Electronic Supplementary Information

Antioxidant-substituted Tetrapyrazinoporphyrazine as a Turn-on Fluorescence Sensor for Basic Anions

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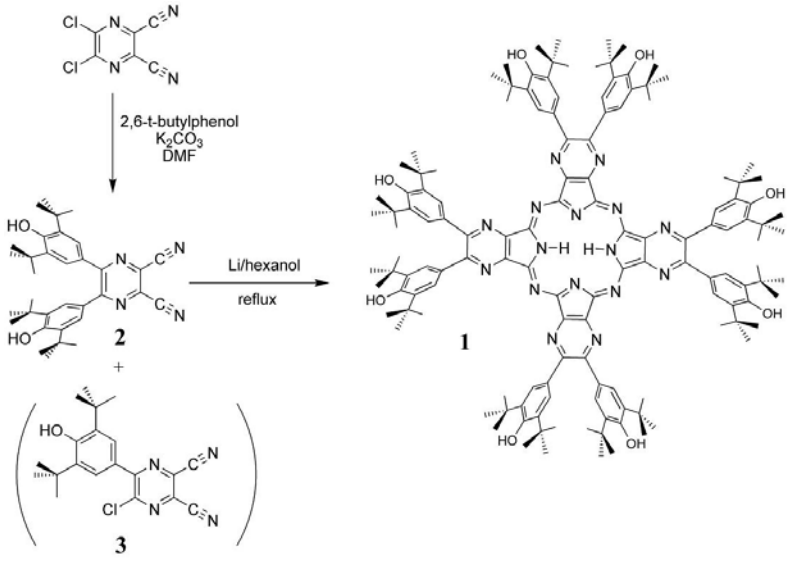
Contents.

1.0. General. Solvents and reagents were obtained from Aldrich Chemical Co., Fischer Chemical Co., Wako Chemical Co., Tokyo Kasei Chemical Co. or Kanto Chemical Co. ^{1}H and ^{13}C NMR spectra were measured at 298 K from $CDCl_3$ or $CDCl_3/d_6$-DMSO solutions of the samples using a JEOL model AL300BX spectrometer with tetramethylsilane as internal standard. Electronic absorption spectra were measured from dichloromethane solutions of the samples using a Shimadzu model UV-3600 UV/Vis/NIR spectrophotometer. FTIR spectra were measured from samples cast on a barium fluoride disc using a Nicolet model 760X FTIR spectrometer. Matrix–assisted laser desorption/ionization time–of–flight mass spectra (MALDI–TOF–MS) were measured using a Shimadzu-Kratos model Axima CFR+ mass spectrometer with dithranol as matrix. Scanning tunneling microscopy (STM) was performed using an Omicron UHV STM. Samples were prepared by dropping a chloroform solution of **1** (10^{-9} M) onto a gold substrate [Au(111)] and allowing it to evaporate. The sample/substrate was dried in vacuo prior to insertion in the STM vacuum chamber.

2.0. Synthesis



Scheme S1. Synthesis of **1**, **2** and **3**.

5,6-Bis(3,5-di-t-butyl-4-hydroxyphenyl)pyrazine-2,3-dicarbonitrile, 2.

5,6-Dichloro-2,3-dicyanopyrazine (1 g, 0.005 mol) and 2,6-di-t-butylphenol (2.5 eq., 2.6 g) were dissolved in N,N-dimethylformamide (50 mL) and the mixture heated to 60 °C. Potassium carbonate (3 g) was gradually added and the suspension heated at 60 °C for 6 hours. The resulting solution was cooled to room temperature, poured into water (100 mL) then extracted with dichloromethane (100 mL × 3). The combined organic fractions were dried (anhydrous Na_2SO_4) then the solvents removed under reduced pressure. The residue was purified by column chromatography on silica eluting with dichloromethane:hexane (40%:60%). Yield: 1.81 g, 67% based on 5,6-dichloro-2,3-dicyanopyrazine. UV/Vis (CH_2Cl_2): λ_{max} = 262, 340, 393 nm. ^{1}H-NMR ($CDCl_3$, 25 °C, 300 MHz): δ = 7.35 (s, 4H, Ar-H), 5.54 (s, 2H, phenolic-H), 1.32 (s, 36H, *t*-butyl-H) ppm. ^{13}C-NMR ($CDCl_3$: 25 °C, 300 MHz): δ = 30.03, 34.33, 113.65, 124.91, 126.95, 128.60, 136.51, 156.17, 156.34 ppm. FT-IR (BaF_2): ν = 775.84(w), 810.07(w), 887.78(w), 902.61(m), 1024.09(w), 1122.90(m), 1153.31(m), 1207.53(m), 1218.59(m), 1239.90(m), 1254.08(m), 1289.69(w), 1322.59(m), 1370.70(s), 1384.35(m), 1425.01(w), 1443.67(w), 1458.28(w), 1510.70(w), 1596.10(m), 2236.86(w), 2872.98(m), 2950.63(s), 3010.39(w), 3601.95(s) cm^{-1}. MALDI-TOF-MS (dithranol): calcd. for $C_{34}H_{43}N_4O_2$ [M + H]$^+$: 539.33; found: 539.55.

5-Chloro-6-(3,5-di-t-butyl-4-hydroxyphenyl)pyrazine-2,3-dicarbonitrile (**3**) can be a major byproduct of the synthesis of 5,6-bis(3,5-di-t-butyl-4-hydroxyphenyl) pyrazine-2,3-dicarbonitrile reaction when not sufficient time is allowed for completion of the reaction. ^{1}H-NMR ($CDCl_3$, 25 °C, 300 MHz): δ = 1.49 (s, 18H, *t*-butyl-H), 5.82 (s, 1H, phenolic-H), 7.84 (s, 2H, Ar-H) ppm. ^{13}C-NMR ($CDCl_3$: 25 °C, 300 MHz): δ = 30.10, 34.51, 112.23, 112.53, 123.76, 127.69, 127.81, 130.55, 136.52, 149.25, 157.01, 157.99 ppm. FT-IR (BaF_2): ν = 865.02(w), 887.53(w), 895.16(w), 913.05(w), 990.11(w), 1024.79(w), 1105.33(m), 1121.80(m), 1132.04(m), 1146.27(m), 1206.63(m), 1240.40(m), 1272.07(m), 1280.85(m), 1293.42(w), 1307.48(w), 1337.28(m), 1376.84(s), 1405.18(w), 1419.21(w), 1456.52(w), 1492.20(w), 1513.01(m), 1590.30(m), 2240.75(w), 2874.77(m), 2920.23(m), 2962.51(s), 3590.47(s) cm^{-1}. MALDI-TOF-MS (dithranol): calcd. for $C_{20}H_{21}ClN_4O$ $[M]^+$: 368.14 ; found: 368.17.

2,3,9,10,16,17,23,24-Octakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-tetrapyrazinoporphyrazine (1). 1 was prepared according to a literature method[1a,b] using 1-hexanol as the solvent. Samples of **1** are usually contaminated with the mono-hexyloxy-substituted product that could not be removed. UV/Vis (CH_2Cl_2): λ_{max} = 330, 384, 526, 596, 620, 648, 676 nm. ^{1}H-NMR ($CDCl_3$, 25 °C, 300 MHz): δ = –0.663 (br. s. 2H, NH), 1.49 (s, 144H, *t*-butyl-H), 5.44 (s, 8H, phenolic-H), 7.84 (s, 16H, Ar-H) ppm. ^{13}C-NMR ($CDCl_3$:

25 °C, 300 MHz): δ = 30.51, 34.57, 127.26, 128.07, 130.86, 136.22, 146.00, 155.13, 157.80 ppm. FT-IR (BaF_2): ν = 760.35(w), 772.14(w), 810.08(w), 866.91(w), 890.54(w), 1004.25(w), 1023.76(w), 1096.90(w), 1121.21(m), 1121.61(w), 1153.28(m), 1203.88(w), 1224.59(s), 1237.85(s), 1255.61(m), 1289.74(w), 1320.81(w), 1356.35(s), 1392.01(w), 1399.94(w), 1433.60(w), 1458.33(w), 1464.94(w), 1536.66(w), 1599.57(w), 1632.61(m), 1727.53(w), 1737.20(w), 2872.16(m), 2955.00(s), 3000.66(w) 3297.88(w), 3640.36(m) cm^{-1}. MALDI-TOF-MS (dithranol): calcd. for $C_{136}H_{170}N_{16}O_8$ $[M + 6H]^+$: 2161.38; found: 2161.29.

Non-phenolic control compounds.

5,6-Diphenylpyrazine-2,3-dicarbonitrile[2] was synthesized according to the method used by Ohta et al.[3] UV/Vis (CH_2Cl_2): λ_{max} = nm. ^{1}H-NMR ($CDCl_3$, 25 °C, 300 MHz): δ = 7.36 (t, 4H, ^3J = 7.4 Hz, phenyl *meta*-H), 7.46 (t, 2H, ^3J = 7.3 Hz, phenyl *para*-H), 7.53 (d, 4H, ^3J = 7.5 Hz, phenyl *ortho*-H ppm. ^{13}C-NMR ($CDCl_3$: 25 °C, 300 MHz): δ = 113.13, 128.86, 129.86, 131.15, 135.34, 155.39 ppm.

2,3,9,10,16,17,23,24-Octaphenyltetrapyrazinoporphyrazine, 1, was synthesized from 5,6-diphenylpyrazine-2,3-dicarbonitrile using literature methods.[1,4]

3.0. X-ray crystallography

Crystals of **2** suitable for X-ray diffraction were grown by refrigerating a dichloromethane/hexane (40:60) solution of **2** at – 20 °C. Crystals of **3** were grown by slow evaporation of a dichloromethane solution. X-ray data for **2** and **3** were collected at 180 K on a Bruker SMART APEX diffractometer using graphite-monochromated MoKα radiation. Structure solutions by direct methods and full-matrix least-squares refinement against F^2 (all data) were carried out using the SHELXTL package.[5] All ordered non-H atoms were refined anisotropically. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 864529 & 864530. 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/cgi-bin/catreq.cgi, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

X-ray Crystallography data for **2**: $C_{34}H_{42}N_4O_2$, M = 538.72 g/mol, space group P 43 21 2, a = 15.9922(12), b = 15.9922(12), c = 12.4393(19) Å, α = 90.00°, V = 3181.36(59) $Å^3$, Z = 4, ρ_{calcd} = 1.125 mg/m^3, $\mu(MoK_\alpha)$ = 0.070 mm^{-1}, 25867 reflections measured, 1997 were unique (Rint. 0.0271); refinement against F2 to wR2:

0.1176, R1 = 0.0473 (1855 reflections with I>2σ(I)), goodness of fit S = 1.074, 193 parameters.

X-ray Crystallography data for **3**: $C_{20}H_{21}ClN_4O$, M = 368.86 g/mol, space group P 2(1)/m, a = 10.639(5), b = 6.969(3), c = 13.260(6) Å, α = γ = 90.00°, β = 109.394(7)°, V = 927.3(7) $Å^3$, Z = 2, ρ_{calcd} = 1.321 mg/m^3, μ(MoK_α) = 0.070 mm^{-1}, 7235 reflections measured, 2040 were unique (Rint. 0.0289); refinement against F2 to wR2: 0.1290, R1 = 0.0499 (1574 reflections with I>2σ(I)), goodness of fit S = 1.027, 155 parameters, 1 restraint.

3.1. Crystal structure of 2

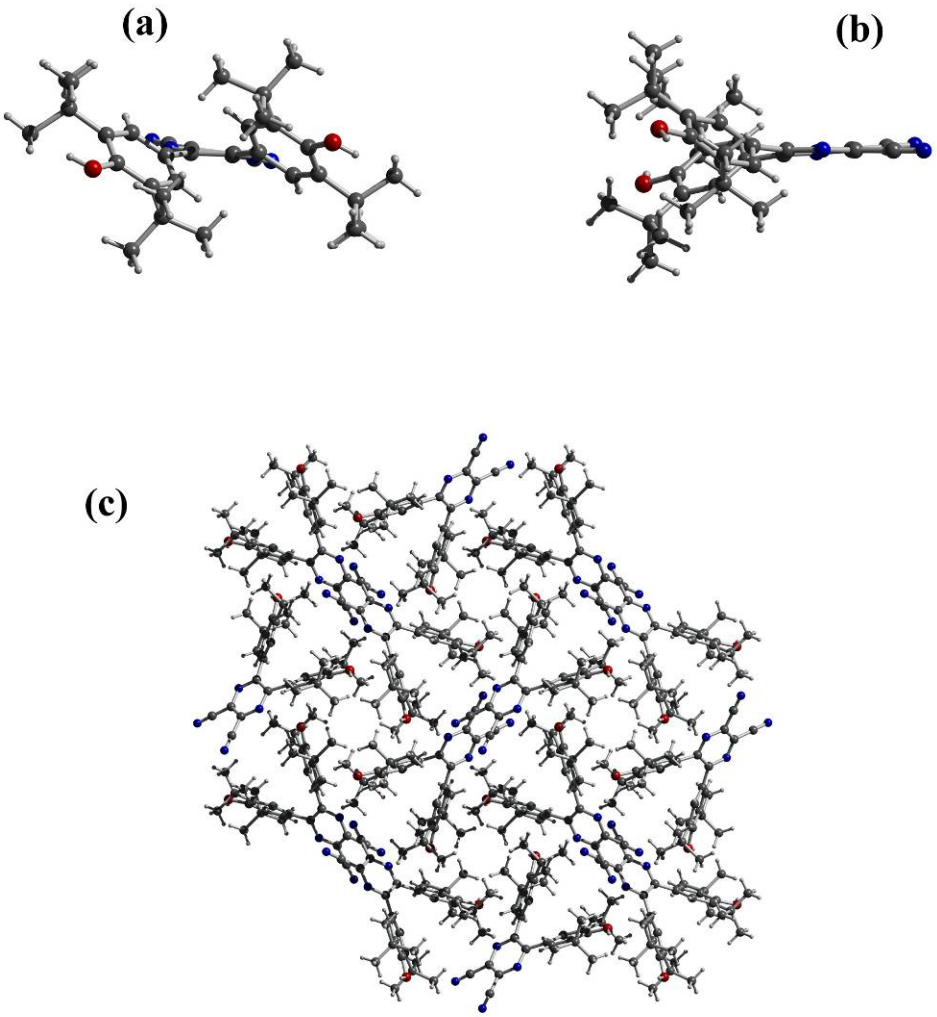


Figure S1. X-ray crystal structure of 5,6-Bis(3,5-di-t-butyl-4-hydroxyphenyl) pyrazine-2,3-dicarbonitrile **2**. (a) View showing the non-coplanarity of the phenyl substituents. (b) Viewed edge-on. The pyrazine-2,3-dicarbonitrile unit is slightly distorted from planarity. (c) Packing diagram of **2** viewed along the *c*-axis.

3.2. Crystal structure of 3

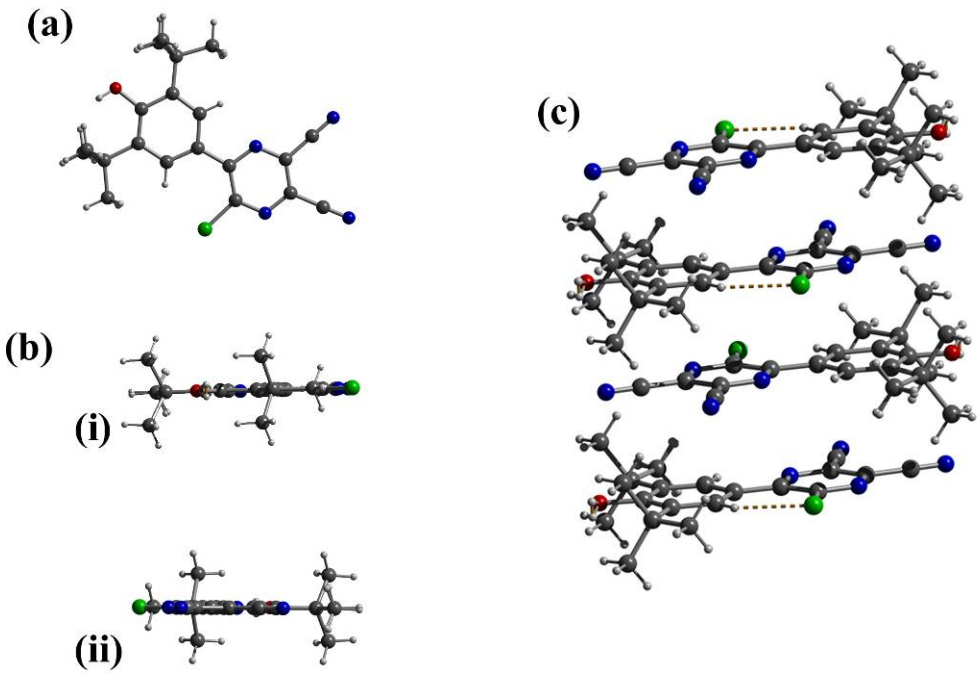


Figure S2. X-ray crystal structure of 5-Chloro-6-(3,5-di-t-butyl-4-hydroxyphenyl) pyrazine-2,3-dicarbonitrile, **3**. (a) Single molecule 3. An intramolecular H-bonding interaction between 5-chloro atom and phenyl substituent leads to coplanarity of the two six-membered rings. (b) Edge-on views of **3** emphasizing the coplanarity: (i) viewed remote from nitrile groups; (ii) viewed from the direction of the nitrile groups. (c) A stack of **3** within the structure where directions of the molecular long axes alternate. Stacking is made possible by the H-bonding induced coplanarity of **3**.

4.0. Molecular model and STM image of 1.

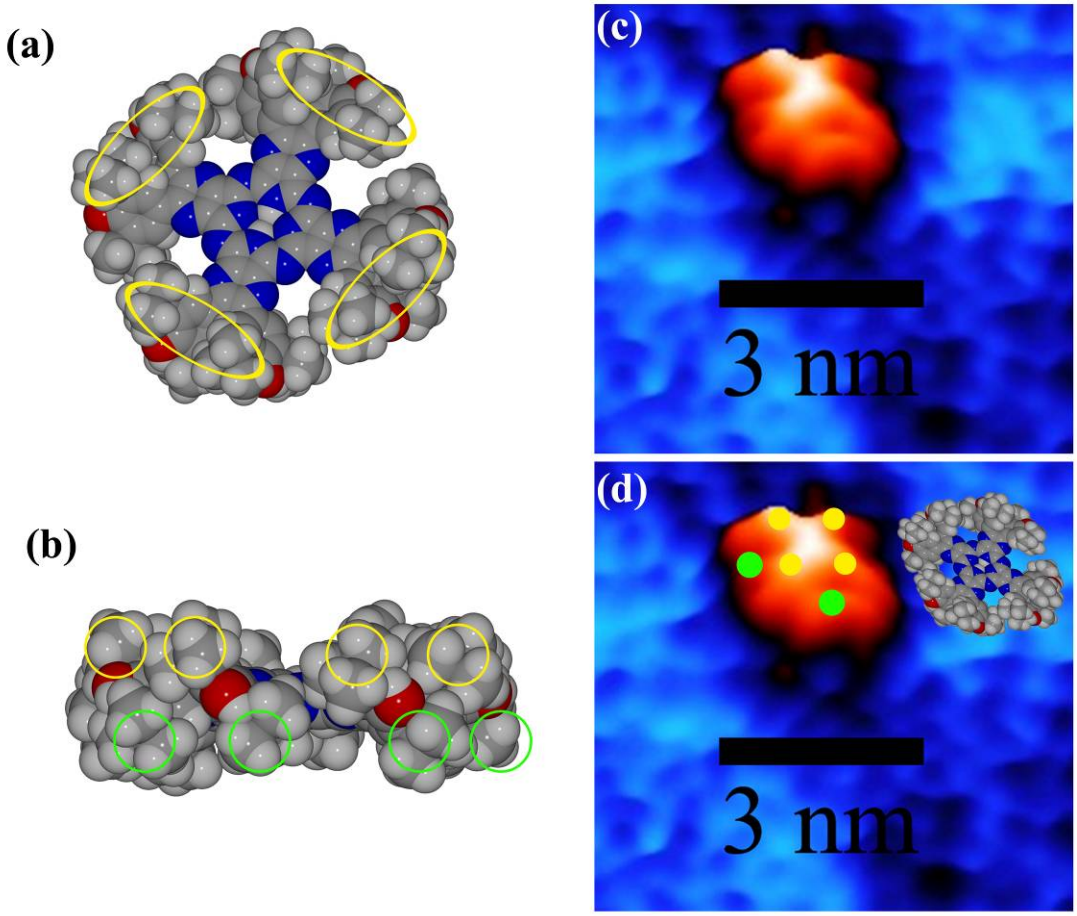


Figure S3. Molecular model of **1** and STM image. (a) Energy minimized structure of **1** (MM2, generated using the Chemdraw3D program). Yellow ellipses indicate the positions oft-butyl groups at the upper rim of the molecule. (b) Edge view of **1** with 'upper' and 'lower' t-butyl groups indicated. (c,d) STM image of **1**. In (d) positions of each type of t-butyl groups are indicated by spots of the same colour as given in (b). A model structure of **1** is also shown in (c) illustrating its approximate positioning.

5.0. Control spectroscopic data for non-phenol derivatives 5,6-Diphenylpyrazine-2,3-dicarbonitrile and 2,3,9,10,16,17,23,24-Octaphenyltetra pyrazinoporphyrazine.

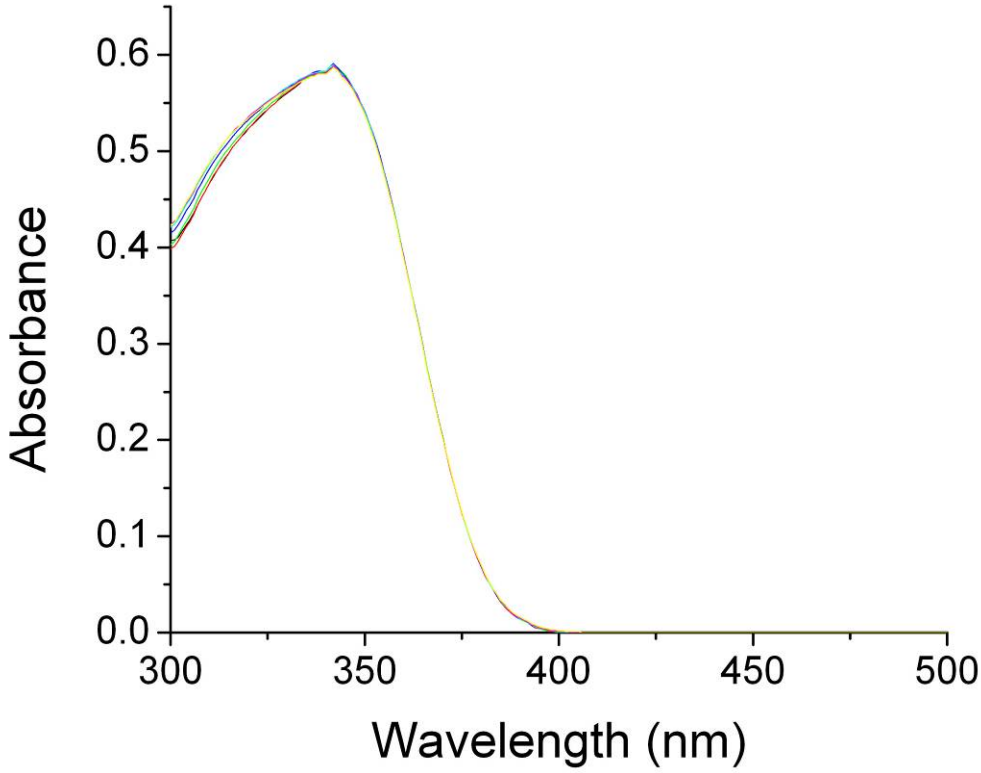


Figure S4. Electronic absorption spectra of 5,6-diphenylpyrazine-2,3-dicarbonitrile in benzonitrile containing increasing amounts of fluoride anion. Almost no variation is observed at any concentration of fluoride anions.

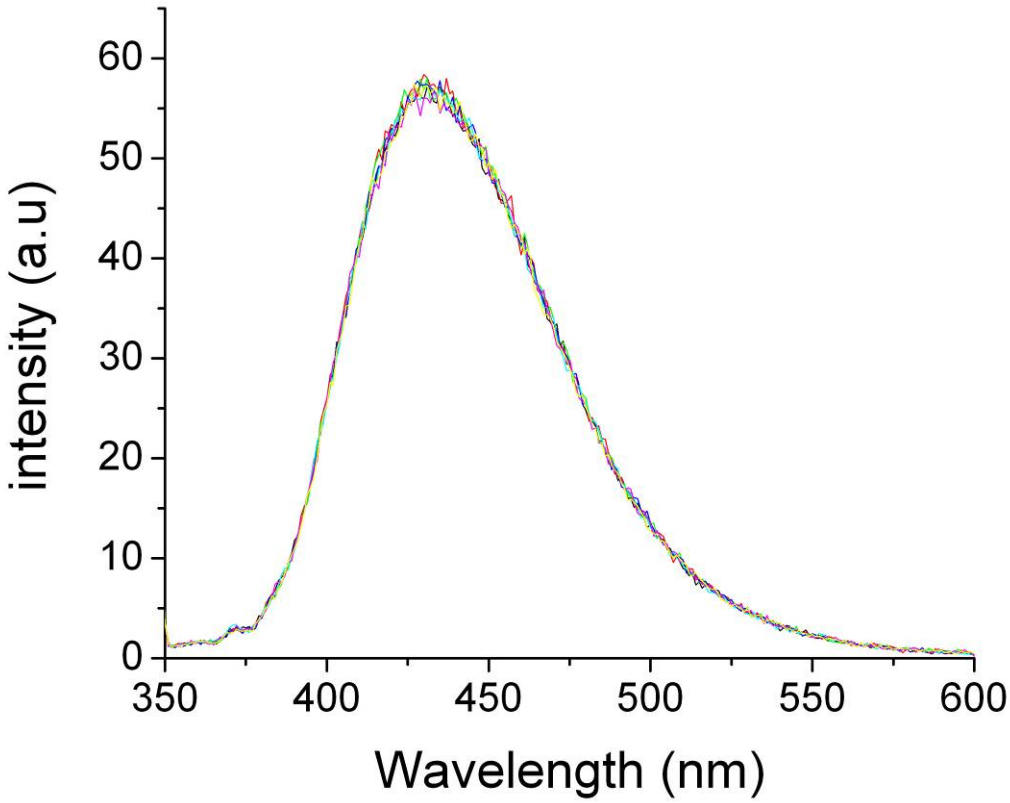


Figure S5. Fluorescence emission (excitation wavelength: 344 nm) spectra of 5,6-diphenylpyrazine-2,3-dicarbonitrile in benzonitrile containing increasing amounts of fluoride anion. Almost no variation is observed at any concentration of fluoride anions.

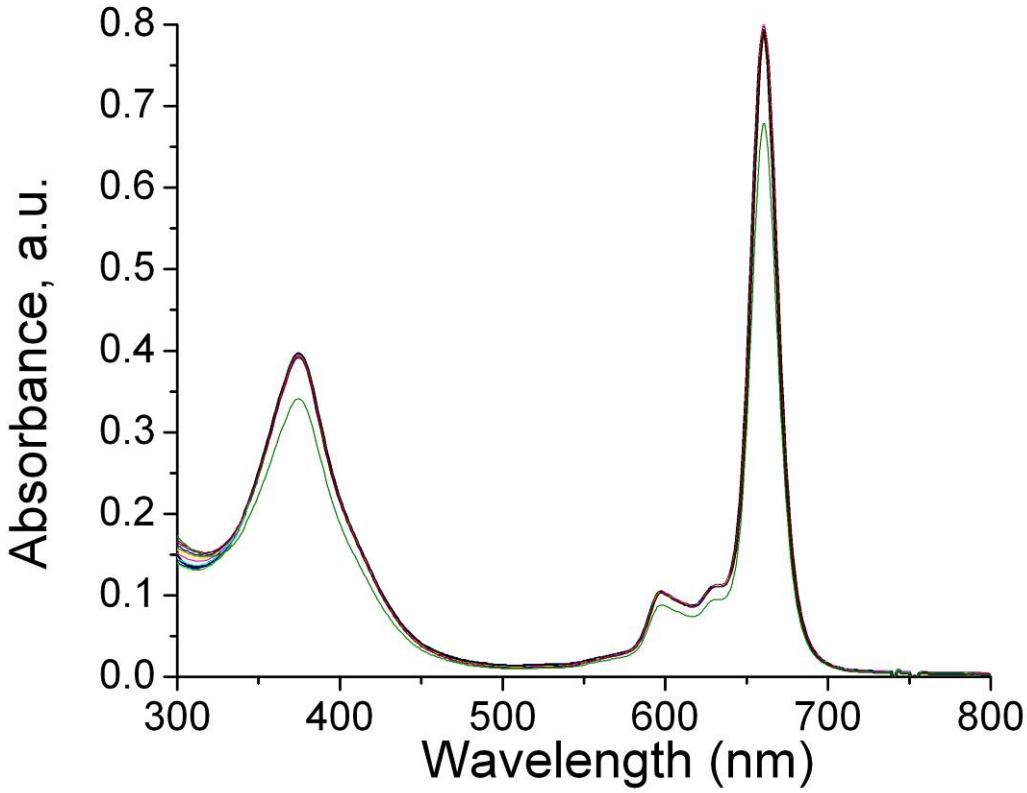


Figure S6. Electronic absorption spectra of 2,3,9,10,16,17,23,24-octaphenyl tetrapyrazinoporphyrazine in benzonitrile containing increasing amounts of fluoride anion. Almost no variation is observed at any concentration of fluoride anions.

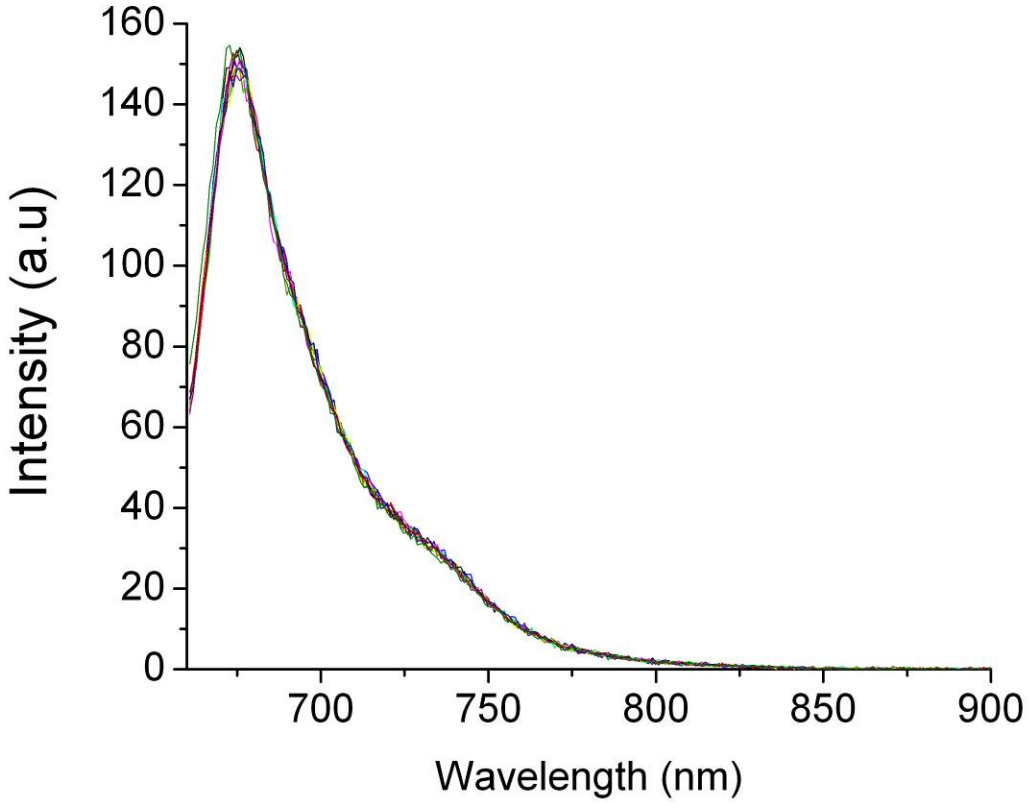


Figure S7. Fluorescence emission (excitation wavelength: 660 nm) spectra of 2,3,9,10,16,17,23,24-octaphenyl tetrapyrazinoporphyrazine in benzonitrile containing increasing amounts of fluoride anion. Almost no variation is observed at any concentration of fluoride anions.

6.0. UV/Vis titrations with other anions.

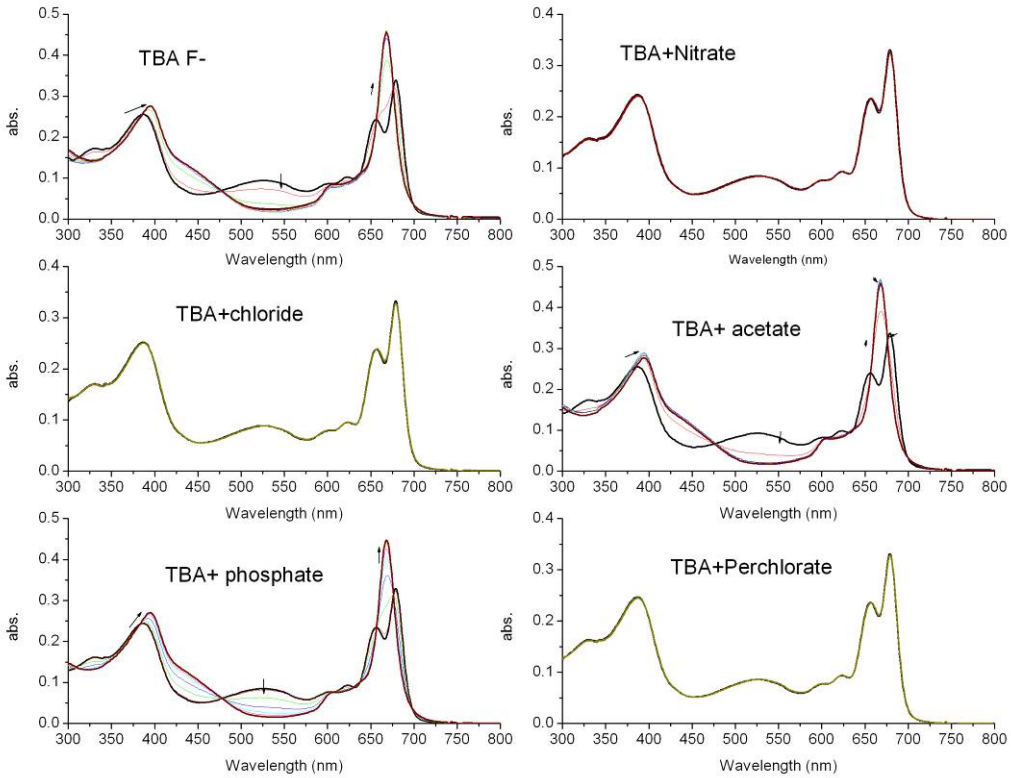


Figure S8. Changes in electronic absorption spectra during titration of solutions of **1** in benzonitrile with the indicated anions.

7.0. Fluorescence emission titrations with other anions.

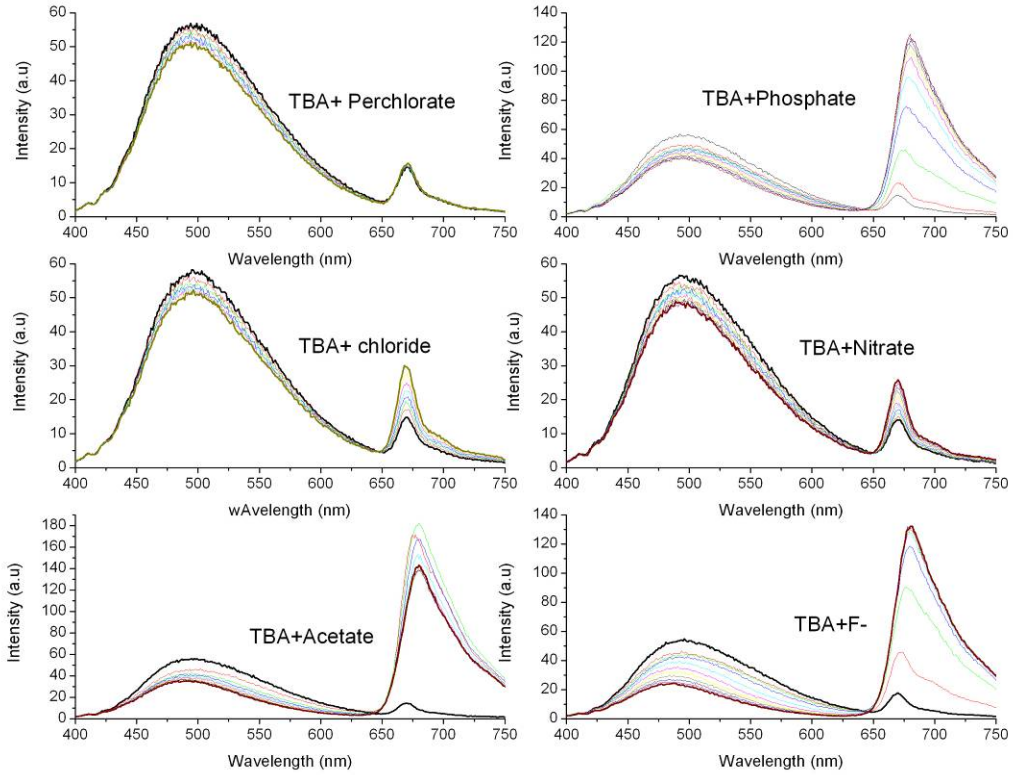


Figure S9. Changes in fluorescence emission spectra during titration of solutions of **1** in benzonitrile with the indicated anions.

8.0 Cyclic voltammetry of compound 2.

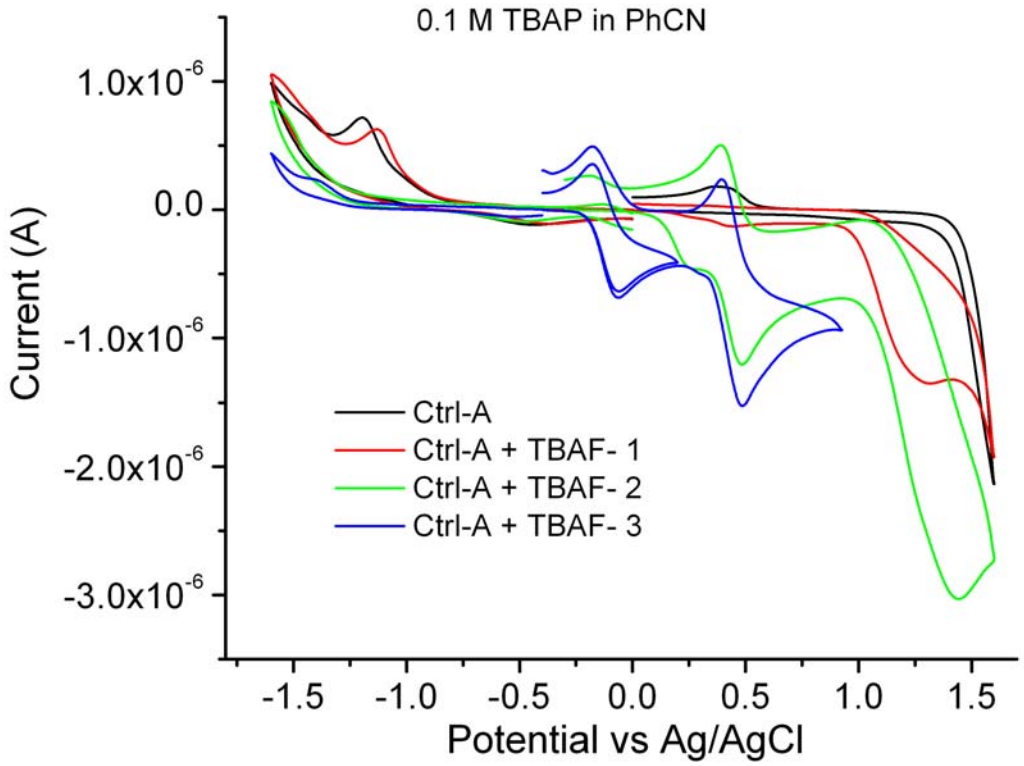


Figure S10. Cyclic voltammograms of **2** revealing eventual emergence of two reversible oxidations in the presence of fluoride anions probably due to oxidation to a quinonoid state.

9.0. References

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