Supplementary Information

Persistent Microporosity of a Non-planar Porphyrinoid based on Multiple

Supramolecular Interactions for Nanomechanical Sensor Applications

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1.0 Experimental

General. Reagents and dehydrated solvents (in septum-sealed bottles) used for syntheses and spectroscopic measurements were obtained from Tokyo Kasei Chemical Co., Wako Chemical Co. or Aldrich Chemical Co. and were used without further purification. Electronic absorption spectra were measured using JASCO V-570 UV/Vis/NIR spectrophotometer or Princeton Applied Research (PAR) diode array rapid scanning spectrometer. ATR-FTIR spectra were obtained using a Thermo-Nicolet 760X FTIR spectrophotometer equipped with a SMART-iTX ATR accessory. Electron spin resonance (ESR) spectra were measured from solid samples using a JEOL JES-FA200 spectrometer equipped with an ES-CT470 liquid He variable temperature system with data recorded and processed using A-System version 1.6.5 PCI J/X-Band and FA-Manager version 1.2.9 V2 series software. Powder X-ray diffraction (pXRD) patterns were recorded at room temperature using with Cu-K α radiation (λ = 1.54184 Å) on a Rigaku MiniFlex 600 diffractometer. ¹H-NMR spectra were obtained using JEOL AL300BX or JEOL AL400SSS spectrometers operating respectively at 300 and 400 MHz and using tetramethylsilane as an internal standard. Proton decoupled ¹³C-NMR spectra were obtained using JEOL AL300BX or JEOL AL400SSS spectrometers operating respectively at 76 and 101 MHz and using tetramethylsilane as an internal standard. Data was processed on Delta version 5.0.5.1, Always JNM-AL version 6.2 and MestReNova 6.0.2. ¹H NMR chemical shifts (δ) are reported in ppm relative to TMS for CDCl₃ (δ 0.00) or the residual solvent peak for other solvents. ¹³C NMR chemical shifts (δ) are reported in ppm relative to the solvent reported. Coupling constants (J) are expressed in Hertz (Hz), shift multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), double doublet (dd), multiplet (m) and broad singlet (bs). High resolution electrospray ionization time-of-flight mass spectra (ESI-TOF-

MS) were measured using a Thermo Scientific Q-Exactive Plus instrument. Tetrakis-(3,5-di-*t*-butyl-4-hydroxyphenyl) porphinatonickel(II) ([T(DtBHP)P]Ni), 2-formyl-*meso*-tetrakis-(3,5-di-*t*-butyl-4-hydroxyphenyl) porphyrinatonickel(II) ([T(DtBHP)P]Ni-CHO), 2-(5,6-Dicyano-1H-imidazo[4,5-b]pyrazin-2-yl)-tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)porphinato nickel(II) and compound **1** were prepared according to literature methods.^{S1,S2}

Specific Surface Area Determinations. Nitrogen adsorption/desorption isotherms were recorded on a BELSORB Max instrument for the estimation of Brunauer–Emmett–Teller (BET) surface area. Samples were loaded into a cell for measurement and heated at 120 °C under reduced pressure for 24 h prior to collection of the adsorption/desorption isotherms.

X-Ray Crystallography. Crystals of 1-ox were grown by slow cooling of a hot solution in toluene. Crystals of **2** were grown by diffusing hexane into a solution in chloroform. Data collections were performed using MoKα radiation ($\lambda = 0.71073$ Å) on a RIGAKU VariMax Saturn diffractometer equipped with a charge-coupled device (CCD) detector or a Bruker APEX CCD diffractometer. Prior to the diffraction experiment the crystals were flash-cooled to the given temperatures in a stream of cold nitrogen gas. Cell refinements and data reductions were carried out using the d*trek program package in the CrystalClear software suite.⁵³ The structures were solved using a dualspace algorithm method (SHELXT)⁵⁴ and refined by full-matrix least squares on F2 using SHELXL-2014⁵⁵ in the WinGX program package.⁵⁶ Non-hydrogen atoms were anisotropically refined and hydrogen atoms were placed on calculated positions with temperature factors fixed at 1.2 times Ueq of the parent atoms and 1.5 times Ueq for methyl groups. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre with CCDC reference numbers 2107801 (1-ox.3(C₆H₅CH₃), 113 K), 2107802 (1-ox.2(C₆H₅CH₃), 113 K), 2107803 (**1**-ox, water, 113 K) and 2107804 (**1**-ox; no solvent 200 K), 2209423 (**2**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi, e-mail: data_request@ ccdc.cam.ac.uk, or fax: +44 1223 336033.

Electrochemistry. Differential pulsed voltammetry (DPV) were recorded on an EG&G Model 263A potentiostat using a three-electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using argon gas. Spectroelectrochemical study was performed by using a cell assembly (SEC-C) supplied by ALS Co., Ltd. (Tokyo, Japan). This assembly comprised of a Pt counter electrode, a 6 mm Pt Gauze working electrode, and an Ag/AgCl reference electrode in a 1.0 mm path length quartz cell. The optical transmission was limited to 6 mm covering the Pt gauze working electrode.

Sensor Preparation. All sensing receptor materials used here were deposited directly onto a four channel MSS membrane by inkjet deposition using an inkjet spotter (LaboJet-500SP, Microjet Corporation) equipped with an IJHBS-300 nozzle (Microjet Corporation). Sensing materials were dissolved in N,N-dimethylformamide (1 mg mL⁻¹) for the inkjet deposition. The number of sequential droplets deposited during this process was varied between 25 and 300. Inkjet stage temperature was set at 70 °C to control the solvent evaporation rate during the deposition process.

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Sensing measurements. Sensitivity tests of the inkjet-spotted receptor materials on the MSS chip were performed at ambient temperature by flowing a carrier gas (nitrogen) alternately containing no analyte vapor and with 20 % v/v of the different VOCs, including alcohols, ketones, esters and hydrocarbons. A gaseous analyte of interest is first introduced to the sensor chamber for 30 s followed by purging with nitrogen gas for 30 s. Four sample-purge cycles were performed for each vapor and data were recorded at a sampling rate of 20 Hz by applying a bridge voltage of - 0.5 V to the Wheatstone bridge composed of four bridges with piezoresistors on the MSS chip. Sensitivity of the receptor materials under different humidity conditions were also investigated at room temperature (25 °C) using a separate automated setup. VOCs were diluted to 2%, 5% and 10% of their saturated vapor concentrations and humidified at 0 %, 10 %, 40 %, 70 % and 90 % relative humidity (RH) prior to injection. 4 sampling (100 sec.)-purging (100 s) cycles were performed for each measurement. Limits of detection were determined from the mean reversible response of the final three cycles, a correction was applied to account for electrical noise inherent in the MSS device (approx. 1 μ V) to give the signal-to-noise ratio. The effective limit of detection was then estimated by dividing the concentration of analyte present by the signal-to-noise ratio. LOD values for acetone were corroborated by using proton-transfer reaction mass spectrometry (PTR-MS) measurements. These were performed using a PTR-TOF-MS 6000 X2 instrument (IONICON) to assess the head space acetone concentration of acetonewater mixtures. Minimum detection limit of this instrument is < 1 pptv with sensitivity > 2000 cps/ppbv and mass resolution > 6000. A range of acetone-water mixtures were prepared by a simple dilution method and their headspace acetone concentrations were calculated by using autosampler technique. Minimum headspace concentration of acetone is 0.8 ppm in water. The

same samples were also measured using **1**-ox coated MSS to corroborate the LOD obtained using the MSS device.

2.0 Synthesis



Scheme S1. Synthesis of **1** and **1**-ox. Condensation of **Ni-CHO** with 5,6-diaminopyrazine-2,3-dicarbonitrile by heating in N,N-dimethylformamide leads to the imidazopyrazine-2,3-dicarbonitrile-substituted **Ni-Benzimd**, which can be oxidized to **1** and **1**-ox by treatment with an oxidant most conveniently 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Lead (IV) oxide can also be used. Treatment of **1**-ox with TBAF in dichloromethane in the presence of water leads to complete migration of a meso-substituent to the benzimidazole beta-substituent (see also Figure S14).

2-(5,6-Dicyano-1H-imidazo[4,5-b]pyrazin-2-yl)-tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)porph inatonickel(II), Ni-BenzImd



A mixture of [T(DtBHP)PNi]-CHO^{S1} (2.00 g, 1.65 mmol) and 5,6-diamino-2,3-dicvanopyrazine (0.40 g, 2.48 mmol) in dimethylformamide (50 mL) were refluxed under air for 30 h. The reaction mixture was then allowed to cool to room temperature and water was added. The solid precipitate was filtered and dried under reduced pressure. The residue was purified by column chromatography (SiO₂) eluting with hexane/dichloromethane (1:1) to give Ni-BenzImd as a green solid (Yield: 1.80 mg, 80%). UV/Vis (CH₂Cl₂): λ (ϵ / M⁻¹cm⁻¹) = 412 (95,000), 442 (119,000), 550 (15,700), 603 (19,800) nm. ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 9.64 (s, 1H), 8.72-8.82 (m, 6H), 8.55 (d, J = 5.1 Hz, 1H), 7.88 (s, 2H), 7.75-7.79 (m, 6H), 5.53 (s, 1H), 5.50 (s, 2H), 5.48 (s, 1H), 1.57-1.58 (m, 54H), 1.36 (s, 18H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 161.53, 154.96, 154.32, 154.14, 154.00, 153.82, 150.30, 145.22, 144.93, 144.75, 144.41, 144.27, 143.07, 142.10, 140.23, 140.05, 139.96, 138.46, 136.48, 134.78, 134.72, 134.69, 134.60, 133.91, 133.68, 133.23, 133.08, 132.40, 131.45, 131.18, 131.01, 130.85, 129.18, 128.22, 125.41, 122.54, 121.19, 120.62, 117.87, 114.28, 114.23, 34.73, 34.64, 30.76, 30.35 ppm. FT-IR(ATR): v = 3627 (m, O-H str.), 3290 (w), 2954 (s), 2911 (m), 2871 (m), 2238 (w, C=N str.), 1601 (w), 1571 (w), 1519 (w), 1466 (w), 1432 (s), 1411 (m), 1393 (w), 1349 (m), 1315 (m), 1223 (s), 1155 (s), 1119 (m), 1077 (w), 1056 (w), 1012 (m), 945 (w), 943 (w), 933 (w), 889 (m), 837 (w), 826 (m), 799 (m), 772 (w), 758 (w), 746 (w), 738 (w), 721 (m), 688 (m), 672 (m), 654 (m), and 631 (m) cm⁻¹. HRMS (ESI-TOF-MS, CH₂Cl₂); calculated for $[C_{83}H_{91}O_4N_{10}Ni]^- = 1349.6573$, found: = 1349.6582.

Oxidation procedures

<u>**1** and **1**-ox</u>

Using DDQ as oxidant.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (336 mg, 1.48 mmol, 4.0 equiv.) was added to a solution of 2-(5,6-dicyano-1H-imidazo[4,5-b]pyrazin-2-yl)-tetrakis(3,5-di-*t*-butyl-4-hydroxy phenyl)porphinatonickel(II), **Ni-Benzimd** (500 mg, 0.37 mmol, 1 equiv.) in dichloromethane (50 mL) and the resulting mixture was stirred for 2 hours. The reaction mixture volume was reduced to an appropriate volume and then subjected to column chromatography (SiO₂) using CH₂Cl₂ as eluent to give **1** (260 mg, 52%). Further elution with CH₂Cl₂ also gave **1**-ox (200 mg, 40%). When a similar reaction mixture was purified using alumina for the column chromatography and dichloromethane as eluent **1**-ox (450 mg, 90%) was the major product. It is likely that **1**-ox is unstable against exposure of its solutions to the silica media used for column chromatography. However, it should be noted that **1** and **1**-ox are interconvertible.

<u>Using PbO₂ as oxidant</u>

<u>From Ni-BenzImd</u>: Lead Oxide (330 mg, 1.48 mmol, 4.0 equiv.) was added to a stirred solution of **Ni-BenzImd** (500 mg, 0.37 mmol, 1 equiv.) in dichloromethane (50 mL) and the resulting mixture stirred for a further 2 hours. The reaction mixture volume was reduced to an appropriate volume then subjected to column chromatography (neutral alumina) using CH₂Cl₂ as eluent to give **1**-ox (450 mg, 90 %).

<u>From 1</u>: Lead Oxide (330 mg, 1.48 mmol, 4.0 equiv.) was added to a stirred solution of **1** (500 mg, 0.37 mmol, 1 equiv.) in dichloromethane (50 mL) and the resulting mixture stirred for a further 2 hours. The reaction mixture volume was reduced to an appropriate volume then subjected to column chromatography (neutral alumina) using CH_2Cl_2 as eluent to give **1**-ox (480 mg, 96 %).

2: Tetrabutylammonium fluoride trihydrate, $[CH_3(CH_2)_3]_4NF$. $3H_2O$ (93.60 mg, 0.297 mmol, 4.0 equiv.) was added to **1**-ox (100 mg, 0.074 mmol, 1.0 equiv.) and left in air for 12 h. The resulting mixture was purified by column chromatography (SiO₂, 0.5% acetone/dichloromethane) to give **2** (85 mg, 84%).



1: UV/Vis (CH₂Cl₂): λ (ϵ / M⁻¹cm⁻¹) = 402 (70,900), 470 (104,900), 566 (9,300), 616 (31,000) nm. ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 9.74 (s, 1H), 9.33 (d, J = 5.5 Hz, 1H), 8.94 (d, J = 5.1 Hz, 1H), 8.79-8.84 (m, 3H), 8.76 (d, J = 5.1 Hz, 1H), 7.82 (s, 2H), 7.75 (s, 2H), 7.74 (s, 2H), 7.08 (s, 2H), 5.61 (s, 1H), 5.53 (s, 1H), 5.52 (s, 1H), 1.54-1.61 (m, 72H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 185.13, 157.72, 154.55, 154.16, 152.45, 147.86, 145.71, 145.50, 144.78, 144.11, 143.62, 143.05, 141.58, 140.39, 138.82, 135.21, 135.05, 135.00, 134.81, 134.74, 134.46, 133.94, 133.72, 131.93, 131.16, 131.11, 131.00, 130.80, 129.39, 129.04, 128.85, 124.64, 124.00, 122.78, 122.38, 121.51, 114.23, 113.70, 107.87, 65.00, 35.87, 34.75, 30.75, 29.92, 29.49 ppm. FT-IR(ATR): v = 3632 (m, O-H str.), 2954 (s), 2921 (m), 2869 (m), 2234 (w, C=N str), 1723 (w), 1669 (w), 1629 (s), 1578 (w), 1545 (w), 1696 (w), 1482 (w), 1455 (w), 1433 (s), 1407 (m), 1391 (w), 1384 (w), 1354 (s), 1320 (m), 1234 (m), 1221 (s), 1201 (w), 1174 (w), 1151 (m), 1131 (s), 1121 (s), 1074 (m), 1011 (m), 958 (w), 934 (m), 920 (w), 888 (w), 856 (w), 822 (w), 799 (m), 781 (w), 722 (w), 757 (w), 740 (w), 722 (m), 714 (m), 692 (w), 682 (w), 656 (w), and 633 cm⁻¹. HRMS (ESI-TOF-MS, CH₂Cl₂); calculated for [C₈₃H₉₀O₄N₁₀Ni]⁺ = 1348.6495, found m/z = 1348.6445.



1-ox: UV/Vis (CH₂Cl₂): λ (ϵ / M⁻¹cm⁻¹) = 411 (62,000), 472 (42,600), 514 (47100), 568 (36700), 741 (48,200), 883 (6,500) nm. ¹H NMR (400 MHz, CDCl₃, 328 K): δ = 7.72 (s, 2H), 7.57 (s, 2H), 7.45 (s, 1H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.34 (s, 2H), 6.86 (d, *J* = 4.6 Hz, 1H), 6.80 (d, *J* = 4.1 Hz, 1H), 6.64-6.69 (m, 3H), 6.62 (s, 2H), 5.50 (s, 1H), 1.50 (s, 18H), 1.33 (s, 18H), 1.29 (s, 36H) ppm. ¹³C NMR (101 MHz, CDCl₃, 328 K): δ = 187.42, 187.19, 184.22, 159.33, 155.70, 155.04, 153.13, 152.86, 151.88, 149.66, 149.57, 149.35, 147.02, 140.87, 139.46, 136.67, 135.68, 134.41, 134.28, 134.11, 133.60, 133.35, 132.83, 131.51, 129.41, 128.70, 127.97, 127.13, 127.07, 124.62, 124.35, 123.84, 122.75, 119.05, 113.93, 113.43, 63.14, 36.16, 35.92, 34.66, 30.52, 29.93, 29.79, 29.25 ppm. FT-IR(ATR): v = 3628 (w, O-H str.), 3181 (w), 3107 (w), 2953 (m), 2913 (m), 2867 (m), 2236 (w, C=N str.), 1672 (m), 1598 (s), 1574 (m), 1553 (m), 1521 (w), 1507 (w), 1483 (w), 1467 (w), 1453 (w), 1437 (w), 1405 (w), 1391 (w), 1360 (s), 1334 (m), 1321 (m), 1283 (m), 1256 (w), 1229 (w), 1217 (w), 1197 (m), 11667 (m), 1146 (w), 1123 (m), 1088 (w), 1063 (s), 1019 (s), 1001 (m), 957 (w), 928 (s), 893 (w), 881 (w), 859 (w), 833 (m), 817 (m), 794 (m), 779 (w), 756 (w), 740 (w), 725 (s), 709 (w), 694 (w), 665 (w), 651 (w), 631 (w), and 620.1(w) cm⁻¹. HRMS (ESI-TOF-MS, CH₂Cl₂); calculated for [C₈₃H₈₇O₄N₁₀Ni]⁻ = 1345.6260, found m/z = 1345.6270.



UV/Vis (CH₂Cl₂): 304 (λ_{max} , ε = 37000 M⁻¹cm⁻¹) nm, 353 (λ_{max} , ε = 39800 M⁻¹cm⁻¹) nm, 464 (λ_{max} , ε = 80100 M⁻¹cm⁻¹) nm, 580 (λ_{max} , ε = 33200 M⁻¹cm⁻¹), 634 (λ_{max} , ε = 38000 M⁻¹cm⁻¹) nm, and 754 (λ_{max} , ε = 3100 M⁻¹cm⁻¹) nm. ¹H NMR (400 MHz, THF-d8): δ = 7.72 (d, J = 4.6 Hz, 2H), 7.40 (s, 2H), 7.29 (s, 2H), 7.13 (d, J = 4.6 Hz, 1H), 7.06 (s, 2H), 6.90 (s, 1H), 6.88 (d, J = 4.6 Hz, 1H), 6.85 (s, 1H), 6.82 (s, 1H), 6.78 (d, J = 4.6 Hz, 1H), 6.65 (d, J = 4.6 Hz, 1H), 6.51 (s, 1H), 6.38 (q, J = 5.3 Hz, 2H), 1.49 (s, 18H), 1.47 (s, 18H), 1.40 (s, 18H), 1.34 (s, 9H), 1.30 (s, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 187.95, 176.47, 162.27, 159.21, 156.20, 155.90, 155.60, 153.93, 149.92, 149.81, 149.62, 149.52, 149.46, 148.22, 144.33, 141.71, 141.25, 140.56, 140.48, 139.75, 136.43, 135.91, 135.56, 135.36, 135.15, 135.05, 134.41, 132.26, 131.08, 129.20, 128.99, 128.13, 128.03, 127.84, 127.24, 126.82, 126.26, 125.91, 125.11, 124.34, 122.49, 120.60, 120.42, 114.49, 114.37, 36.13, 34.68, 34.63, 34.60, 30.49, 30.43, 30.21, 29.83 ppm. FT-IR(ATR): v = 3621.7 (m), 3203.6 (w), 2954.3 (s), 2912.2 (m), 2869.4 (m), 2236.8 (w), 1610.2 (m), 1560.0 (s), 152.9 (m), 1455.9 (m), 1436.2 (m), 1389.7 (w), 1360.9 (w), 1329.6 (s), 1316.5 (s), 1279.4 (m), 1251.2 (m), 1222.2 (m), 1157.4 (m), 1119.6 (w), 1076.2 (w), 1056.7 (w), 1024.5 (s), 946.5 (w), 950.0 (w), 930.0 (m), 888.0 (w), 858.5 (w), 836.3 (s), 779.7 (m), 756.4 (w), 742.9 (w), 727.4 (m), 713.5 (w), 690.4 (m), 664.9 (w), and 614.2 (w) cm⁻¹. HRMS (ESI-TOF-MS, CH₂Cl₂/CH₃OH); calculated for [C₈₃H₉₁O₅N₁₀Ni]⁺ = 1365.6527, found: m/z = 1365.6580.

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3.0 Additional Figures



Figure S1. X-ray crystal structure of **1**-ox. (a) Plan view shows the metalloporphyrin with fused N-heterocycle unit and spiro hemiquinonoid substituent. (b) Saddle structure of the macrocycle with almost orthogonal arrangement of the radical-bearing substituents at opposing meso positions of the porphyrin.



Figure S2. Dimer-1 unit of **1**-ox (see Fig. 1b main manuscript). (a) Dimer with solvating toluene molecules stacked at 5,6-dinitrile-pyrazine unit. (b) Edge-on view of intermolecular pi-pi stacking of **1**-ox. (c) Plan view of stacking interaction.



Figure S3. Dimer-2 unit of **1**-ox formed by interleaving of saddle-forms of the porphyrinoid unit (see Fig. 1c main manuscript).



Figure S4. How dimer units are arranged in the crystals of **1**-ox. Yellow ellipse highlights the π - π stacking dimer-1 unit. Blue circle highlights the dimer-2 unit involving saddle-saddle interleaving with Ni-O coordination.



Figure S5. X-ray crystal structure of **1**-ox viewed along a-axis. (a) Ball-and-stick representation. (b) Space-filling representation.



Figure S6. Ball-and-stick representations of the X-ray crystal structure of **1**-ox viewed along (a) b-axis, (b) c-axis.



Figure S7. X-ray crystal structure of **1**-ox viewed along a-axis (same as shown in Fig. 1g in the main manuscript).



Figure S8. Wall binding site of toluene molecules of solvation in **1**-ox. (a) For the toluene molecule in yellow, light yellow broken bonds denote hydrogen bonds with nitriles and a possible C-H... π interaction between its methyl group and the adjacent porphyrin unit. Important distances: methine (H(89)) C-H...N(9) (2.8872(1) Å), methyl (H85(C)) C-H...N(10) (3.1945(1) Å), methyl (H(85A)) C-H...C(68) (3.0171(3) Å). methyl (H(85B)) C-H...C(65) (3.1535(3) Å). Broken light green bond indicates closest approaches of the green toluene to the fused unit. Important distances (see (b)): C(201)...N(8) (3.3461(5) Å), C(203)...C(80) (3.4259(5) Å). (b) Stacking of toluene molecules in adjacent pores at the N-heterocycle component. (c) Space-filling depiction of the stack.



Figure S9. Wall binding site for water. Two water molecules occupy the hydrogen bonding sites of the yellow toluene molecule. Important distances (from left): N(10)...OW(2) (3.7303(1) Å), OW(2)...OW(1) (4.3160(1) Å). N(9)...OW(1) (3.8729(2) Å). Protons could not be located but these bond distances indicate C=N...H-O hydrogen bonds at N(9), N(10) and a mutual intervening hydrogen bonding between the water molecules.



Figure S10. Progression in the X-ray crystal structure measurements of **1**-ox. Arrows indicate the positions of solvating toluene. (a) Solvate containing approx. 3 molecules of toluene (one at the pore centroid is highly disordered, two are bound at the pore wall). (b) X-ray structure of a different crystal of **1**-ox containing predominantly 2 toluene solvent molecules. (c) X-ray crystal structure of **1**-ox (as in (a)) where the SQUEEZE routine has been applied during refinement. (d) X-ray crystal structure of **1**-ox containing 2 equivs. of water (protons could not be refined). (e) X-ray crystal structure of **1**-ox obtained at 200 K where any residual electron density due to solvent has been eliminated using the SQUEEZE routine in Platon.



Figure S11. Thermogravimetric analyses on samples of the toluene solvate of **1**-ox prior to (red trace) and following (black trace) drying in air.



Figure S12. (a) Nitrogen adsorption isotherms of **1**-ox obtained from a sample after slow evaporation of a solution in N,N-dimethylformamide. (b) Half pore widths of **1**-ox (DMF) obtained by using DFT methods. Inset shows well-defined micropore at 0.8 nm half pore width. (c) Nitrogen adsorption isotherm of a recrystallized sample of **1**-ox which had been stored in a vial under air under ambient conditions for a period of 12 months (subjected to the same specific surface area measurement technique as other samples). (d) Half pore widths of the sample in (c) revealing long term persistence of the micropore structure but with an increasing contribution from mesopores (S_{micro} = 557.4 m² g⁻¹; S_{meso} = 220.4 m² g⁻¹) compared to the initially isolated material.



Figure S13. Powder X-ray diffraction patterns for 1-ox. (a) Crystalline film of 1-ox obtained by slow evaporation of a solution (10 mg mL⁻¹) of 1-ox in *N*,*N*-dimethylformamide (red). (b) Partially air-dried crystals of 1-ox obtained by cooling a hot toluene solution (blue). (c) Polycrystalline 1-ox obtained by rotary evaporation of a solution in CH_2Cl_2 . (d) Powder pattern of 1-ox simulated from single crystal data. Correlation between spectra is poor indicating differences between the crystal structures of 1-ox obtained from different solvents. Surface area is lower in samples prepared from DMF but this solvent is preferred for the ink-jet printing deposition of the material onto the MSS sensor.



Figure S14. Electrochemical measurements on **1**-ox. (a) Spectroelectrochemical changes observed during the first reduction (V = -0.4 V). Note emergence of peaks due to **1**. Peak at 414 nm decreases in intensity and shifts to 406 nm; 473 nm intensity increases; 516, 579, 753, 900 nm decrease in intensity; new peak emerges at 616 nm. (b) Differential pulsed voltammetry of **1**-ox revealing three reduction peaks assigned to reduction to its precursor structures shown in (c). An additional oxidation peak at 1.21 V occurs at characteristic potential for oxidation 2,6-di-t-butylphenyl moieties presumably due to oxidation involving the remaining phenol meso-substituent. (c) Chemical structures of species obtained by consecutive reductions at -0.34 V (to **1**), -0.88 V (to **Ni-benzimd**) and -1.56 V (species provisionally assigned as being due to reduction of the N-heterocyclic β -substituent although reduction of Ni(II) to Ni(I) might also occur in this region).



Figure S15. Mechanism of the conversion of **1**-ox to **2** in the presence of TBAF. Hydroxide anions formed by the reaction of fluoride with adventitious water undergo nucleophilic substitution at the meso position adjacent to the spiro-linkage leading to ring opening thus completing the transfer of the 3,5-di-t-butyl-4-hydroxyphenyl substituent from meso position to benzimidazole N atom. Aqueous work-up leads to neutralization of phenoxide to phenol with subsequent protic keto-enol tautomerization of the opposing hydroxyl substituents to their adjacent positions as revealed by the crystal structure of **2** (see Figure 5, main manuscript).



Figure S16. Nitrogen adsorption isotherm of 2. Total surface area based on DFT and Barrett-Joyner-Halenda analyses: $21.2 \text{ m}^2 \text{ g}^{-1}$.



Figure S17. (a) Typical sensing responses of receptor layer **1** and MSS measured at room temperature (25 °C). (b) Relative signal strength of different vapors. The responses for acetone, alcohols and ethyl acetate have approx. 4-fold weaker MSS signal outputs than **1**-ox@MSS.

4.0 Chemical analytical data



Figure S18. ¹H NMR spectrum of 2-(5,6-dicyano-1H-imidazo[4,5-b]pyrazin-2-yl)-tetrakis(3,5-di-*t*-butyl-4-hydroxy phenyl)porphinatonickel(II), **Ni-BenzImd** in CDCl₃. Upper panel: full spectrum. Lower panel: expansion of the low field region.



Figure S19. D₂O shake disclosing exchangeable protons in **Ni-BenzImd**. ¹H NMR spectra of 2-(5,6-dicyano-1H-imidazo[4,5-b]pyrazin-2-yl)-tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)porphinatonick el(n), **Ni-BenzImd** in CDCl₃ (a) in the presence of D₂O, (b) without D₂O.



Figure S20. ¹³C NMR spectrum of 2-(5,6-dicyano-1H-imidazo[4,5-b]pyrazin-2-yl)-Tetrakis(3,5-di*t*-butyl-4-hydroxy phenyl)porphinatonickel(II), **Ni-BenzImd** in CDCl₃



Figure S21. ESI-TOF-MS spectrum of 2-(5,6-dicyano-1H-imidazo[4,5-b]pyrazin-2-yl)-Tetrakis(3,5-di-*t*-butyl-4-hydroxy phenyl)porphinatonickel(II), **Ni-BenzImd**.



Figure S22. Electronic absorption spectrum of 2-(5,6-dicyano-1H-imidazo[4,5-b]pyrazin-2-yl)-Tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl) porphinatonickel(II), **Ni-BenzImd** in CH₂Cl₂



Figure S23. ¹H NMR spectrum of **1** in CDCl₃. Upper panel: full spectrum. Lower panel: expansion of the low field region.



Figure S24. D₂O shake disclosing exchangeable protons in **1**. ¹H NMR spectra of **1** in CDCl₃ (a) in the presence of D₂O, (b) without D₂O.



Figure S25. ¹³C NMR spectrum of 1 in CDCl₃.



Figure S26. ESI-TOF-MS spectrum of 1



Figure S27. Electronic absorption spectrum of $\mathbf{1}$ in CH_2Cl_2



Figure S28. ¹H NMR spectrum of 1-ox in CDCl₃ at 55 °C. Lower panel: expansion of the low field region.



Figure S29. D₂O shake disclosing exchangeable protons in 1-ox. ¹H NMR spectra of 1-ox in CDCl₃ (a) in the presence of D₂O, (b) without D₂O.



Figure S30. ¹³C NMR spectrum of 1-ox in CDCl₃.



Figure S31. ESI-TOF-MS spectrum of 1-ox



Figure S32. Electronic absorption spectrum of 1-ox in CH₂Cl₂







Figure S34. D₂O shake disclosing exchangeable protons in **2**. ¹H NMR spectra of **2** in CDCl₃ (a) in the presence of D₂O, (b) without D₂O.



Figure S35. ¹³C NMR spectrum of 2 in CDCl₃.



Figure S36. ESI-TOF-MS spectrum of 2.



Figure S37. Electronic absorption spectrum of 2 in CH₂Cl₂.

5.0 References

S1. Chahal, M. K., Labuta, J., Březina, V., Karr, P. A., Matsushita, Y., Webre, W. A., Payne, D. T., Ariga, K., D'Souza F., Hill, J. P. Knock-on synthesis of tritopic calix[4]pyrrole host for enhanced anion interactions. *Dalton Trans.* **2019**, *48*, 15583–15596.

S2. Chahal, M. K.; Liyanage, A.; Alsaleh, A. Z.; Karr, P. A.; Hill, J. P.; D'Souza, F. Anion-enhanced excited state charge separation in a spiro-locked N-heterocycle-fused push-pull zinc porphyrin. *Chem. Sci.* **2021**, *12*, 4925–4930.

S3. CrystalClear (Rigaku Corporation, Tokyo, 2005).

S4. Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst.* **A71**, 3–8 (2015).

S5. Sheldrick, G. M. A short history of SHELX. Acta Cryst. A64, 112–122 (2008).

S6. Farrugia, L. J. WinGX suite for small-molecule single-crystal crystallography. J. Appl. Cryst.

32, 837–838 (1999).