Electron Sponge from Naphthalenediimide-Viologen Conjugates: Water Stable, Highly Electron-Deficient Polyions with 1 V Potential Window

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Supporting Information

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Experimental Section

General: Chemicals were sourced either from Sigma-Aldrich, Spectrochem India, Loba-chemie, or Thomas-Baker-India and were used as received. Thin layer chromatography (TLC) was carried out on aluminium plates coated with silica gel mixed with fluorescent indicator and was sourced from Merck, Germany. NMR (¹H, ¹³C, DEPT 135 and APT) spectra were recorded on a Bruker 500 MHz spectrometer in CDCl₃ with TMS as a standard. Spin multiplicities are reported as a singlet (s), doublet (d), and triplet (t) with coupling constants (*J*) given in Hz, or multiplet (m). MALDI-TOF mass spectral data were obtained using a Bruker made Auto flex TOF/TOF instrument with laser repetition rate of 50 psec. α -Cyano-4-hydroxycinnamic acid and 1,8,9-Anthracenetriol were used as the matrix for MALDI-TOF mass spectrometry.

UV-vis-NIR and IR Spectroscopy: UV-vis-NIR spectra were recorded on a JASCO V-670UV-vis-NIR Spectrophotometer. All the spectroscopic experiments were carried out in UV Grade Methanol or MeCN which was sourced from Spectrochem, India. Infrared spectra were recorded in KBr pellet using a Varian 3100 FT-IR instrument.

Cyclic and Differential Pulse Voltammetry (CV/DPV): CV and DPV were carried out using a computer controlled potentiostat (CHI 650C) and a standard three electrode arrangement that consisted of both platinum working and auxiliary electrodes and saturated calomel (SCE) as reference electrode. All electrochemical measurements were carried out in Ar-purged DMF with n-Bu₄NPF₆ as the supporting electrolyte. CV studies of the all molecules (0.5 mM) were performed in degassed DMF under Ar atmosphere and the scan rate for the measurements was typically 500 mV/s. DPV was carried out keeping peak amplitude 50 mV, pulse width 0.01 sec, pulse period 0.05 sec and increment E at 20 mV.

Theoretical calculations: The ground-state geometry optimization was carried out applying the density functional theory (DFT) with the Becke three-parameter¹ hybrid exchange functional in concurrence with the Lee-Yang-Parr gradient-corrected correlation function $(B3LYP \text{ functional})^2$ with the 6-311G++(d,p) basis set as implemented in Gaussian 09W.³ All the geometries were optimized without any constrain.

X-ray Crystallography: Crystals of $2a^{4+}4PF6^{-}$ were grown in mixture of solvent using *o*-xylene and acetonitrile solution by slow evaporation method at R.T. The crystals were adequately stable under ambient conditions, losing the crystalline nature upon long exposure to air. The reported data set was collected by mounting the crystal with paratone oil in a loop. X-ray reflections were

collected on Bruker D8 Quest diffractometer with CMOS detector using Mo-K α radiation, generated from the micro-focus sealed tube. Data collection was performed using φ and ω -scans of 0.5° steps at 100 K. Cell determination, data collection and data reduction were performed with the help of Bruker APEX2 (version: 2014.3-0) software. The structure were solved by intrinsic phasing method (SHELXS-97) and refined by full-matrix least squares refinement method based on F², using, SHELXL-2014. A total of 74141 reflections were measured out of which 9119 were independent and 6247 were observed [I > 2\s(I)] for theta 28.38°. All non-hydrogen atoms were refined anisotropically. All non-hydrogen atoms were refined anisotropically. All non-hydrogen atoms were fixed geometrically with their U_{iso} values 1.2 times of the phenylene and methylene carbons and 1.5 times of the methyl carbon using a riding model. A final refinement of 499 parameters has given R1 = 0.0665, wR2 = 0.1811 for the observed data. The ORTEP diagram is given in Figure 2 of the manuscript. The crystal structure data are deposited to Cambridge Structural Database with CCDC number 1478518.

Synthesis of $1a^{2+}$:



In a 50 mL round bottomed (RB) flask containing 15 mL dry p-dioxane, N, N'-dibutyl-2,3dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (500 mg, 0.84 mmol) and 4,4'-bipyridine (518 mg, 3.37 mmol) were added. The mixture was refluxed under N₂ atmosphere. After 24 h, the reaction mixture was gradually brought to room temperature, and then diluted with diethyl ether. The obtained pale orange solid was thoroughly washed with CHCl₃ and then MeCN. Yield = 88%. Melting Point: 268°C. ¹H NMR (500 MHz, MeOD, 300 K): δ = 9.52 (d, *J* = 6.5 Hz, 4H, BiPy⁺*H*), 9.17 (s, 2H, NDI*H*), 8.93 (d, 4H, *J* = 5 Hz, BiPy⁺*H*), 8.84 (d, 4H, *J* = 6.4 Hz, BiPy⁺*H*), 8.18 (d, 4H, *J* = 5 Hz, BiPy⁺*H*), 4.05 (t, 4H, *J* = 7.5 Hz, NDI*CH*₂), 1.66 (p, 4H, *alkylCH*₂), 1.38 (hex, 4H, *CH*₂), 0.94 (t, 6H, *J* = 6.5 Hz, *CH*₃). ¹³C NMR (125 MHz, MeOD, 300 K): δ = 160.61, 160.53, 156.25, 150.59, 146.18, 142.92, 142.12, 130.71, 129.13, 128.46, 125.50, 122.44, 121.69, 40.72, 29.40, 19.87, 12.66. MS (MALDI-TOF, matrix–1,8,9-Anthracenetriol): calculated for C₄₂H₃₆N₆O₄ (m/z) 688.28, found 688.28 (m/z). FTIR (KBr, cm⁻¹): 3423, 3016, 2960, 1713, 1666, 1635, 1319, 1213, 821. Anal Calcd. for C₄₂H₃₆Br₂N₆O₄: C 59.45, H 4.28, N 9.90; Found: C 59.52, H 4.20, N 9.84.

Synthesis of 1b²⁺:



In a 50 mL round bottomed (RB) flask containing 5 mL dry p-dioxane, N, N'-dimesityl-2,3dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (253 mg, 0.38 mmol) and 4,4'-bipyridine (240 mg, 1.53 mmol) were added. The mixture was refluxed under N₂ atmosphere. After 24 h, the reaction mixture was gradually brought to room temperature and then diluted with diethyl ether. The obtained orange solid was thoroughly washed with CHCl₃ MeCN and then MeOH. Yield = 75%. Melting Point: 258°C. ¹H NMR (500 MHz, DMSO, 300 K): δ = 9.63 (d, *J* = 6.5 Hz, 4H, BiPy⁺H), 9.38 (s, 2H, NDIH), 8.93 (d, 4H, *J* = 4 Hz, BiPy⁺H), 8.89 (d, 4H, *J* = 6.5 Hz, BiPy⁺H), 8.15 (d, 4H, *J* = 5.5 Hz, BiPy⁺H), 7.03 (s, 4H, Mes*CH*), 2.27 (s, 6H, Mes*CH*₃), 2.04 (s, 12H, Mes*CH*₃). ¹³C NMR (125 MHz, DMSO, 300 K): δ = 160.61, 160.10, 155.31, 151.56, 146.82, 143.68, 141.12, 139.10, 135.58, 132.88, 130.22, 129.51, 128.79, 128.17, 125.49, 122.63, 122.13, 20.97, 17.86. MS (MALDI-TOF, matrix – 1,8,9-Anthracenetriol): calculated for C₅₂H₄₀N₆O₄ (m/z) 812.31, found 812.22 (m/z). FTIR (KBr, cm⁻¹): 3425, 3025, 2923, 1717, 1676, 1637, 1437, 1329, 1253, 827. Anal Calcd. for C₅₂H₄₀ Br₂N₆O₄: C 64.21, H 4.14, N 8.64; Found: C 64.27, H 4.21, N 8.67.



In a 50 mL round bottomed (RB) flask containing 12 mL dry DMF, $1a^{2+}$ (250 mg, 0.29 mmol) and benzyl bromide (0.541 mL, 4.56 mmol) were added. The mixture heated at 50 °C under N₂ atmosphere. After 24 h, the reaction mixture was gradually brought to room temperature washed with excess of MeCN. The obtained orange solid was thoroughly washed with excess of diethyl ether (70 mL) and followed by MeCN (25 mL). Yield = 90%. Melting Point: 260 °C. ¹H NMR (500 MHz, MeOD, 300 K): $\delta = 9.71$ (d, J = 6.0 Hz, 4H, BiPy²⁺H), 9.43 (d, J = 6.5 Hz, 4H, BiPy²⁺H), 9.17 (s, 2H, NDIH), 8.98 (d, J = 6.5 Hz, 4H, BiPy²⁺H), 8.87 (d, J = 6.5 Hz, 4H, BiPy²⁺H), 7.65 (t, J = 6 Hz,4H, Bz*CH*), 7.55 (m, J = 6 Hz, 6H, Bz*CH*), 6.03 (s, 4H, Bz*CH*₂), 4.03 (t, 4H, J = 7.5 Hz, NDICH₂),), 1.66 (p, 4H, *alkylCH*₂), 1.38 (hex, 4H, *CH*₂), 0.92 (t, 6H, J = 6.5 Hz, *CH*₃). ¹³C NMR (125 MHz, MeOD, 300 K): $\delta = 160.59$, 160.57, 152.27, 150.18, 146.86, 145.83, 142.72, 132.87, 130.58, 129.95, 129.48, 129.19, 129.05, 128.55, 127.47, 126.71, 121.71, 64.66, 40.73, 29.38, 19.88, 12.65. MS (MALDI-TOF, matrix – 1,8,9-Anthracenetriol): calculated for C₅₆H₅₀N₆O₄ (m/z) 870.39, found 870.36 (m/z). FTIR (KBr, cm⁻¹): 3421, 3027, 2958, 1707, 1663, 1635, 1445, 1325, 1213, 1094. Anal Calcd. for C₅₆H₅₀Br₄N₆O₄: C 56.49, H 4.23, N 7.06; Found: C 56.41, H 4.27, N 7.01.

Synthesis of 2b⁴⁺:



In a 50 mL round bottomed (RB) flask containing 7 mL dry DMF, $1b^{2+}$ (300 mg, 0.308 mmol) and benzyl bromide (0.549 mL, 4.626 mmol) were added. The mixture heated at 55 °C under N₂ atmosphere. After 24 h, the reaction mixture was gradually brought to room temperature and then diluted with diethyl ether. The obtained pale yellow solid was thoroughly washed with CHCl₃. MeCN and then MeOH. Yield = 80%. Melting Point: 248 °C. ¹H NMR (500 MHz, MeOD, 300 K): $\delta = 9.85$ (d, J = 6.5 Hz, 4H, BiPy²⁺H), 9.54 (d, J = 6.5 Hz, 4H, BiPy²⁺H), 9.39 (s, 2H, NDIH), 9.01 (d, J = 6.5 Hz, 4H, BiPy²⁺H), 8.88 (d, J = 6.5 Hz, 4H, BiPy²⁺H), 7.62 (d, J = 7 Hz,4H, Bz*CH*), 7.48 (m, 6H, Bz*CH*), 7.01 (s, 4H, Mes*CH*), 5.98 (s, 4H, Bz*CH*₂), 2.27 (s, 6H, Mes*CH*₃), 2.04 (s, 12H, Mes*CH*₃). ¹³C NMR (125 MHz, MeOD, 300 K): $\delta = 160.56$, 160.07, 151.63, 149.37, 147.35, 146.25, 143.57, 139.15, 135.57, 134.41, 130.16, 130.10, 129.82, 129.48, 129.36, 128.78, 128.12, 127.90, 126.82, 122.13, 64.07, 20.95, 17.84. MS (MALDI-TOF, matrix – 1,8,9-Anthracenetriol): calculated for C₆₆H₅₄N₆O₄ (m/z) 994.42, found 994.21 (m/z). FTIR (KBr, cm⁻¹): 3033, 1716, 1677, 1636, 1438, 1329, 1252. Anal Calcd. for C₆₆H₅₄Br₄N₆O₄: C 60.29, H 4.14, N 6.39; Found: C 60.21, H 4.17, N 6.36.

Synthesis of 2c⁴⁺:



In a 50 mL round bottomed (RB) flask containing 6 mL dry DMF, **1a** (150 mg, 0.17 mmol) and 2,3,4,5,6-pentafluoro-benzyl bromide (0.267 mL, 1.76 mmol) were added. The mixture heated at 50 °C under N₂ atmosphere. After 24 h, the reaction mixture was gradually brought to room temperature and diluted with MeCN. The obtained yellow solid was thoroughly washed with excess of diethyl ether (50 mL) and followed by MeCN (25 mL). Yield = 85%. Melting Point: 220 °C. ¹H NMR (500 MHz, MeOD, 300 K): δ = 9.72 (d, *J* = 6.0 Hz, 4H, BiPy²⁺*H*), 9.42 (d, *J* = 6.5 Hz, 4H, BiPy²⁺*H*), 9.17 (s, 2H, NDI*H*), 9.01 (d, *J* = 6.0 Hz, 4H, BiPy²⁺*H*), 8.91 (d, *J* = 6.5 Hz, 4H, BiPy²⁺*H*), 6.26 (s, 4H, Bz*CH*₂), 4.03 (t, 4H, *J* = 7.5 Hz, NDI*CH*₂),), 1.66 (p, 4H, *alkylCH*₂), 1.38 (hex, 4H, *CH*₂), 0.92 (t, 6H, *J* = 6.5 Hz, *CH*₃). ¹³C NMR (125 MHz, MeOD, 300 K): δ = 160.61, 152.04, 150.85, 146.92, 146.32, 142.73, 130.57, 129.23, 128.55, 127.71, 126.82, 121.71, 52.04, 40.78, 29.36, 19.88, 12.67. MS (MALDI-TOF, matrix – 1,8,9-Anthracenetriol): calculated for C₅₆H₄₀F₁₀N₆O₄ (m/z) 1050.29, found 1050.21 (m/z). FTIR (KBr, cm⁻¹): 3421, 3019, 2962, 1707,

1666, 1635, 1510, 1448, 1032. Anal Calcd. For C₅₆H₄₀Br₄F₁₀N₆O₄: C 49.08, H 2.94, N 6.13; Found: C 49.02, H 2.97, N 6.07.

Synthesis of NDI-Py₂²⁺:



In a 50 mL round bottomed (RB) flask containing 6 mL dry p-dioxane, N, N'-dibutyl-2,3dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (150 mg, 0.28 mmol) and pyridine in excess (1.1 gm, 13.98 mmol) were added. The mixture was refluxed under N₂ atmosphere. After 24 h, the reaction mixture was gradually brought to room temperature and diluted with diethyl ether. The obtained pale yellow solid was thoroughly washed with CHCl₃ and then MeCN. Yield = 72%. Melting Point: 290°C. ¹H NMR (500 MHz, MeOD, 300 K): δ = 9.36 (d, *J* = 6 Hz, 4H, Py⁺H), 9.11 (s, 2H, NDI*H*), 8.97 (t, 2H, *J* = 7.5 Hz, Py⁺H), 8.42 (t, 4H, *J* = 7 Hz, Py⁺H), 4.04 (t, 4H, *J* = 7.5 Hz, NDI*CH*₂), 1.66 (p, 4H, *alkylCH*₂), 1.38 (hex, 4H, *CH*₂), 0.94 (t, 6H, *J* = 6.5 Hz, *CH*₃). ¹³C NMR (125 MHz, MeOD, 300 K): 160.61, 160.41, 148.21, 145.63, 143.14, 130.61, 129.09, 128.44, 127.95, 121.61, 40.63, 29.38, 19.84, 12.64. MS (MALDI-TOF, matrix – 1,8,9-Anthracenetriol): calculated for C₃₂H₃₀N₄O₄ (m/z) 534.23, found 534.20 (m/z). FTIR (KBr, cm⁻¹): 3415, 3042, 2962, 1710, 1658, 1626, 1449, 1324, 1272. Anal Calcd. for C₃₂H₃₀Br₂N₄O₄: C 55.35, H 4.35, N 8.07; Found: C 55.40, H 4.39, N 8.02. **Table S1:** Selected bond length and torsion angles of the crystal $2a^{4+}4PF_6^{-}$.

Atoms	Selected Bond length [Å] Crystal Data
C7 – O1, C7' – O1'	1.210 Å
C6 – O2, C6' – O2'	1.213 Å
C6 – N1, C6' –N1'	1.383 Å
C7 – N1, C7' – N1'	1.394 Å
N1 –C8, N1' – C8'	1.483 Å
N2 – C3, N2' – C3'	1.451 Å
N3 – C22, N3' – C22'	1.497 Å
C1 – C6, C1' – C6'	1.486 Å
C4 - C7, C4' - C7'	1.488 Å
C2 - C3, C2' - C3'	1.400 Å
C14 – C17, C14' – C17'	1.483 Å

Atom	Selected Dihedral angles (Degree)
C2 - C3 - N2 - C12, C2' - C3' - N2' - C12'	67.65°
C4 – N3 – C2 – C16, C4' – N3' – C2' – C16'	65.57°
C13 - C14 - C17 - C18, C13' - C14' - C17' - C18'	-32.52°
C15 - C14 - C17 - C21, C15' - C14' - C17' - C21'	-31.75°
N3 - C22 - C23 - C28, N3' - C22' - C23' - C28'	113.08°
N3 - C22 - C23 - C24, N3' - C22' - C23' - C24'	-66.57°

Table S2: P-F--- π non-bonding interactions in crystal of $2a^{4+}4PF_6^-$.

P–F π , Anion- π Interactions			
	Fπ (Å)	Ρ π (Å)	
(Ct1), (Ct1')	2.865	4.066	
(Ct2), (Ct2')	3.018	4.067	

Mol.		E ¹ _{red}	E ² _{red}	E ³ _{red}	E ⁴ _{red}	E ⁵ _{red}	E ⁶ red	HOMO ^e
1a ²⁺	$\frac{\mathrm{E}_{1/2}\mathrm{vs.\;SCE}}{\mathrm{(V)}^a}$	-0.00	-0.40	-1.02	-1.15	-1.76		-7.870 eV
	$\Delta E_{\rm p} ({\rm mV})^b$	66	78	64	74	-1.61 ^d	-1.83 ^d	
	I_{pa}/I_{pc}^{c}	1.15	1.43	n.d.	n.d.			
1b ²⁺	E _{1/2} vs. SCE (V)	0.07	-0.33	-1.00	-1.11		•••••	
	$\Delta E_{p} (mV)$	67	76	58	76			
	I_{pa}/I_{pc}	0.91	1.00	n.d.	n.d.			
2a ⁴⁺	E _{1/2} vs. SCE (V)	0.05	-0.21	-0.31	-0.64	-0.82	-1.04	-7.674 eV
	$\Delta E_{\rm p} ({\rm mV})$	77	54	64	72	82	76	
	I_{pa}/I_{pc}	1.04	n.d.	n.d.	1.14	0.97	0.81	
2b ⁴⁺	E _{1/2} vs. SCE (V)	0.09	-0.22	-0.34	-0.64	-0.83	-1.03	
	$\Delta E_{p} (mV)$	79	64	79	77	81	73	
	I_{pa}/I_{pc}	0.97	n.d.	n.d.	1.3	0.94	1.00	
2c ⁴⁺	E _{1/2} vs. SCE (V)	0.05	-0.18	-0.27	-0.58	-0.75	-1.00	-7.917 eV
	$\Delta E_{p} (mV)$	70	61	56	74	78	78	
	I _{pa} /I _{pc}	0.98	n.d.	n.d.	1.3	0.82	0.92	

Table S3. Voltammetric data of $1a^{2+}$ to $2c^{4+}$.

- a) $E_{1/2} = (E_{pa} + E_{pc})/2$ at 0.500 V s⁻¹.
- b) $\Delta Ep = Epa-Epc \text{ at } 0.500V \text{ s}^{-1}$.
- c) $I_{pa}/I_{pc} = Ratio of the anodic to cathodic peak currents.$
- *d*) *At* -30 °C.
- e) Calculated by DFT [B3LYP/6311++g(dp) (IEFPCM-DMF)].

n.d. = not determined (All four CV spectra have two electron redox couple peaks, for them I_{pa} and I_{pc} value could not be calculated).

Table S4: Calculated dihedral angles and bond distance for all seven redox states of compound $1a^{2+}$ by DFT calculations [B3LYP/6311++g(dp) and UB3LYP/6311++g(dp) (IEFPCM-DMF)].

Entry	Dihedral angle b/w two hetrocyclic rings of Bipyridinium	Dihedral angle b/w NDI & Bipyridinium	Distance of C-C bond of two hetrocylclic rings of Bipyridinium	Distance of C-N Bond b/w NDI & Bipyridinium
$1a^{2+}$	31.95°	87.00°	1.47 Å	1.45Å
1a ^{+.}	28.00°	56.53°	1.47 Å	1.44 Å
1a	13.12°	48.47°	1.44 Å	1.42 Å
1a ⁻	4.32°	51.62°	1.42 Å	1.42 Å
1a ²⁻	1.70°	45.22°	1.39 Å	1.40 Å

Table S5: Calculated value of selected dihedral angle and bond distance for all seven redox states of compound $2a^{4+}$ by DFT calculation on UB3LYP/6311++g(dp) (IEFPCM-DMF).

Entry	Dihedral angle b/w two hetrocyclic rings of Bipyridinium	Dihedral angle b/w NDI & Bipyridinium	Distance of C-C bond of two hetrocylclic rings of Bipyridinium	Distance of C-N Bond b/w NDI & Bipyridinium
$2a^{4+}$	41.74°	88.48°	1.48 Å	1.46 Å
$2a^{3+.}$	28.00°	56.53°	1.47 Å	1.44 Å
$2a^{2+}$	13.12°	48.47°	1.44 Å	1.42 Å
2a ^{+.}	4.31 °	51.61°	1.42 Å	1.42 Å
2a	1.70°	45.22°	1.39 Å	1.40 Å
2a	0.92°	52.12°	1.38 Å	1.42 Å
$2a^{2-}$	0.69°	59.37°	1.39 Å	1.44 Å



Figure S1: a) POV-ray diagram of $2a^{4+}4PF_6^-$ showing the atom numbering scheme, b) Space filing model showing the anion- π interactions in $2a^{4+}$.



Figure S2: DPV plots in degassed DMF (5×10^{-4} M) at RT.



Figure S3: CV results of $1b^{2+}$ at -30 °C.



Figure S4: 1–100 CV redox scans of $2a^{4+}$ in degassed DMF (5 × 10⁻⁴ M) at RT.



Figure S5. Calculated spin density plot of $1a^{2+}$, occupied with 2 (1a), 3 ($1a^{-}$), and 4 ($1a^{2-}$) electrons bottom to top respectively.



Figure S6. Calculated spin density plot of $2a^{4+}$, occupied with 2 $(2a^{2+})$, 3 $(2a^{+})$, and 4 (2a) electrons (left side), 4 (2a), 5 $(2a^{-})$, and 6 $(2a^{2-})$ electrons (right side) bottom to top respectively.



Figure S7: ESP maps of $2a^{4+}$ with successive addition of electrons [B3LYP/6-311++G(d,p)], ESP contours are colour-coded from red (electron-rich) to blue (electron-deficient).



Figure S8: UV-vis-NIR spectra showing the spectral response of $1a^{2+}2PF_6$ (4 × 10⁻⁵ M) (a), $2a^{4+}4PF_6$ (4 × 10⁻⁵ M) (b) in MeCN with gradual addition of Na₂S.



Figure 9: UV-vis-NIR spectra showing the light stability of $2a^{4+}$ (4 × 10⁻⁴ M) in H₂O with the exposure of light: in diffused laboratory CFL light (a), direct exposure to CFL light (15 W) with a distance of ~27 cm.



Figure S10: FT-IR spectra of 1a²⁺, 1b²⁺, 2a⁴⁺, 2b⁴⁺, 2c⁴⁺ and NDI-Py₂²⁺.



Figure S11: MALDI-TOF mass spectrum of 1a²⁺.



Figure S12: MALDI-TOF mass spectrum of 1b²⁺.



Figure S13: MALDI-TOF mass spectrum of 2a⁴⁺.



Figure S14: MALDI-TOF mass spectrum of 2b⁴⁺.



Figure S15: MALDI-TOF mass spectrum of 2c⁴⁺.



Figure S16: MALDI-TOF mass spectrum of **NDI-Py**₂²⁺.



Figure S17: 500 MHz ¹H NMR spectrum of $1a^{2+}$ in deuterated MeOH at room temperature.



Figure S18: 125 MHz ¹³C, DEPT-135 and APT spectra of $1a^{2+}$ in deuterated MeOH at room temperature.



Figure S19: 500 MHz ¹H NMR spectrum of $1b^{2+}$ in deuterated DMSO at room temperature.



Figure S20: 125 MHz ¹³C, DEPT-135 and APT spectra of $1b^{2+}$ in deuterated MeOH at room temperature.



Figure S21: 500 MHz ¹H NMR spectrum of $2a^{4+}$ in deuterated MeOH at room temperature.



Figure S22: 125 MHz ¹³C, DEPT-135 and APT spectra of $2a^{4+}$ in deuterated MeOH at room temperature.



Figure S23: 500 MHz ¹H NMR spectrum of $2b^{4+}$ in deuterated MeOH at room temperature.



Figure S24: 125 MHz ¹³C, DEPT-135 and APT spectra of **2b**⁴⁺ in deuterated MeOH at room temperature.



Figure S25: 500 MHz ¹H NMR spectrum of $2c^{4+}$ in deuterated MeOH at room temperature.



Figure S26: 125 MHz ¹³C, DEPT-135 and APT spectra of $2c^{4+}$ in deuterated MeOH at room temperature.



Figure S27: 500 MHz ¹H NMR spectrum of $NDI-Py_2^{2+}$ in deuterated MeOH at room temperature.



Figure S28: 125 MHz ¹³C, DEPT-135 and APT spectra of $NDI-Py_2^{2+}$ in deuterated MeOH at room temperature.

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