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Electronic Supplementary Information (ESI)

Hydrophilic and Hydrophobic Carboxamide Pincers as Anion Hosts

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Table of Contents

S1 Materials and instrumentation

S1.1 Materials

All reagents, chemicals and deuterated solvents were purchased from commercial suppliers and used as such without further purification.

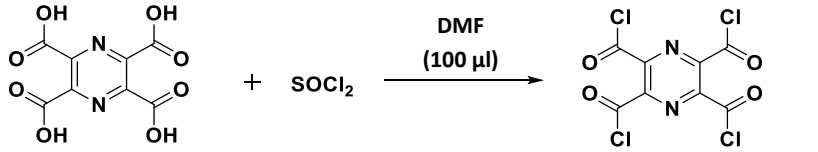
S1.2 Instrumentation

All NMR spectra were recorded at 25°C and referenced according to the deutatred solvents. 1D ^{1}H NMRs spectra were recorded on Bruker AVIIIHD 400 MHz spectrometer. ^{13}C and 2D NMR spectra were recorded in Avance AVIII 500 MHz spectrometer. HREIMS+ was recorded in Waters Micromass LCT Premier spectrometer.

S2 Synthesis and characterization of ligands

Synthesis

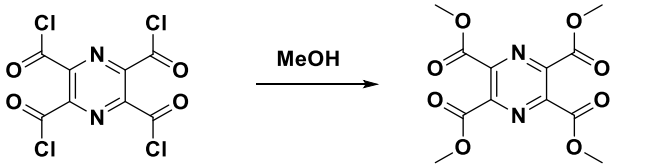
S2.1 Pyrazine-2,3,5,6-tetracarbonyl tetrachloride:



Pyrazine-2,3,5,6-tetracarbonyl tetrachloride

A suspension of pyrazine-2,3,5,6-tetracarboxylic acid (6.0 g, 23.44 mmol) in thionyl chloride (50 mL, 695 mmol) and a catalytic amount (100 µL)) of DMF were heated at reflux temperature for 10 hours and a clear solution was observed. Excess thionyl chloride was distilled off under reduced pressure to furnish pyrazine-2,3,5,6-tetracarbonyl tetrachloride as a white solid, which was kept under sealed condition and used without purification to prepare the methyl ester.

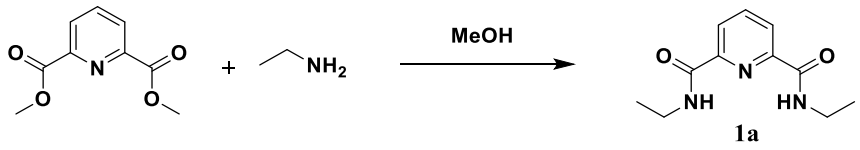
S2.2 Tetramethyl pyrazine-2,3,5,6-tetracarboxylate:



Tetramethyl pyrazine-2,3,5,6-tetracarboxylate

A cooled solution of methanol (200 mL) was slowly added to the above white solid and stirred at room temperature for one hour. The resulting white solid was filtered and washed with methanol to provide the crude product which was further purified by column chromatography on silica (230-400 mesh) using eluent DCM to MeOH:DCM (0.5:9.5). The white crystalline tetramethylpyrazine-2,3,5,6-tetracarboxylate product (2.2 g, yield 30%) was obtained. *^{1}H NMR (400 MHz, DMSO-d_6, ppm)*: δ = 3.96 (s, 12H, OC*H*$_3$). *^{13}C NMR (125 MHz, DMSO-d_6)*, δ = 163.23 (*CO*), 144.23 (Ar), 53.64 (O*C*H$_3$). Exact mass for $[C_{12}H_{12}N_2O_8+Na]^+$ 335.0486, found (HREIMS+) 335.0515.

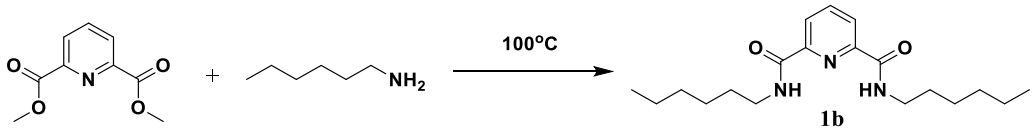
S2.3 N,N-diethylpyridine-2,6-dicarboxamide,[S1] 1a:



1a

A slightly modified procedure compared to that previously published[S1] was used. Dimethyl 2,6-pyridinedicarboxylate (0.31 g, 1.57 mmol) was added to a sealed tube with 10 mL of methanol. A 2M solution of ethylamine (in THF) was added (3.14 mL, 6.28 mmol) to the reaction vessel, which was then sealed and stirred at 60°C for 1 days. Solvent was removed under reduced pressure and recrystallized with ether to yield a white solid of **1a** (0.32 g, yield 92%). *^{1}H NMR (400 MHz, DMSO-d_6)*: δ = 9.33 (t, *J* = 6.0 Hz, 2H, *NH*), 8.19-8.12 (m, 3H, *Ar*), 3.40 (quint, 4H, *J* = 7.0 Hz, NH-*CH*$_2$-CH$_3$), 1.18 (t, *J* = 6.0 Hz, 6H, NH-CH$_2$-*CH*$_3$). *^{13}C NMR (125 MHz, DMSO-d_6)*: δ = 162.83 (CO), 148.80 (Ar), 139.41 (Ar), 124.05 (Ar), 33.64 (NH-*C*H$_2$-CH$_3$), 15.15 (NH-CH$_2$-*C*H$_3$). Exact mass for $[C_{11}H_{15}N_3O_2+Na]^+$ 244.1056, found (HREIMS+) 244.0305.

S2.4 N,N-dihexylpyridine-2,6-dicarboxamide, 1b:[S2]

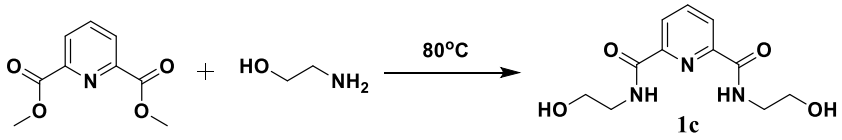


1b

A modified procedure compared to that previously published[S2] was used. Dimethyl pyridine-2,6-dicarboxylate (0.5 g, 2.6 mmol) was dissolved in 10 mL MeOH followed by addition of hexylamine (1.35 mL, 10.25 mmol) and heated at 80°C for 24 hours. The reaction mixture was concentrated under reduced pressure and recrystallized with CH$_3$CN:MeOH (4:1) to furnish white fluffy solid of **1b** (0.5 g, yield 58%). *^{1}H NMR (400 MHz, DMSO-d_6)*: δ = 9.30 (t, *J* = 6.1 Hz, 2H, *NH*), 8.20-8.14 (m, 3H, ArH), 3.36 (q, *J* = 5.3 Hz, 4H, N-*CH*$_2$), 1.58 (quint, *J* = 7.3 Hz, 4H, NCH$_2$-

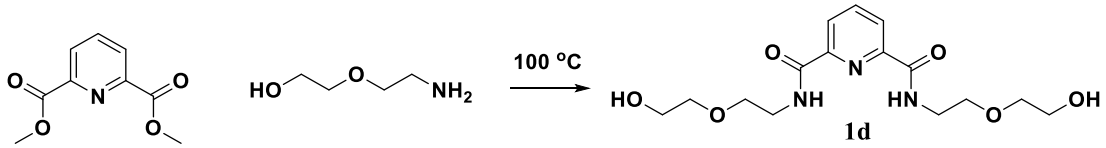
CH₂-(CH₂)₃-CH₃), 1.35-1.28 (m, 12H, NCH₂-CH₂-*(CH₂)₃*-CH₃), 0.87 (t, *J* = 6.0 Hz, 6H, N(CH₂)₅-*CH₃*, 6H). *[13]C NMR (125 MHz, DMSO-d₆)*: δ = 162.92 (*CO*), 148.78, 139.39, 124.07, 38.86, 31.06, 29.49, 26.25, 22.09, 13.93. Exact mass for $[C_{19}H_{31}N_3O_2+ Na]^+$ 356.2308, found (HREIMS+) 356.2319.

S2.5 N,N-bis(2-hydroxyethyl)pyridine-2,6-dicarboxamide, 1c:[S3]



A slightly modified procedure compared to that previously published[S3] was used. Dimethyl pyridine-2,6-dicarboxylate (0.5 g, 2.6 mmol) was added to aminoethanol (0.63 g, 10.3 mmol) and heated at 80°C for 24 hours in a sealed tube. The reaction mixture was evaporated to dryness and recrystallized from acetonitrile to provide **1c** as a white solid (0.57 g, yield 88%). *[1]H NMR (400 MHz, DMSO-d₆)*: δ = 9.35 (t, *J* = 6.0 Hz, 2H, *NH*), 8.20-8.12 (m, 3H, ArH), 4.82 (t, *J* = 6.0 Hz, 2H, *OH*), 3.56 (q, *J* = 5.3 Hz, 4H, *CH₂*-OH), 3.43 (q, *J* = 5.3 Hz, 4H, N-*CH₂*). *[13]C NMR (125 MHz, DMSO-d₆)*: δ = 163.28 (*CO*), 148.77 (Ar), 139.38 (Ar), 124.16 (Ar), 59.77 (*C*H₂-OH), 41.78 (N-*C*H₂). Exact mass for $[C_{11}H_{15}N_3O_4+Na]^+$ 276.0955, found (HREIMS+) 276.0967.

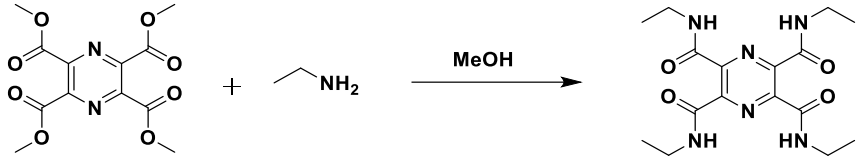
S2.6 N,N-bis(2-(2-hydroxyethoxy)ethyl)pyridine-2,6-dicarboxamide, 1d:[S4]



A slightly modified procedure compared to that previously published[S4] was used. A solution 2,6-pyridinedicarboxylic acid, 2,6-dimethyl ester (0.3 g, 1.5 mmol) in 10 mL methanol, 2-(2-aminoethoxy)ethanol (0.33 ml, 3.3 mmol) was heated at 80°C for 24 hours. The solution was concentrated under reduced pressure to remove methanol and solidified through ether followed by acetonitrile to get **1d** as waxy white solid (0.37g, yield 70%). *[1]H NMR (400 MHz, DMSO-d₆)*: δ = 9.37 (t, *J* = 5.9 Hz, 2H, *NH*), 8.21-8.15 (m, 3H, ArH), 4.62 (t, *J* = 5.2 Hz, 2H, *OH*), 3.60 (t, *J* = 6.3 Hz, 4H, NCH₂*CH₂*), 3.54 (t, *J* = 4 Hz, 4H, N*CH₂*), 3.51 (t, *J* = 4 Hz, 4H, *CH₂*OH), 3.47 (d, *J* = 4.6 Hz, 4H, O*CH₂*-CH₂OH). *[13]C NMR (125 MHz, DMSO-d₆)*: δ = 163.73 (*CO*), 149.12, 139.94,

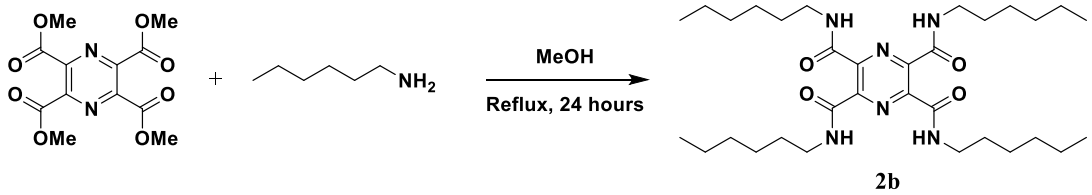
124.73, 72.68, 69.48, 60.67, 39.44. Exact mass found for $[C_{15}H_{23}N_3O_4+Na]^+$ 364.1479, found (HREIMS+) 364.1523.

S2.7 N,N,N,N-tetraethylpyrazine-2,3,5,6-tetracarboxamide, 2a:[S5]



A slightly modified procedure compared to that previously published[S5] was used. To a sealed tube containing suspension of tetramethylpyrazine-2,3,5,6-tetracarboxylate (0.3 g, 0.96 mmol) in 8 mL of methanol was added 2M ethylamine solution in THF (3.86 mL, 7.66 mmol). The reaction was capped and heated to 60°C. Within 2 hours the reaction mixture clears and was stirred up to 24 hours. Solvent was removed under reduced pressure to produce a white solid, which was recrystallized from MeOH:CH_3CN (1:3) to give the white crystalline product **2a** (0.30 g, yield 87%). Crystals of **2a** were grown through slow evaporation of methanol. *^{1}H NMR (400 MHz, DMSO-d_6)*: δ = 8.76 (t, *J* = 6.0 Hz, 4H, *NH*), 3.29 (q, *J* = 5.3 Hz, 8H, NH-*CH_2*-CH_3), 1.14 (t, *J* = 6.0 Hz, 12H, NH-CH_2-*CH_3*). *^{13}C NMR (125 MHz, DMSO-d_6)*: δ = 163.61 (*CO*), 145.82 (Ar), 34.24 (NH-*CH_2*-CH_3), 15.02 (NH-CH_2-*CH_3*). Exact mass for $[C_{16}H_{24}N_6O_4+Na]^+$ 387.1751, found (HREIMS+) 387.1777.

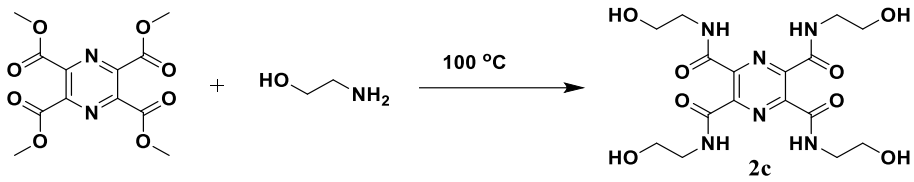
S2.8 N,N,N,N-tetrahexylpyrazine-2,3,5,6-tetracarboxamide, 2b:[S6]



A slightly modified procedure compared to that previously published[S6] was used. To a solution of tetramethylpyrazine-2,3,5,6-tetracarboxylate (0.3 g, 0.96 mmol) in 10 mL methanol, n-hexylamine (0.39 g, 3.84 mmol) was added followed by refluxing at 80℃ for 24 hours. The reaction mixture was evaporated to dryness under reduced pressure, and the solid crude product was recrystallized with acetonitrile to provide white fluffy crystalline solid of **2b** (0.36 g, yield 64%). Needle-like crystals of **2b** suitable for X-ray diffraction were grown from slow evaporation of ethanol solution at room temperature. ^{1}H NMR (500 MHz, *$CDCl_3$*) δ = 8.09 (t, *J* = 10.0 Hz, 4H, *NH*), 3.30 (q, *J* =

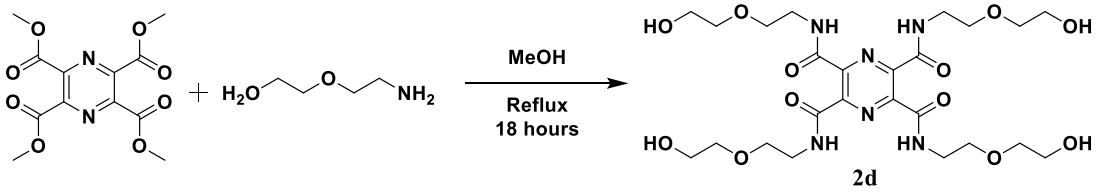
6.4 Hz, 8H, N-CH_2), 1.64 (quint, J = 7.5 Hz, 8H, NCH_2-CH_2), 1.41 (quint, J = 7.9 Hz, 8H, NCH_2-CH_2-CH_2), 1.36-1.33 (m, 16H, $N(CH_2)_3$-(CH_2)$_2$-CH_3), 0.93 (t, J = 6.7 Hz, 12H, $N(CH_2)_5$-CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 163.26 (*CO*), 144.76, 40.23, 31.70, 28.84, 26.94, 22.71, 14.10. Exact mass for $[C_{32}H_{56}N_6O_4+Na]^+$ 611.4255, found (HREIMS+) 611.4252.

S2.9 N,N,N,N-tetrakis(2-hydroxyethyl)pyrazine-2,3,5,6-tetracarboxamide, 2c:



To 10 mL methanol solution of aminoethanol (0.62 g, 10.2 mmol), tetramethylpyrazine-2,3,5,6-tetracarboxylate (0.4 g, 1.3 mmol) was added and heated at 80°C for 36 hours. The reaction mixture was concentrated and recrystallized from acetonitrile to furnish **2c** as a white solid (0.45g, yield 83%). Crystals of **2c** were grown through from slow evaporation of methanol solution at room temperature. *^{1}H NMR (400 MHz, DMSO-d_6)*: δ = 8.95 (t, J = 6.0 Hz, 4H, *NH*), 4.77 (t, J = 6.0 Hz, 4H, *OH*), 3.55 (q, J = 5.3 Hz, 8H, CH_2-OH), 3.35 (q, J = 5.3 Hz, 8H, N-CH_2). *^{13}C NMR (125 MHz, DMSO-d_6)*: δ = 163.59 (*CO*), 145.21, 59.52 (CH_2-OH), 41.86 (N-CH_2). Exact mass for $[C_{16}H_{25}N_6O_8+Na]^+$ 451.1548, found (HREIMS+) 451.1521.

S2.10 N,N,N,N-tetrakis(2-(2-hydroxyethoxy)ethyl)pyrazine-2,3,5,6-tetracarboxamide, 2d:



To a suspension of tetramethylpyrazine-2,3,5,6-tetracarboxylate(0.7 g, 2.24 mmol) in 10 ml methanol, 2-(2-aminoethoxy)ethanol (1.8 mL, 17.84 mmol) was added and refluxed at 80°C for 18 hours. The clear reaction mixture solution, which was evaporated to dryness under reduced pressure, recrystallized from acetonitrile within 15 minutes to provide the solid crystalline tetrakis[2-(2-hydroxyethoxy)ethyl]pyrazine-2,3,5,6-tetracarboxamide (0.89 g, yield 66%). Suitable crystals of **2d** for X-ray diffraction were grown from slow evaporation of a methanol solution. *^{1}H NMR (400 MHz, DMSO-d_6)*: δ = 8.93 (t, J = 6.0 Hz, 4H, *NH*), 4.61 (t, J = 6.0 Hz, 4H,

OH), 3.56 (t, *J* = 6.0 Hz, 8H, NCH$_2$-*CH$_2$*), 3.50 (q, *J* = 4.0 Hz, 8H, *CH$_2$*OH), 3.47-3.43 (m, 16H, N*CH$_2$*- and O*CH$_2$*-CH$_2$OH). *^{13}C NMR (125 MHz, DMSO-d$_6$)*: δ = 163.51 (*CO*), 145.18 (Ar), 72.22 (O*CH$_2$*-CH$_2$OH), 68.70 (NCH$_2$-*CH$_2$*), 60.18 (*CH$_2$*OH), 39.00 (N*CH$_2$*). Exact mass for [C$_{24}$H$_{40}$N$_6$O$_{12}$+Na]$^+$ 627.2596, found (HREIMS) 627.2631.

Characterization (NMR and MS)

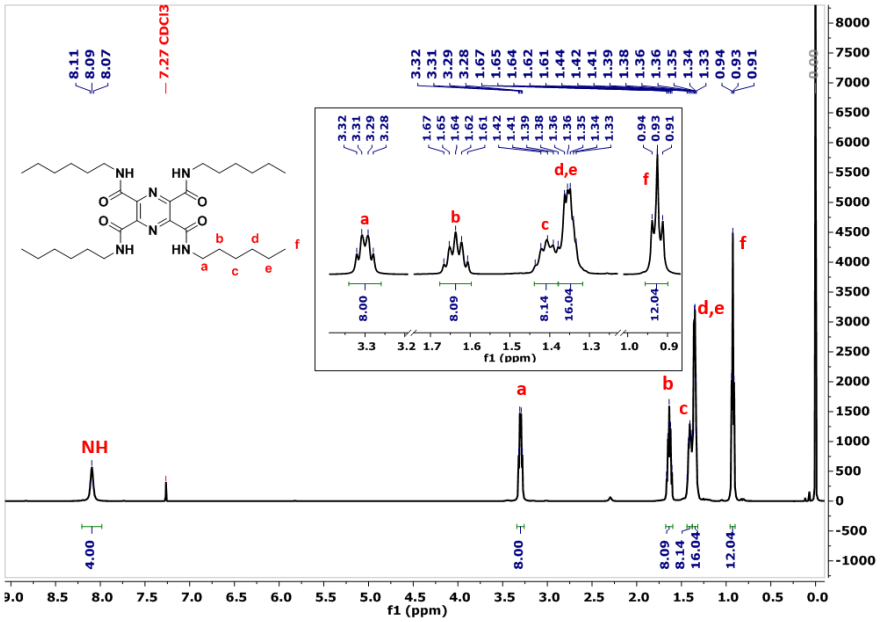


Fig. S1A. ^{1}H NMR (500 MHz, $CDCl_3$) of **2b**.

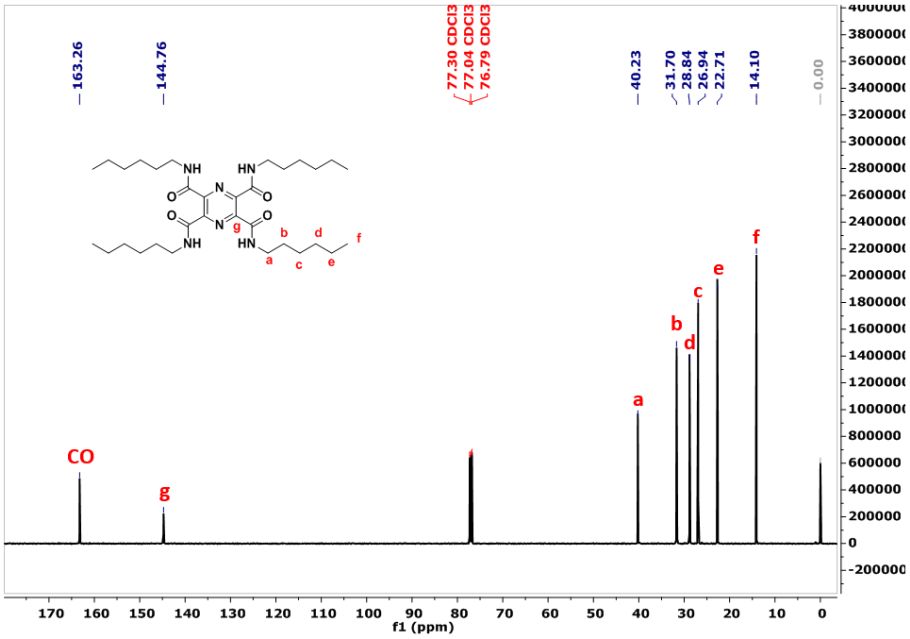


Fig. S1B. ^{13}C NMR (125 MHz, $CDCl_3$) of **2b**.

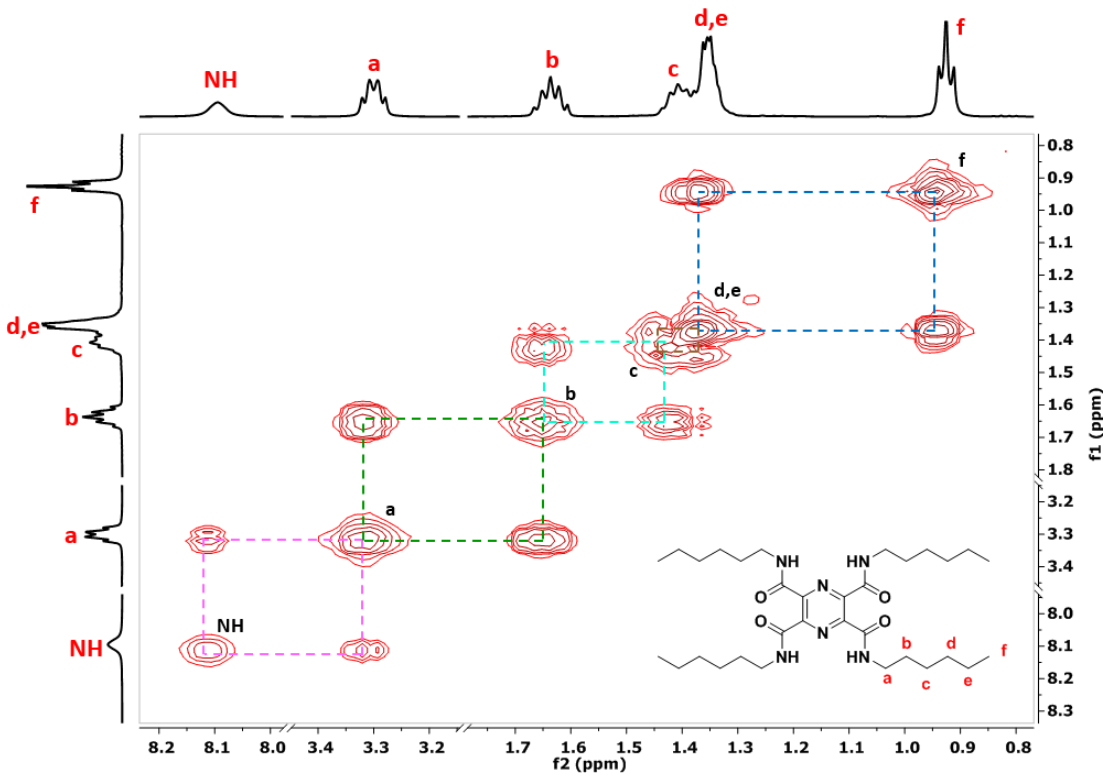


Fig. S1C. ^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d_6) of **2b**.

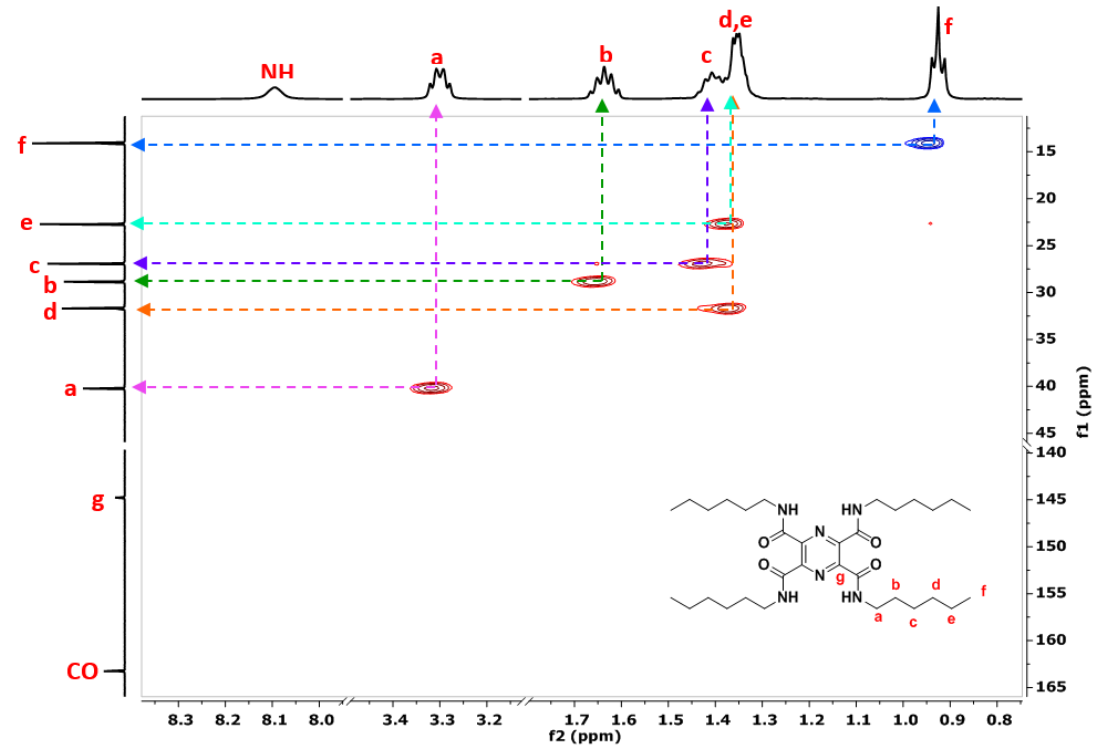


Fig. S1D. ^{1}H-^{13}C HSQC NMR (500 MHz, DMSO-d_6) of **2b**.

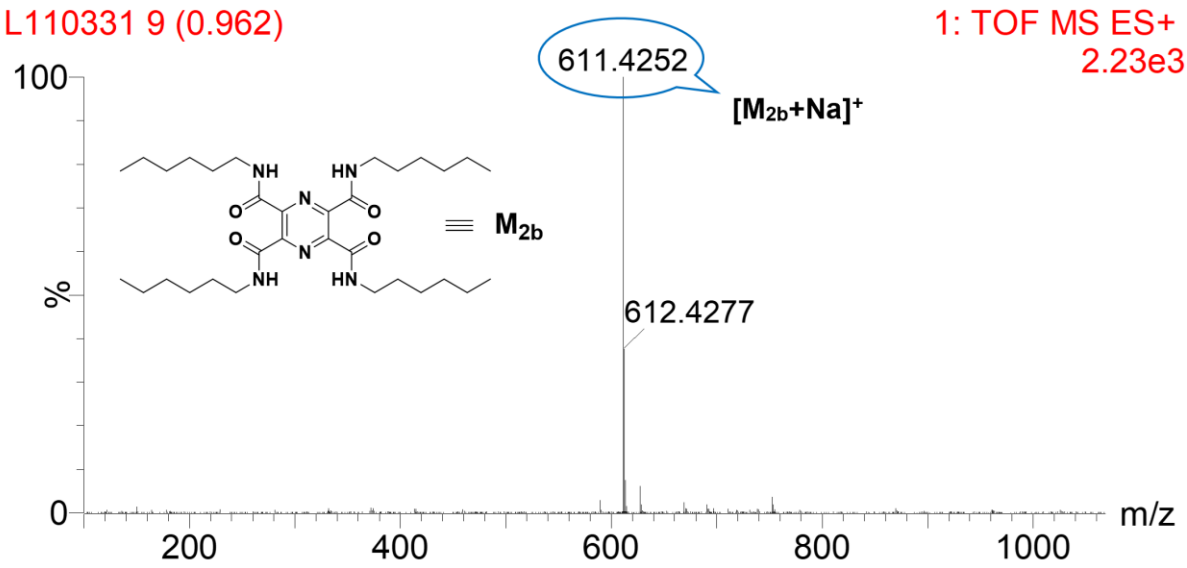


Fig. S1E. ESI-MS of **2b**.

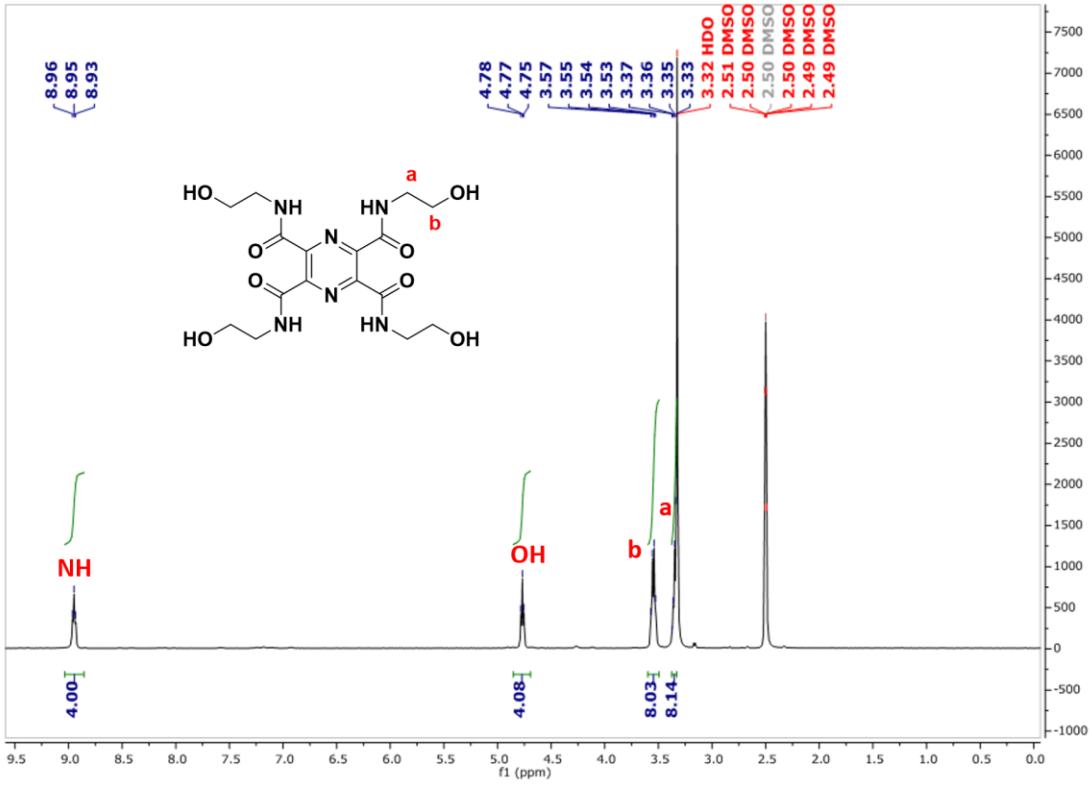


Fig. S2A. ^{1}H NMR (400 MHz, DMSO-d_6) of **2c.**

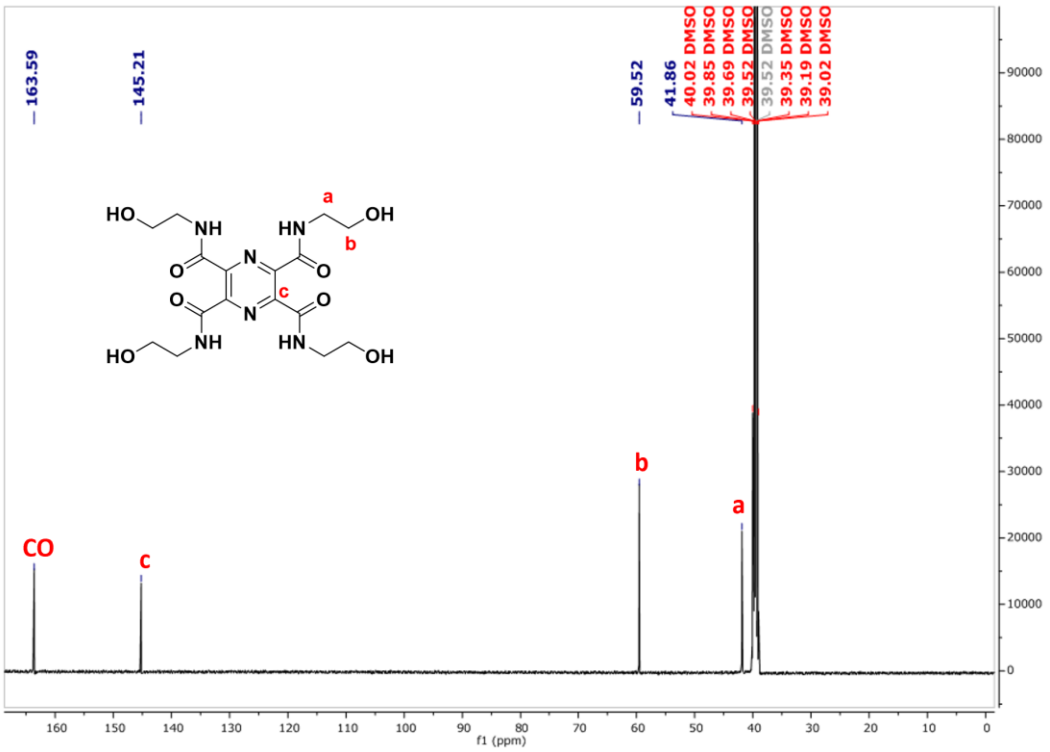


Fig. S2B. ^{13}C NMR (125 MHz, DMSO-d_6) of **2c.**

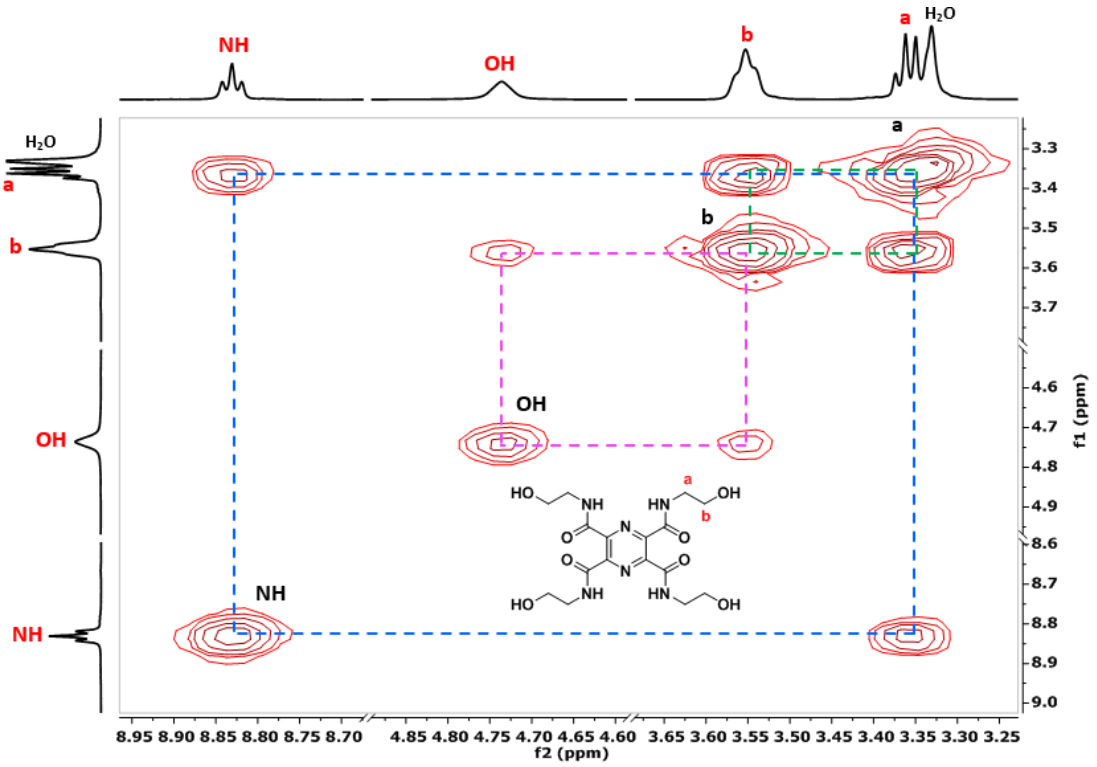


Fig. S2C. ^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d_6) of **2c**.

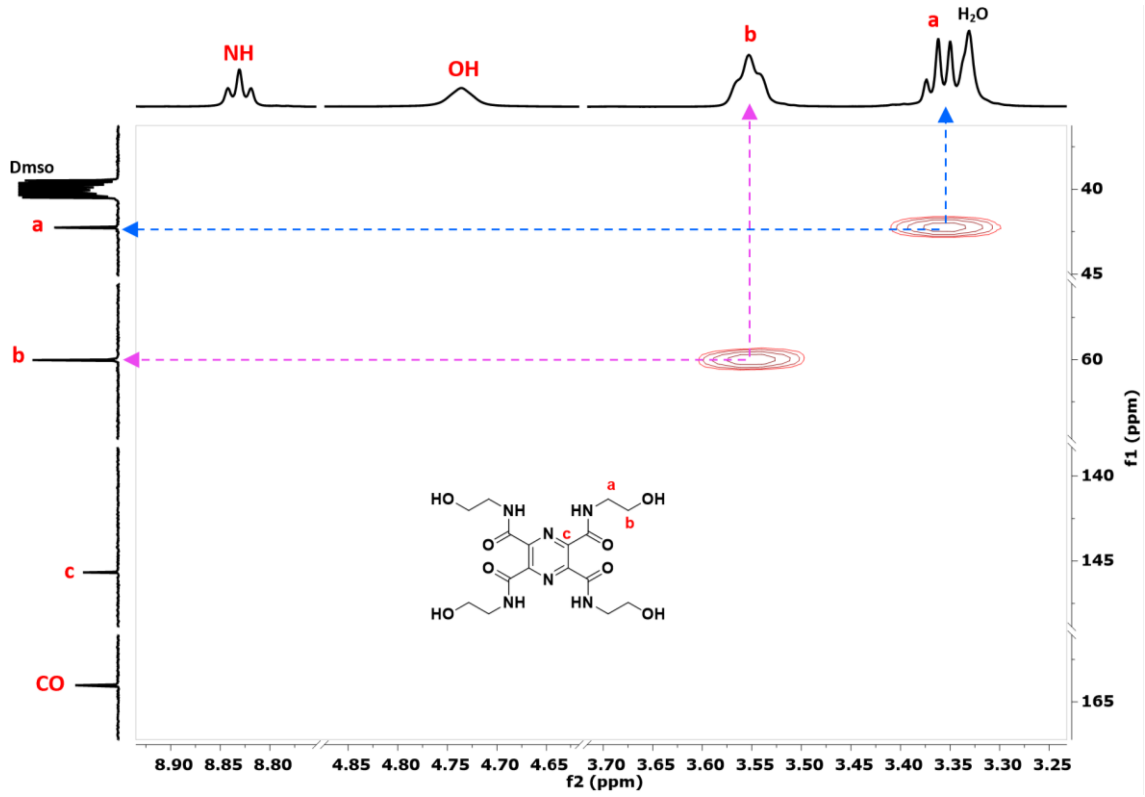


Fig. S2D. ^{1}H-^{13}C HSQC NMR (500 MHz, DMSO-d_6) of **2c**.

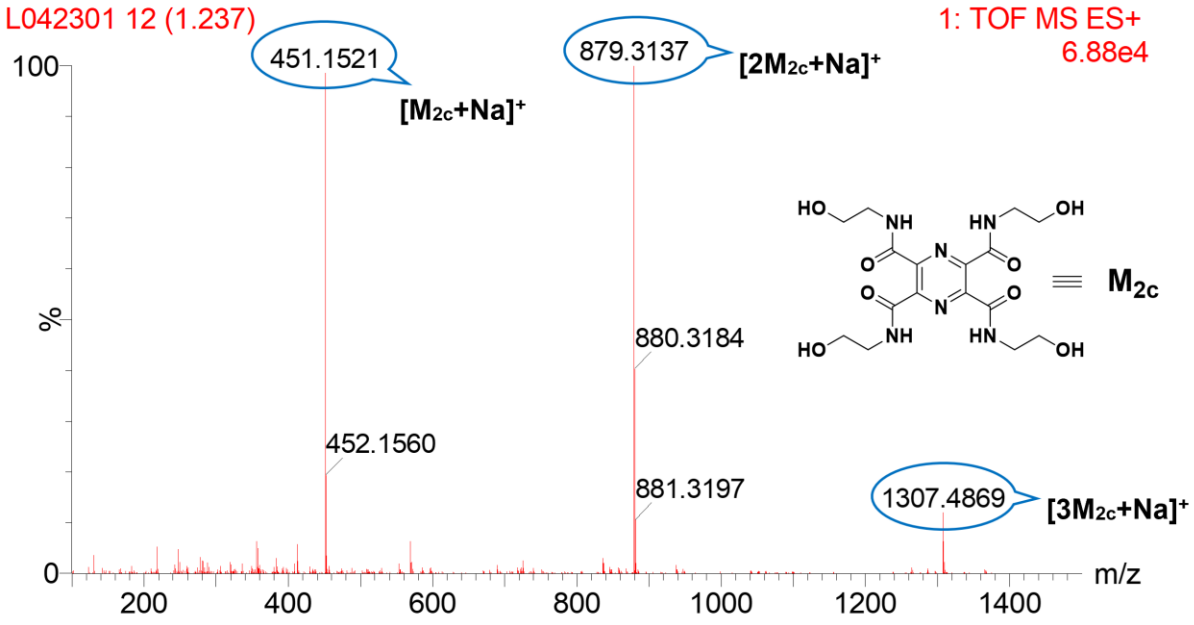


Fig. S2E. ESI-MS of **2c.**

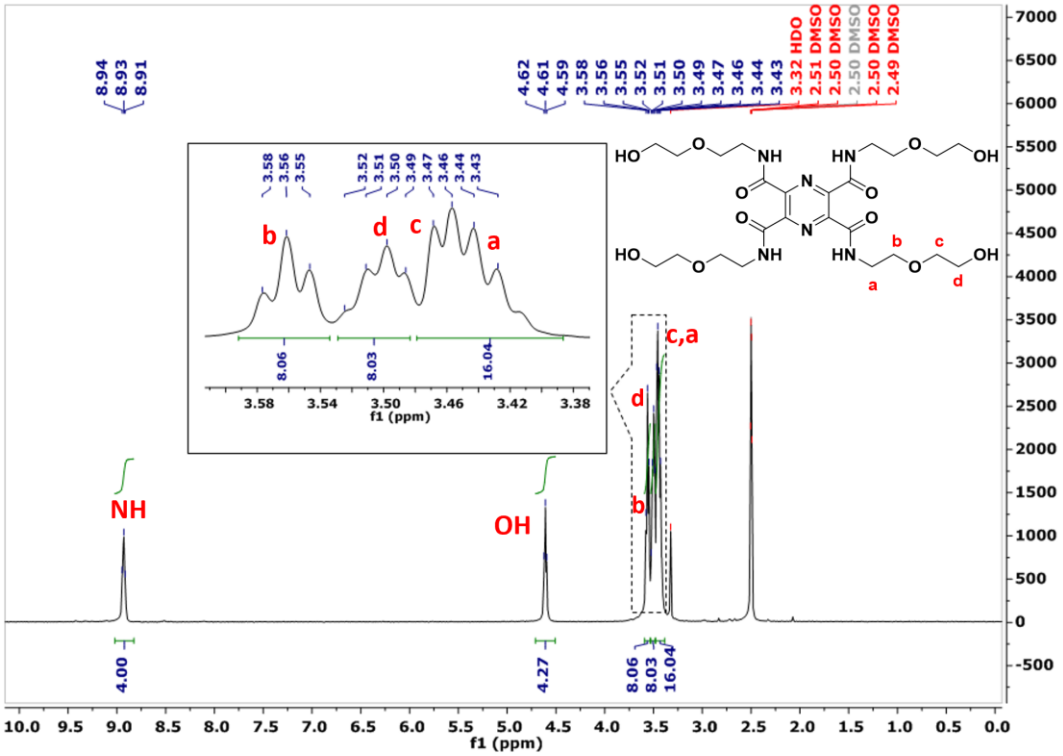


Fig. S3A. ^{1}H NMR (400 MHz, DMSO-d_6) of **2d.**

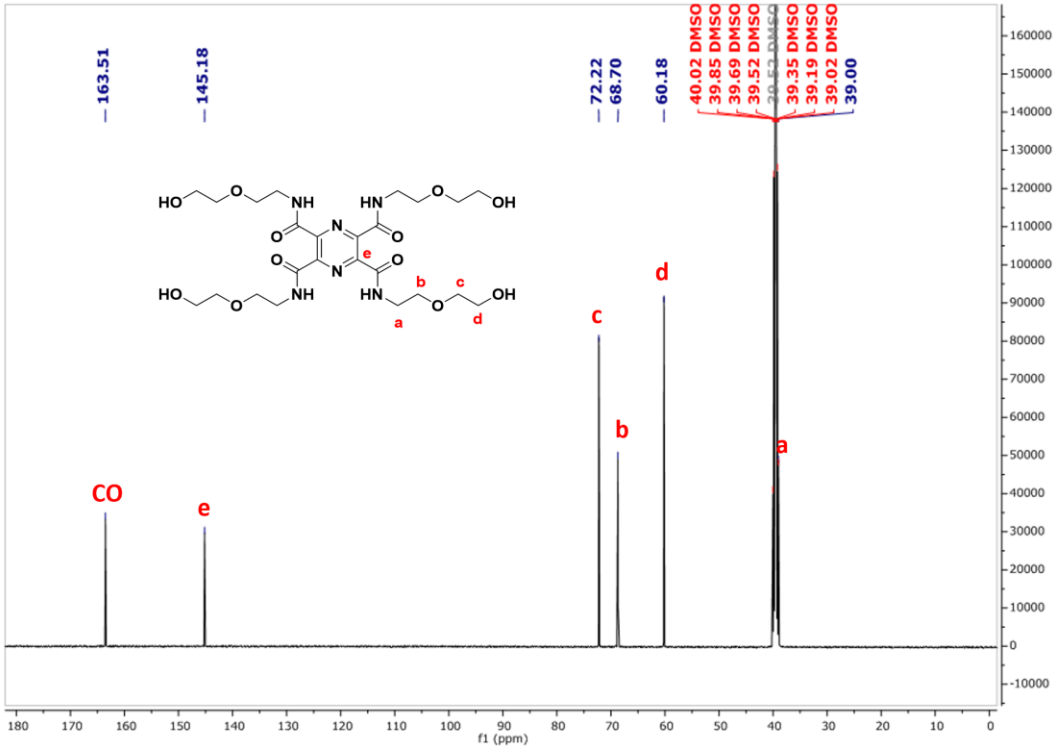


Fig. S3B. ^{13}C NMR (125 MHz, DMSO-d_6) of **2d.**

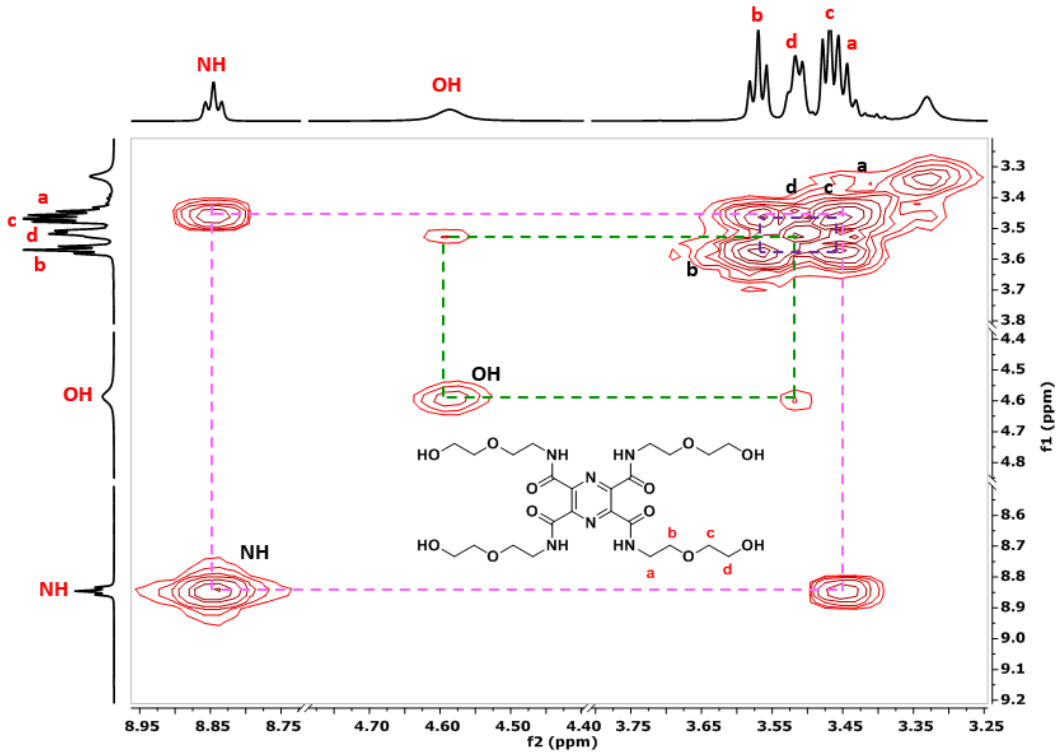


Fig. S3C. ^{1}H-^{1}H COSY NMR (500 MHz, DMSO-d_6) of **2d**.

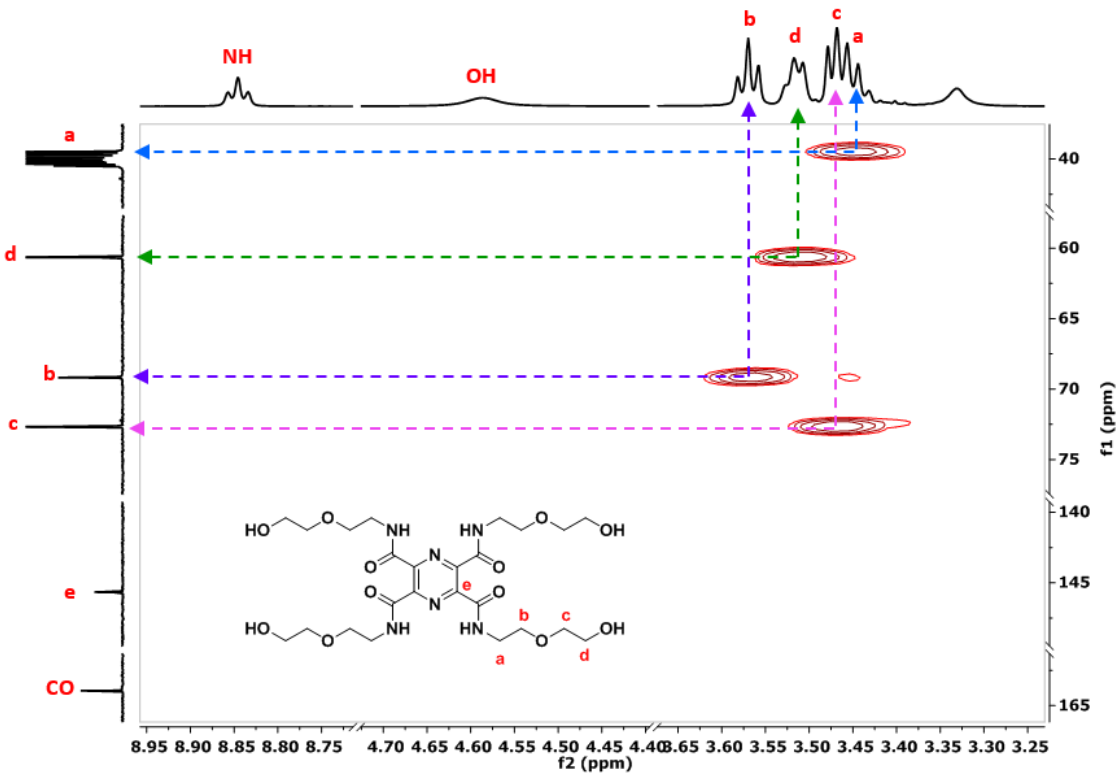


Fig. S3D. ^{1}H-^{13}C HSQC NMR (500 MHz, DMSO-d_6) of **2d**.

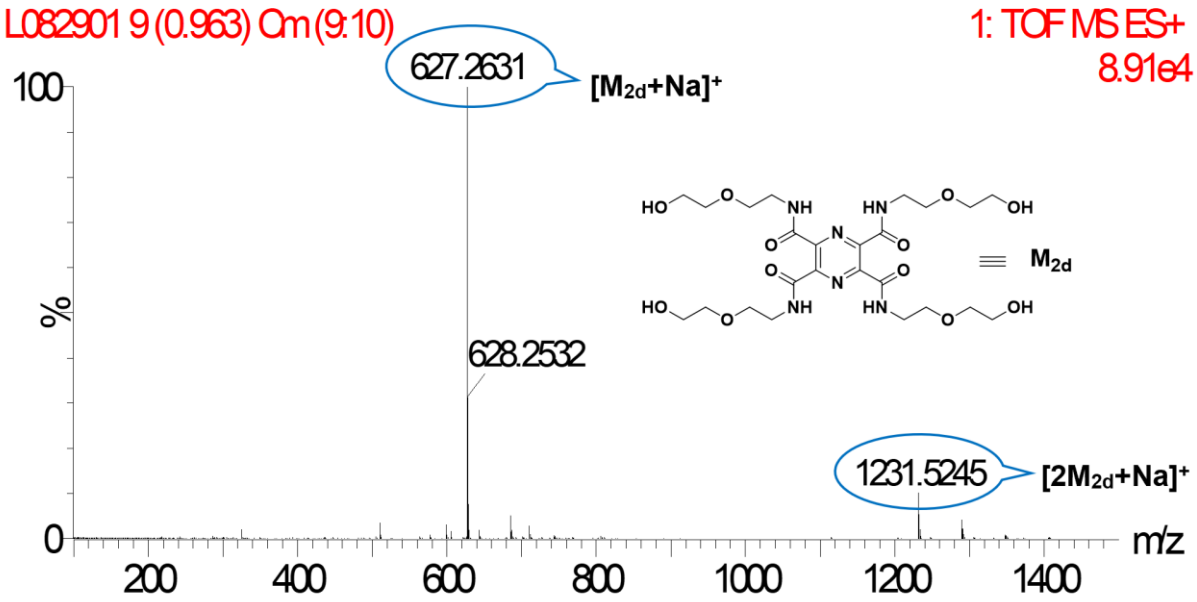


Fig. S3E. ESI-MS of **2d**.

S3 NMR titration experiments and binding studies

^{1}H NMR titrations were conducted for each host on a Bruker DRX 500 MHz spectrometer. Tetrabutylammonium (TBA) salts of $H_2PO_4^-$, F^-, and OAc^- were used to make the guest titrant solution in CD_3CN:DMSO-d_6 (9:1). A 20 mM solution of guest anions was titrated into 0.5 mL of 2 mM host (**1a-1d**, **2a-2d**) solutions to examine anion binding (Fig. S4-S11). All NMR additions were recorded manually and each proton NMR spectrum was acquired for five minutes (16 scans each). A given titration, 20 NMRs, required about 1 hour 20 minutes. Association constants, K for 1:1 and K_{11} and K_{12} for 1:2, were obtained by fitting ^{1}H NMR titration data (shifting of the amide proton) with EQNMR[S7] and Bindfit [S8] software.

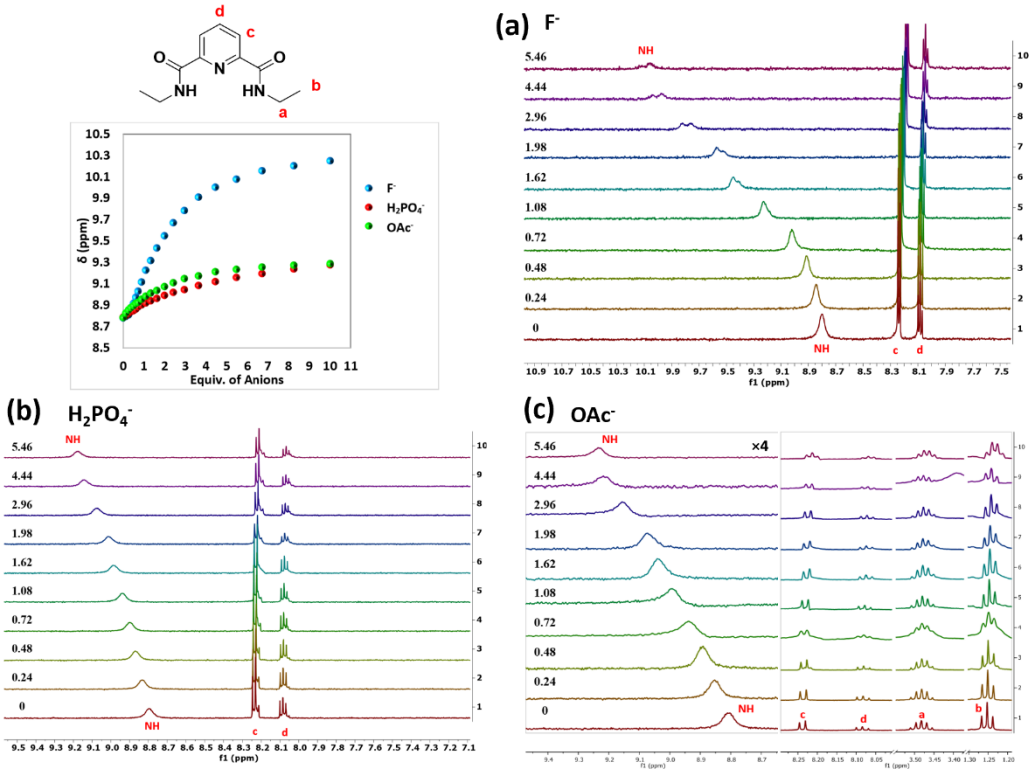


Fig.S4. Anion binding titration of **1a** with (a) TBAF, (b) $TBAH_2PO_4$, and (c) TBAOAc in 9:1 CD_3CN:DMSO-d_6.

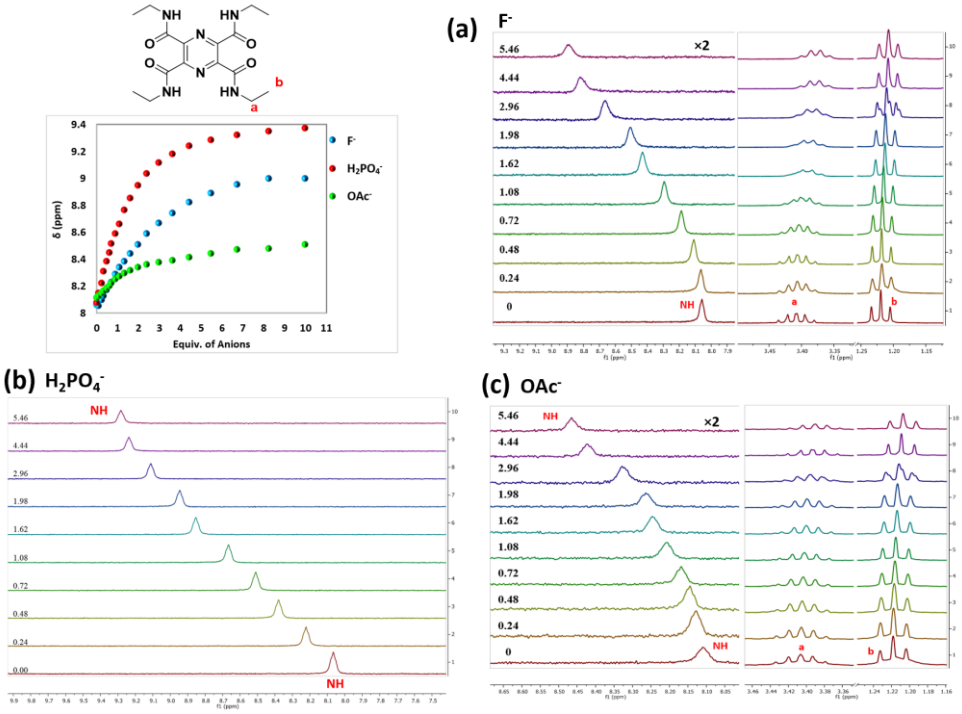


Fig. S5. Anion binding titration of **2a** with (a) TBAF, (b) $TBAH_2PO_4$, and (c) TBAOAc in 9:1 CD_3CN:DMSO-d_6.

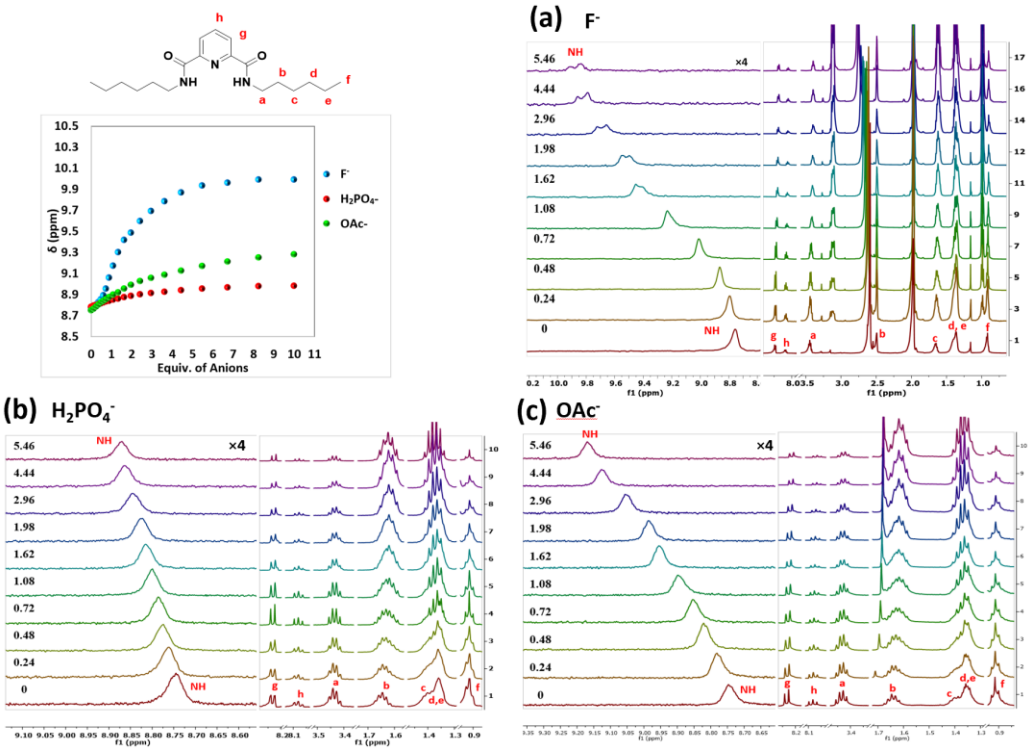


Fig. S6. Anion binding titration of **1b** with (a) TBAF, (b) $TBAH_2PO_4$, and (c) TBAOAc in 9:1 CD_3CN:DMSO-d_6.

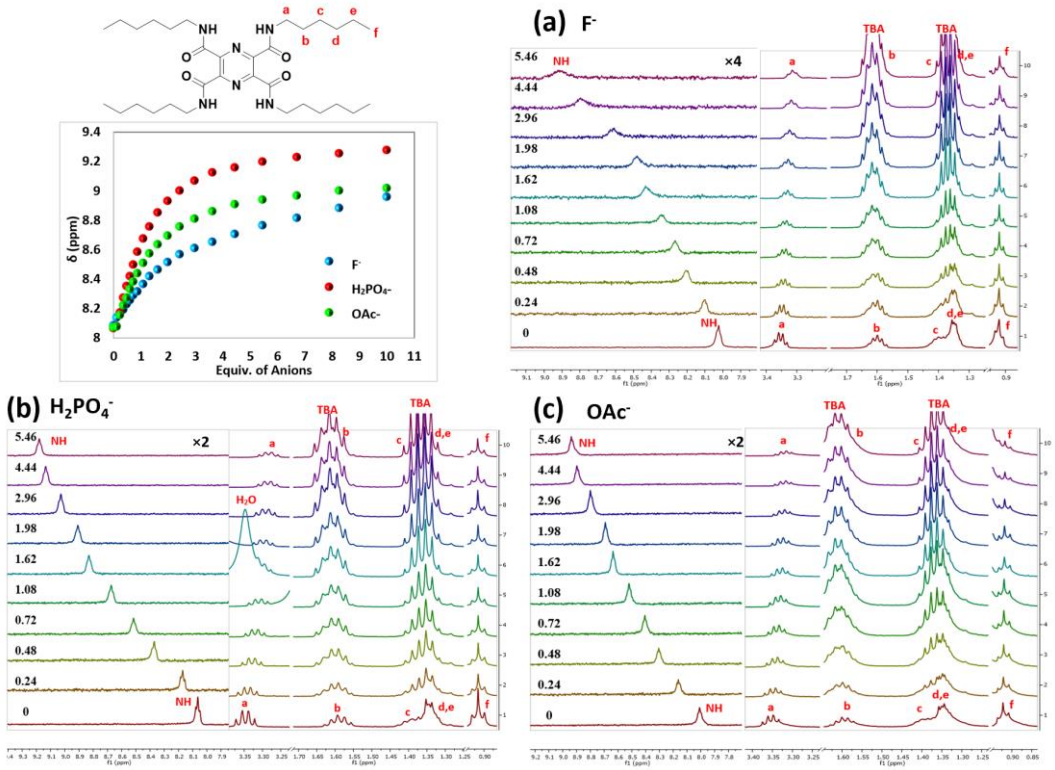


Fig. S7. Anion binding titration of **2b** with (a) TBAF, (b) $TBAH_2PO_4$, and (c) TBAOAc in 9:1 CD_3CN:DMSO-d_6.

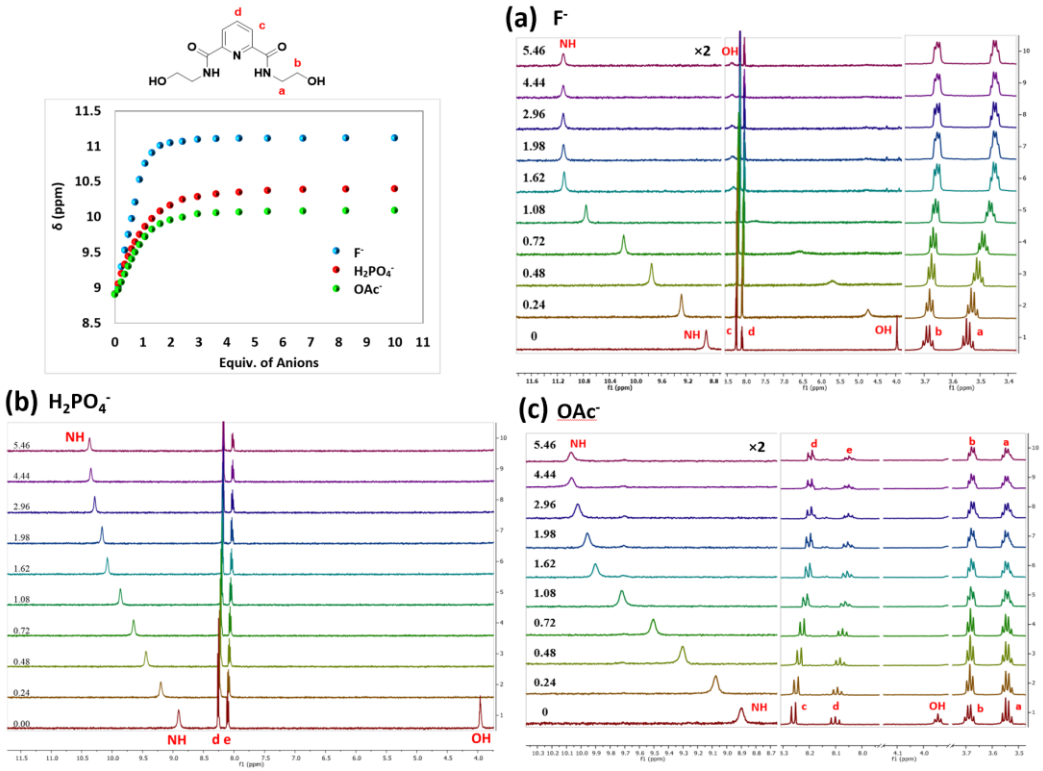


Fig. S8. Anion binding titration of **1c** with (a) TBAF, (b) $TBAH_2PO_4$, and (c) TBAOAc in 9:1 CD_3CN:DMSO-d_6.

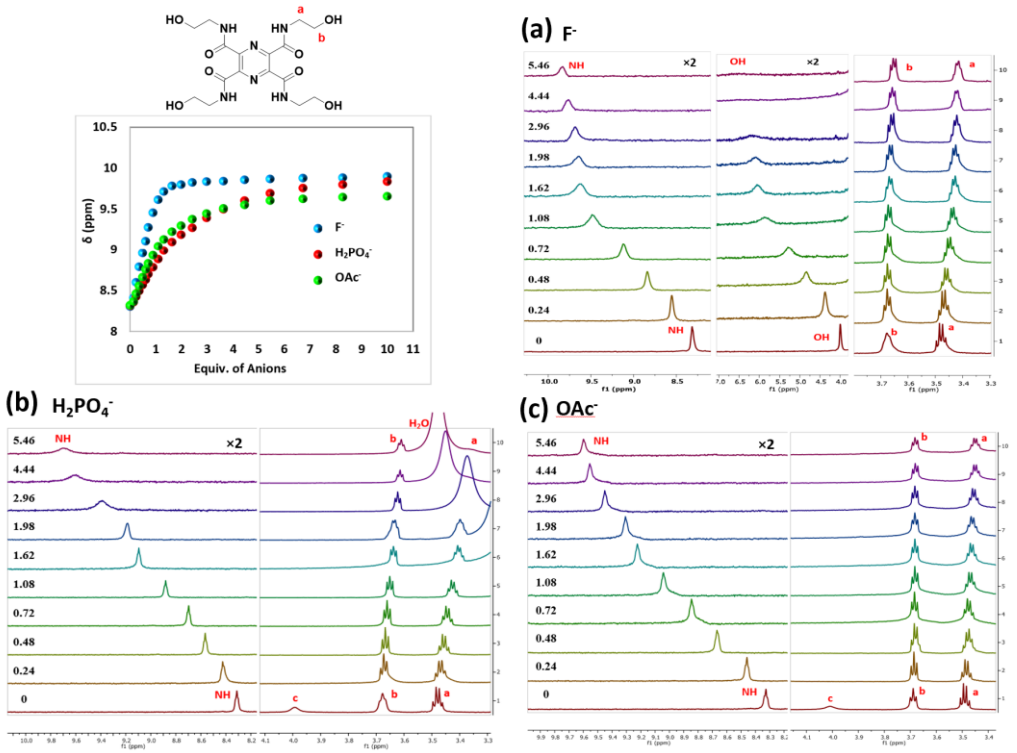


Fig. S9. Anion binding titration of **2c** with (a) TBAF, (b) $TBAH_2PO_4$, and (c) TBAOAc in 9:1 CD_3CN:DMSO-d_6.

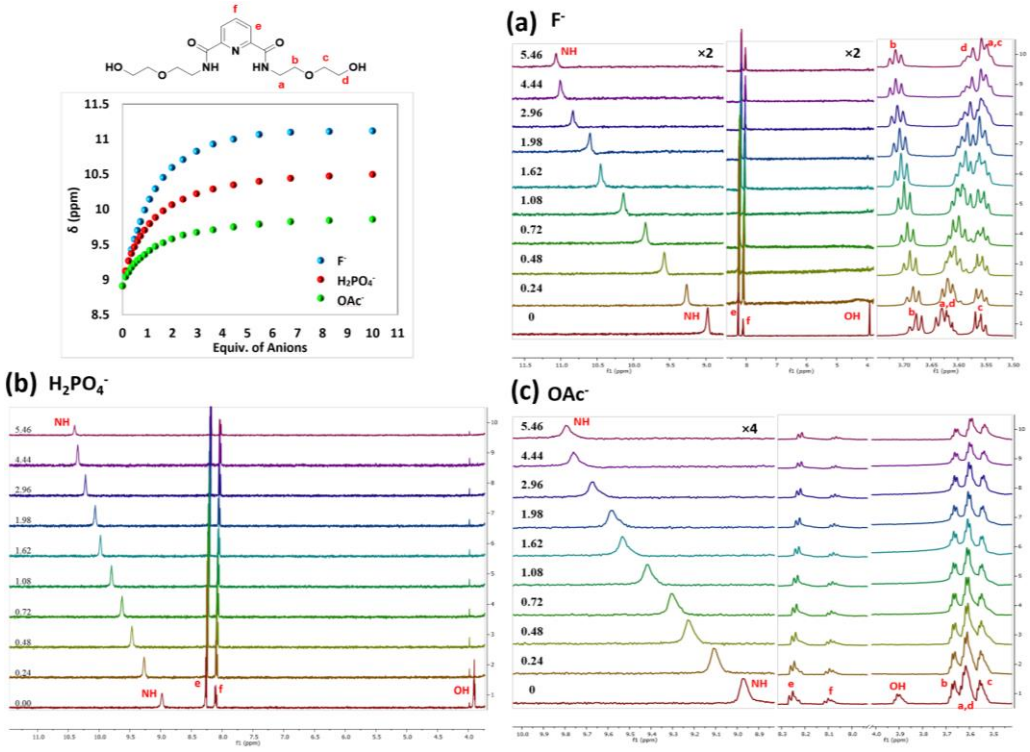


Fig. S10. Anion binding titration of **1d** with (a) TBAF, (b) $TBAH_2PO_4$, and (c) TBAOAc in 9:1 CD_3CN:DMSO-d_6.

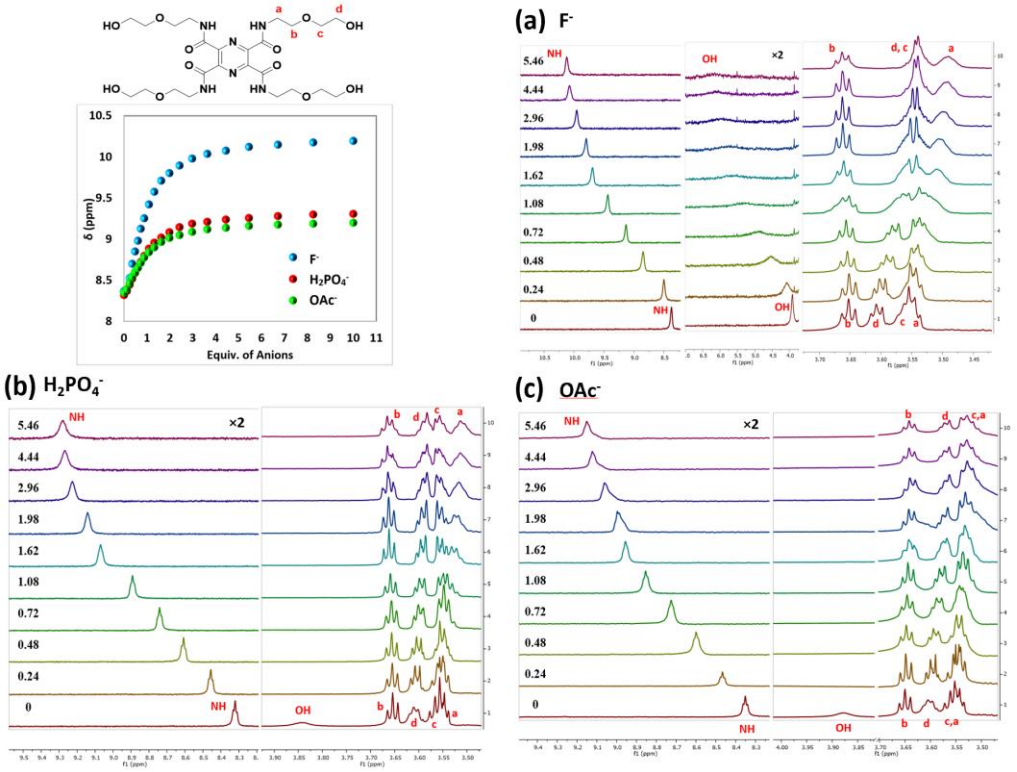


Fig. S11. Anion binding titration of **2d** with (a) TBAF, (b) $TBAH_2PO_4$, and (c) TBAOAc in 9:1 CD_3CN:DMSO-d_6.

Table S1. Solubility chart for pincers **1a-1d** and **2a-2d** where (**S** is soluble, **L** is low solubility, and **N** is insoluble).

Solvent	1a (DiEt)	2a (TetraEt)	1b (DiHex)	2b (TetraHex)	1c (DiEtOH)	2c (TetraEtOH)	1d (DiGly)	2d (TetraGly)
Acetone	S	N	S	S	S	N	S	L
Acetonitrile	S	N	S	S	L	N	S	L
Methanol	S	S	S	S	S	L	S	S
Ethanol	S	S	S	S	S	N	S	S
Toluene	L	N	S	S	L	N	N	L
Hexane	N	N	N	S	N	N	N	N
Chloroform	S	S	S	S	L	N	S	L
DMF	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S
THF	S	L	S	S	L	N	S	N
Cyclohexane	N	N	N	S	N	N	N	N
Water	N	N	N	N	S	S	S	S

***** Solubilities were checked by both sonication and heating (50-60 ^{o}C).

Table S2. Association constants (Log$K$, M^{-1}) of **1a-1d** and **2a-2d** for selected anions ($TBAH_2PO_4$, TBAOAc, and TBAF) in CD_3CN:DMSO-d_6 (9:1).[*]

Anions	1a (DiEt)	2a (TetraEt)	1b (DiHex)	2b (Tetra-Hex)	1c (DiEtOH)	2c (Tetra-EtOH)	1d (DiGly)	2d (TetraGly)
$H_2PO_4^-$	**1.64**	K_{11} **2.77** K_{12} **2.05**	**2.01**	K_{11} **2.99** K_{12} **n.o.**	**3.29**	K_{11} **2.67** K_{12} **2.13**	**2.87**	K_{11} **2.80** K_{12} **3.26**
OAc^-	**2.17**	K_{11} **2.58** K_{12} **n.o.**	**2.05**	K_{11} **2.95** K_{12} **n.o.**	**3.49**	K_{11} **3.21** K_{12} **1.87**	**2.79**	K_{11} **3.30** K_{12} **1.60**
F^-	**2.40**	K_{11} **2.69** K_{12} **3.75**	**2.43**	K_{11} **2.79** K_{12} **n.o.**	**>4.00**	K_{11} **>4.00** K_{12} **n.o.**	**3.00**	K_{11} **3.15** K_{12} **n.o.**

[*]Abbreviation **n.o.** (not observed) denotes log $K \leq 1.0$.

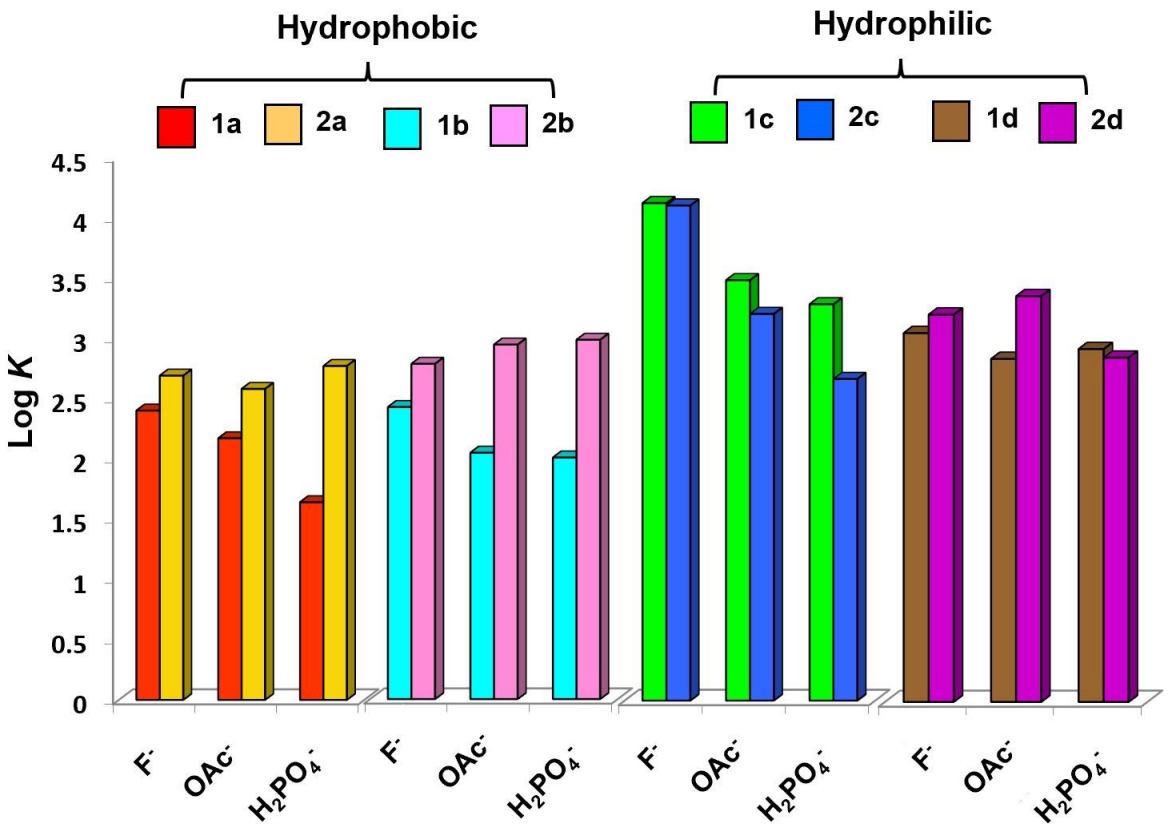


Fig. S12. Bar diagram showing association constants (Log K_1, M^{-1}) of **1a-1d** and **2a-2d** for selected anions (TBAF, TBAOAc, and $TBAH_2PO_4$) in CD_3CN:DMSO-d_6 (9:1).

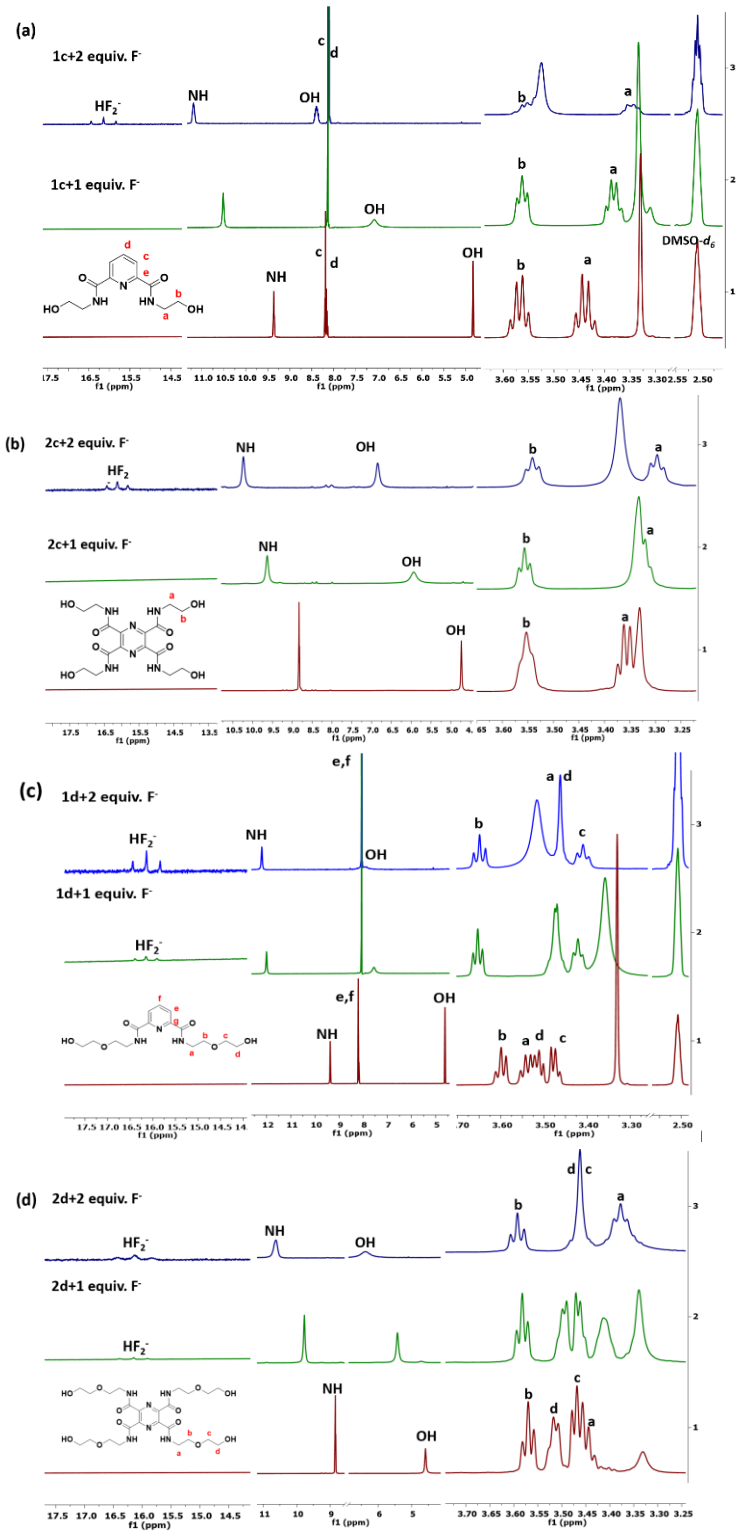


Fig. S13. ^{1}H NMR spectra showing the chemical shift of (a) **1c**, (b) **2c**, (b) **1d** and (b) **2d** in the presence of 1 and 2 equiv. of TBAF in DMSO-*d*$_6$ showing the appearance of FHF^- signal at 16.1 ppm.

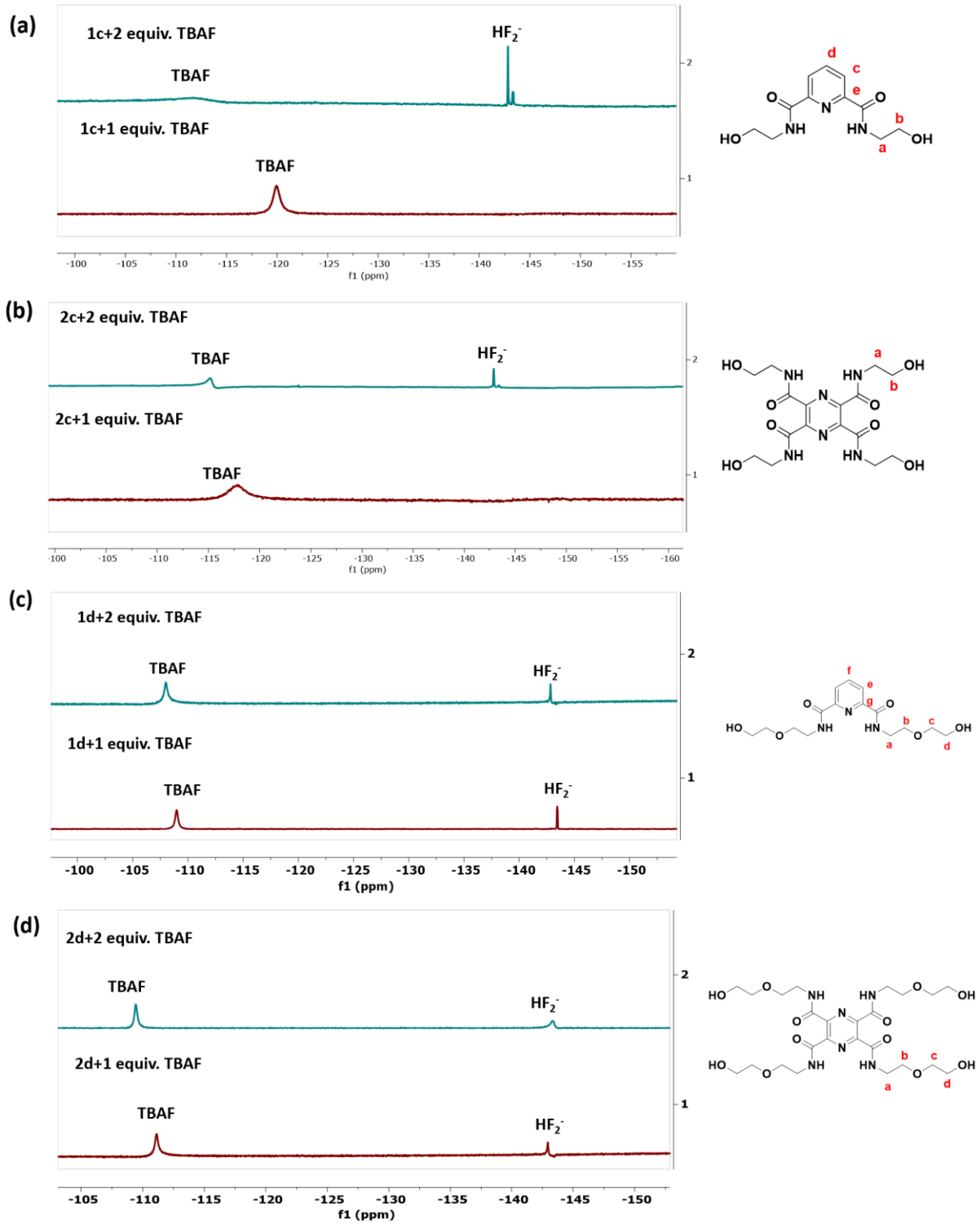


Fig. S14. ^{19}F NMR spectra showing the chemical shift of (a) **1c**, (b) **2c**, (b) **1d** and (b) **2d** in the presence of 1 and 2 equiv. of TBAF in DMSO-*d*$_6$ showing the appearance of FHF^- signal at -143 ppm.

S4 Single crystal X-ray diffraction studies of (2b), (2c) and (2d)

Complete sets of unique reflections were collected with monochromated CuKa radiation (**2b** and **2c**) (CuK_α = 1.54178 Å) or monochromated Mo Ka radiation (**2d**) (MoK_α = 0.71073 Å) for single-domain crystals of all three compounds. Totals of 3880 (**2b**), 5237 (**2c**) and 560 (**2d**) 1°-wide omega- or phi-scan frames with counting times of 6-20 seconds for **2b**, 4-8 seconds for **2c** and 5 seconds for **2d** were collected with a Bruker Platinum 135 CCD area detector (**2b**), a Bruker APEX II CCD area detector (**2c**) or a Bruker SMART APEX CCD area detector (**2d**). X-rays for **2b** and **2c** were provided by a Bruker MicroStar microfocus rotating anode operating at 45kV and 60 mA and equipped dual CCD detectors and Helios multilayer x-ray optics. X-rays for **2d** were provide by a microfocus sealed X-ray tube operating at 50 kV and 35 mA and equipped with a MonoCap collimator and graphite monochromator. Preliminary lattice constants were obtained with the Bruker program SMART.[S9] Integrated reflection intensities for all crystals were produced using the Bruker program SAINT.[S10] All three data sets were corrected empirically for variable absorption effects using equivalent reflections. The Bruker software package SHELXTL was used to solve each structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using Fo^2 data with the SHELXTL v2014 software package.[S11]

The final structural model for all three structures incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The non-methyl hydrogen atoms in **2b** were placed at idealized riding model sp^2- or sp^3-hybridized positions with N-H bond lengths of 0.88 Å or C-H bond lengths of 0.99 Å. The methyl groups in **2b** were included in their structural models as riding model sp^3-hybridized rigid groups (with a C-H bond length of 0.98 Å) at idealized "staggered" positions. The isotropic thermal parameters of idealized hydrogen atoms in **2b** were fixed at values 1.2 (non-methyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon or nitrogen atom to which they are covalently bonded. All hydrogen atoms in **2c** and **2d** were located from a difference Fourier and included in the structural model as independent isotropic atoms whose parameters were allowed to vary in least-squares refinement cycles. The B-alert for **2b** is obviously due to slight disorder for the terminal C16-C17 unit of the second hexyl group.

CCDC: 2092504 **(2b)**, 1974541 **(2c)** and 1453984 **(2d)**

Table S3. Crystal Data and Structure Refinement for **2b**, **2c**·H_2O and **2d**.

	2b	**2c**·H_2O	**2d**
Empirical formula	$C_{32}H_{56}N_6O_4$	$C_{16}H_{26}N_6O_9$	$C_{24}H_{40}N_6O_{12}$
Formula weight	588.82	446.43	604.62
Temperature	200(2) K	200(2) K	228(2) K
Wavelength	1.54178 Å	1.54178 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/c$	$P2_1/c$
a	44.553(4) Å	8.7091(6) Å	11.0587(19) Å
b	4.9317(4) Å	24.6511(16) Å	14.955(3) Å
c	15.7652(15) Å	9.7352(7) Å	8.8548(15) Å
a	90°	90°	90°
β	90.399(6)°	94.492(3)°	101.133(2)°
γ	90°	90°	90°
Volume	3463.9(5) $Å^3$	2083.6(2) $Å^3$	1436.9(4) $Å^3$
Z	4	4	2
Density (calculated)	1.129 mg/m^3	1.423 mg/m^3	1.397 mg/m^3
Absorption coefficient	0.597 mm^{-1}	1.004 mm^{-1}	0.113 mm^{-1}
F(000)	1288	944	644
Crystal size	0.700 × 0.190 × 0.030 mm^3	0.450 × 0.055 × 0.025 mm^3	0.490 × 0.330 × 0.180 mm^3
Theta range	1.983 to 68.246°	3.586 to 70.069°.	2.319 to 30.521°
Index ranges	-52≤h≤52, -3≤k≤5, -18≤l≤18	-10≤h≤8, -29≤k≤28, -11≤l≤10	-15≤h≤15, -21≤k≤21, -10≤l≤12
Reflections collected	11408	23676	11256
Independent reflections	3042 [R_{int} = 0.0808]	3853 [R_{int} = 0.0606]	4319 [R_{int} = 0.0541]
Completeness to theta = 66.000°	98.0 %	99.5 %	99.3 %
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	1.000 and 0.497	1.000 and 0.461	1.000 and 0.622
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3042 / 0 / 190	3853 / 0 / 384	4319 / 0 / 270
Goodness-of-fit on F^2	1.122	1.024	1.025
Final R indices [I>2σ(I)]	R1 = 0.1242, wR2 = 0.2927	R1 = 0.0511, wR2 = 0.1429	R1 = 0.0512, wR2 = 0.1084

R indices (all data)	R1 = 0.1406, wR2 = 0.3011	R1 = 0.0561, wR2 = 0.1480	R1 = 0.1009, wR2 = 0.1334
Largest diff. peak and hole	0.351 and -0.348 $e^-/Å^3$	0.246 and -0.313 $e^-/Å^3$	0.341 and -0.269 $e^-/Å^3$

S5 References

S1 T. J. Bartczak, Z. M. Michalska, B. Ostaszewski, P. Sobota and K. Strzelec, *Inorg. Chim. Acta*, 2001, **319**, 229-234.

S2 H. Horino, H. Sakaba and M. Arai, *Synthesis*, 1989, **9**, 715-718.

S3 S. Kumar, R. Singh and K. Singh, *Bioorg. Med. Chem. Lett.*, 1993, **3**, 363-364.

S4 A. M. Costero, M. J. Bañuls, M. J. Aurell, M. D. Ward and S. Argent, *Tetrahedron*, 2004, **60**, 9471-9478.

S5 J. Lohrman, H. Telikepalli, T. S. Johnson, T. A. Jackson, V. W. Day and K. Bowman-James, *Inorg. Chem.*, 2016, **55**, 5098-5100.

S6 J. Lohrman, E. A. Vãzquez-Montelongo, S. Pramanik, V. W. Day, M. A. Hix, K. Bowman-James and G. A. Cisneros, *Inorg. Chem.*, 2018, **57**, 9775-9778.

S7 M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, **2**, 311-312.

S8 (a) P. Thordarson, *Chem. Soc. Rev.*, **2011**, *40*, 1305-1323; (b) For BindFit online software see www.supramolecular.org.

S9 Data Collection: SMART Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

S10 Data Reduction: SAINT Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

S11 Refinement: SHELXTL Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.