz, C9), 156.2 (s, C2) ppm. IR ν_{max}: 829 (P=S); 970, 1003 (P-O-C); 2121 (C≡C); 3287 (C≡CH) cm^{-1}. Anal. Calcd. for $C_{96}H_{92}O_{20}P_4S_4$ (%): C, 63.44; H, 5.07; P, 6.83; S, 7.05. Found (%): C, 63.46; H, 4.62; P, 6.85; S, 7.04. MALDI-MS: *m/z* = 1817 [M+H]$^+$, 1855 [M+K]$^+$ (calcd. M = 1816).

Calix[4]resorcinol 2b was obtained as an orange powder by a method analogous to that used to prepare **2a** by the treatment of calix[4]resorcinol **1b** (1.00 g, 0.64 mmol) with dry potassium carbonate (1.41 g, 10.20 mmol) and propargyl bromide (1.21 g, 10.20 mmol) in acetonitrile (100 ml). Yield 1.18 g (99 %), mp > 110 ºC (dec). ^{31}P NMR (242.9 MHz, DMSO-d_6, 30 ºC): δ 54.4 ppm. ^{1}H NMR (600.1 MHz, $CDCl_3$, 30 ºC): δ 0.96 (s, 12H, H12), 1.34 (s, 12H, H12), 2.15 (s, 12H, C1-CH_3^h), 2.29 (s, 12H, C1-CH_3^v), 2.47 (br.m, 4H, H2.3^h), 2.48 (br.m, 4H, H2.3^v), 3.89 – 4.13 (m, 32H, H10, H2.1^h,H2.1^v), 5.94 (s, 2H, H4^h), 5.98 (s, 4H, H5), 6.09 (s, 2H, H4^v), 6.86 (d, $^3J_{HH}$ 8.0 Hz, 8H, H7), 7.13 (d, $^3J_{HH}$ 8.0 Hz, 8H, H8) ppm. IR ν_{max}: 828 (P=S); 971, 1004 (P-O-C); 2125 (C≡C); 3291 (C≡CH) cm^{-1}. Anal. Calcd. for $C_{100}H_{100}O_{20}P_4S_4$ (%): C, 64.03; H, 5.34; P, 6.61; S, 6.83. Found (%): C, 64.07; H, 5.41; P, 6.57; S, 6.91. MALDI-MS: *m/z* = 1874 [M+H]$^+$, 1896 [M+Na]$^+$ (calcd. M = 1873).

Calix[4]resorcinol 2c was obtained as an orange powder by a method analogous to that used to prepare **2a** by treatment of calix[4]resorcinol **1c** (0.25 g, 0.16 mmol) with dry potassium carbonate (0.35 g, 2.55 mmol) and propargyl bromide (0.30 g, 2.55 mmol) in acetonitrile (50 ml). Yield 0.23 g (77 %), mp > 120 ºC (dec). ^{31}P NMR (242.9 MHz, $CDCl_3$, 30 ºC): δ 54.1 ppm. ^{1}H NMR (600.1 MHz, $CDCl_3$, 30 ºC): δ 0.92 (s, 12H, H12), 1.33 (s, 12H, H12), 2.31 (s, 6H, C1-$C\underline{H}_3^h$), 2.39 (s, 6H, C1-$C\underline{H}_3^v$), 2.46 (t, 4H, $^4J_{HH}$ 2.4 Hz, H2.3^h), 2.50 (t, $^4J_{HH}$ 2.4 Hz, 4H, H2.3^v), 3.90 – 4.46 (m, 32H, H10, H2.1^h,H2.1^v), 5.81 (s, 2H, H4^h), 6.03 (s, 4H, H5), 6.29 (s, 2H, H4^v), 6.63 (d, $^3J_{HH}$ 8.1 Hz, H7), 6.96 (d, $^3J_{HH}$ 8.1 Hz, H8) ppm. IR ν_{max}: 830 (P=S); 971, 1003 (P-O-C); 2125 (C≡C); 3289 (C≡CH) cm^{-1}. Anal. Calcd. for $C_{100}H_{100}O_{20}P_4S_4$ (%): C, 64.10; H, 5.34; P, 6.62; S, 6.84. Found (%): C, 64.07; H, 5.41; P, 6.57; S, 6.91. MALDI-MS: *m/z* = 1874 [M+H]$^+$, 1896 [M+Na]$^+$ (calcd. M = 1873).

Experimental procedure for the preparation and spectroscopic data of 3a-d



Scheme S2 *Reagents and conditions*: *ii*, BnN_3 or 9-(azidomethyl)anthracene, $CuSO_4 \cdot 5H_2O$, sodium ascorbate, THF/H_2O, reflux.

Calix[4]resorcinol 3a. To a suspension of calix[4[resorcinol **2a** (0.15 g, 0.08 mmol), sodium ascorbate (0.03 g, 0.13 mmol) and $CuSO_4 \cdot 5H_2O$ (0.03 g, 0.13 mmol) in THF/H_2O mixture (1:1, 30 ml), benzyl azide (0.18 g, 1.32 mmol) was added. The mixture was stirred at 60–65 ºC for 24 h under inert atmosphere. The mixture was diluted with $CHCl_3$ (25 ml), washed with H_2O, and concentrated *in vacuo*. The residue was purified by precipitation from chloroform with diethyl ether. After drying *in vacuo* (40 ºC, 0.06 Torr), pure **3a** as its *rccc*-isomer and *boat* conformation was obtained (0.17 g, 71%) as a beige powder. Mp 134–135 ºC. ^{31}P NMR (242.9 MHz, acetone-d_6, 30 ºC): δ 54.9 ppm. ^{1}H NMR (600.1 MHz, acetone-d_6, 30 ºC): δ 1.04 (s, 12H, H12), 1.36 (s, 12H, H12), 4.13 (m, 8H, H10), 4.54 (m, 8H, H10), 4.63 (d, $^2J_{HH}$ 12.0 Hz, 8H, H2.1^h), 4.79 (d, $^2J_{HH}$ 11.6 Hz, 8H, H2.1^v), 5.03 (d, $^2J_{HH}$ 11.6 Hz, 8H, H2.1^v), 5.08 (d, $^2J_{HH}$ 12.0 Hz, 8H, H2.1^h), 5.59 (m, 16H, H2.4), 5.73 (s, 4H, H5), 5.98 (s, 2H, H4^h), 6.35 (s, 2H, H4^v), 6.74 (d, $^3J_{HH}$ 8.0 Hz, 8H, H7), 6.87 (s, 2H, H1^v), 6.99 (d, $^3J_{HH}$ 8.0 Hz, 8H, H8), 7.04 (s, 2H, H1^h), 7.36

(m, 40H, H2.6, H2.7, H2.8), 7.37 (s, 4H, H2.3), 7.46 (s, 4H, H2.3) ppm. ^{13}C NMR (150.9 MHz, acetone-d_6, 30 ºC): δ 21.4 (s, C12), 22.6 (s, C12), 33.6 (d, $^3J_{PC}$ 6.1 Hz, C11), 44.5 (s, C5), 54.9 (s, C2.7), 64.5 (s, C2.1), 79.4 (s, C10), 100.8 (s, C1^{v}), 101.8 (s, C1^{h}), 121.6 (s, C8), 125.1 (s, C2.3), 125.3 (s, C2.3), 126.9 (s, C3), 129.5 (s, C2.6), 129.6 (s, C2.8), 129.9 (s, C4^{v}), 130.4 (s, C2.7), 131.5 (s, C7), 133.7 (s, C4^{h}), 137.6 (s, C2.5), 137.8 (s, C2.5), 142.6 (s, C6), 145.6 (s, C2.2), 150.2 (s, C9), 156.7 (s, C2^{h}), 156.8 (s, C2^{v}) ppm. IR ν_{max}: 829 (P=S); 970, 1003 (P-O-C) cm^{-1}. Anal. Calcd for $C_{152}H_{148}N_{24}O_{20}P_4S_4$ (%): C, 63.32; H, 5.17; N, 11.66; P, 4.30; S, 4.45. Found: C, 63.55; H, 5.23; N, 11.87; P, 4.48; S, 4.51. MALDI-MS: *m/z* = 2884.0 [M+H]$^+$ (calcd M = 2883.0).

Calix[4]resorcinol 3b was obtained as a pale-yellow powder with an yield of 0.20 g (87%) analogously to compound **3a** by the treatment of calix[4]resorcinol **2b** (0.15 g, 0.08 mmol) with sodium ascorbate (0.03 g, 0.13 mmol), $CuSO_4{\cdot}5H_2O$ (0.03 g, 0.13 mmol) and benzyl azide (0.18 g, 1.28 mmol). Mp 110–111 ºC. ^{31}P NMR (242.9 MHz, acetone-d_6, 30 ºC): δ 54.3 ppm. ^{1}H NMR (600.1 MHz, acetone-d_6, 30 ºC): δ 0.98 (s, 12H, H12), 1.32 (s, 12H, H12), 2.10 (s, 6H, C1-CH$_3$^{h}), 2.22 (s, 6H, C1-CH$_3$^{v}), 4.10 (m, 8H, H10), 4.32 (m, 8H, H10), 4.45 (br.m, 8H, H2.1^{h}), 4.50 (br.m, 8H, H2.1^{v}), 4.81 (d, $^2J_{HH}$ 12.0 Hz, 8H, H2.1^{v}), 4.83 (d, $^2J_{HH}$ 12.0 Hz, 8H, H2.1^{h}), 5.48 (m, 16H, H2.4), 5.61 (s, 4H, H5), 5.99 (s, 2H, H4^{h}), 6.37 (s, 2H, H4^{v}), 6.81 (d, $^3J_{HH}$ 8.0 Hz, 8H, H7), 7.06 (d, $^3J_{HH}$ 8.0 Hz, 8H, H8), 7.35 (m, 40H, H2.6, H2.7, H2.8), 7.80 (s, 4H, H2.3), 7.84 (s, 4H, H2.3) ppm. IR ν_{max}: 828 (P=S); 970, 1003 (P-O-C) cm^{-1}. Anal. Calcd. for $C_{156}H_{156}N_{24}O_{20}P_4S_4$ (%): C, 63.75; H, 5.35; N, 11.44; P, 4.22; S, 4.36. Found (%): C, 63.72; H, 5.11; N, 11.60; P, 4.11; S, 4.34. MALDI-MS: *m/z* = 2962.0 [M+Na]$^+$, 2978.0 [M+K]$^+$ (calcd. M = 2939.0).

Calix[4]resorcinol 3c was obtained as a pale-yellow powder with an yield of 0.22 g (94%) according to a method analogous to that used to prepare **3a** by the treatment of calix[4]resorcinol **2c** (0.15 g, 0.08 mmol) with sodium ascorbate (0.03 g, 0.13 mmol), $CuSO_4{\cdot}5H_2O$ (0.03 g, 0.13 mmol) and benzyl azide (0.18 g, 1.28 mmol). Mp > 100 ºC (dec.). ^{31}P NMR (166.9 MHz, acetone-d_6, 30 ºC): δ 54.0 ppm. ^{1}H NMR (600.1 MHz, acetone-d_6, 30 ºC): δ 0.85 (s, 12H, H12), 1.20 (s, 12H, H12), 2.04 (s, 6H, C1-C$\underline{H}_3$^{h}), 2.40 (s, 6H, C1-C$\underline{H}_3$^{v}), 3.96 (m, 8H, H10), 4.36 (m, 8H, H10), 4.38 (m, 8H, H2.1^{h}), 4.49 (d, $^2J_{HH}$ 12.0 Hz, 8H, H2.1^{v}), 4.79 (d, $^2J_{HH}$ 11.6 Hz, 8H, H2.1^{v}), 4.94 (d, $^2J_{HH}$ 11.6 Hz, 8H, H2.1^{h}), 5.46 (s, 8H, H2.4), 5.55 (s, 8H, H2.4), 5.78 (s, 2H, H4^{h}), 5.91 (s, 4H, H5), 6.40 (s, 2H, H4^{v}), 6.54 (d, $^3J_{HH}$ 8.0 Hz, 8H, H7), 6.82 (d, $^3J_{HH}$ 8.0 Hz, 8H, H8), 7.29 (m, 40H, H2.6, H2.7, H2.8), 7.81 (s, 4H, H2.3), 7.98 (s, 4H, H2.3) ppm. IR ν_{max}: 830 (P=S); 971, 1002 (P-O-C) cm^{-1}. Anal. Calcd. for $C_{156}H_{156}N_{24}O_{20}P_4S_4$ (%): C, 63.75; H, 5.35; N, 11.44; P, 4.22; S, 4.36. Found (%): C, 63.55; H, 5.24; N, 11.26; P, 4.26; S, 4.37. MALDI-MS: *m/z* = 2978.0 $[M+K]^+$ (calcd. M = 2939.0).

Calix[4]resorcinol 3d was obtained as a beige powder with an yield of 0.28 g (72%) according to a method analogous to that used to prepare **3a** by the treatment of calix[4]resorcinol **2b** (0.20 g, 0.11 mmol) with sodium ascorbate (0.03 g, 0.17 mmol), $CuSO_4{\cdot}5H_2O$ (0.04 g, 0.17 mmol) and 9-(azidomethyl)anthracene (0.40 g, 1.71 mmol). ^{31}P NMR (242.9 MHz, DMSO-d_6, 30 ºC): δ 54.0 ppm. Mp > 180 ºC (dec). ^1H NMR (600.1 MHz, DMSO-d_6, 30 ºC): δ 0.82 (s, 12H, H12), 1.18 (s, 12H, H12), 4.09 (m, 8H, H10), 4.28 (m, 8H, H10), 5.60 (s, 4H, H5), 5.84 (s, 16H, H2.1), 6.23 (m, 16 H, H2.4), 6.40 (d, $^3J_{HH}$ 8.6 Hz, 8H, H7), 6.72 (d, $^3J_{HH}$ 8.6 Hz, 8H, H8), 7.16 (t, $^3J_{HH}$ 8.8 Hz, 16H, H2.11), 7.25 (t, $^3J_{HH}$ 8.8 Hz, 16H, H2.10), 7.35 (s, 8H, H2.3), 8.08 (d, $^3J_{HH}$ 8.8 Hz, 16H, H2.12), 8.29 (d, $^3J_{HH}$ 8.8 Hz, 16H, H2.9), 8.66 (s, 8H, H2.8) ppm. ^{13}C NMR (150.9 MHz, DMSO-d_6, 30 ºC): δ 19.7 (s, C12), 21.1 (s, C12), 31.8 (d, $^3J_{PC}$ 6.2 Hz, C11), 45.4 (s, C2.4), 43.6 (s, C5), 64.6 (s, C2.1), 77.5 (d, $^2J_{PC}$ 7.2 Hz, C10), 119.8 (s, C8), 123.4 (s, C2.9), 123.6 (s, C2.7), 123.9 (s, C2.3), 125.5 (s, C2.11), 127.1 (s, C2.10), 129.6 (s, C2.12), 129.7 (s, C2.8), 129.9 (s, C7), 130.2 (s, C2.6), 131.0 (s, C2.5), 139.3 (s, C3), 142.6 (s, C6, C2.2), 147.9 (s, C9), 153.6 (s, C2) ppm. IR ν_{max}: 827 (P=S); 971, 1003 (P-O-C) cm^{-1}. Anal. Calcd for $C_{220}H_{188}N_{24}O_{20}P_4S_4$ (%): C, 70.65; H, 5.07; N, 8.99; P, 3.31; S, 3.43. Found: C, 70.55; H, 5.03; N, 9.01; P, 3.46; S, 3.50. MALDI-MS: *m/z* = 3741.0 $[M+H]^+$ (calcd M = 3740.0).

Nickel complexes with triazole-containing thiophosphorylated ligands have been prepared *in situ* by mixing 1 equiv. calix[4]resorcinols **3a,b,d** with 1 equiv. $Ni(BF_4)_2{\cdot}6H_2O$.

Ni^{2+}L (L = 3a): ^{31}P NMR (242.9 MHz, DMSO-d_6, 30 ºC): δ 54.7 ppm. MALDI-MS: calcd for $C_{152}H_{148}N_{24}NiO_{20}P_4S_4$ *m/z* = 2941.0; found *m/z* = 2941.5.

Ni^{2+}L (L = 3b): ^{31}P NMR (242.9 MHz, DMSO-d_6, 30 ºC): δ 54.2 ppm.
MALDI-MS: calcd for $C_{156}H_{156}N_{24}NiO_{20}P_4S_4$ *m/z* = 2997; found *m/z* = 2997.3.

Ni^{2+}L (L = 3d): ^{31}P NMR (242.9 MHz, DMSO-d_6, 30 ºC): δ 54.2 ppm.
MALDI-MS: calcd for $C_{220}H_{188}N_{24}NiO_{20}P_4S_4$ *m/z* = 3798; found *m/z* = 3798.1.