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Supporting Information

Pyrazolium salts as a new class of ionic liquid crystals

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Pyrazolium compounds of the type $[H_2pz^{R(n)}][A]$ ([A] = Cl^-, BF_4^-, ReO_4^-, SbF_6^-, $CF_3SO_3^-$, CH_3-*p*-$C_6H_4SO_3^-$; R = $C_6H_4OC_nH_{2n+1}$, n = 1, 8, 10, 12, 14, 16, 18)

$[H_2pz^{R(1)}][Cl]$ (Cl-1): colourless solid (42%). Elemental analysis: Found: C, 56.6; H, 5.2; N, 13.3%. $C_{10}H_{11}N_2OCl$ requires C, 57.0; H, 5.3; N, 13.3%. ν_{max}(KBr)/cm^{-1}: 3152, 3083 ν(NH), 1610 ν(C=C + C=N). δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.87 (3 H, s, CH_3), 6.72 (1 H, d, *J* 2.8, H4), 7.05 (2 H, d, *J* 8.9, H_m), 7.91 (1 H, d, *J* 2.8, H5), 7.96 (2 H, d, *J* 8.9, H_o).

$[H_2pz^{R(8)}][Cl]$ (Cl-8): colourless solid (80%). Elemental analysis: Found: C, 65.8; H, 7.8; N, 9.1%. $C_{17}H_{25}N_2OCl$ requires C, 66.1; H, 8.2; N, 9.1%. ν_{max}(KBr)/cm^{-1}: 3144, 3080 ν(NH), 1615 ν(C=C + C=N). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.89 (3 H, t, *J* 6.7, CH_3), 1.30 (10 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.01 (2 H, t, *J* 6.7, OCH_2), 6.71 (1 H, d, *J* 2.8, H4), 7.02 (2 H, d, *J* 8.9, H_m), 7.90 (1 H, d, *J* 2.8, H5), 7.93 (2 H, d, *J* 8.9, H_o).

$[H_2pz^{R(10)}][Cl]$ (Cl-10): colourless solid (86%). Elemental analysis: Found: C, 67.9; H, 8.4; N, 8.4%. $C_{19}H_{29}N_2OCl$ requires C, 67.7; H, 8.7; N, 8.3%. ν_{max}(KBr)/cm^{-1}: 3144, 3083 ν(NH), 1615 ν(C=C + C=N). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.27 (14 H, m, CH_2), 1.80 (2 H, m, CH_2), 4.00 (2 H, t, *J* 6.7, OCH_2), 6.71 (1 H, d, *J* 2.8, H4), 7.02 (2 H, d, *J* 8.9, H_m), 7.91 (1 H, d, *J* 2.8, H5), 7.93 (2 H, d, *J* 8.9, H_o).

$[H_2pz^{R(12)}][Cl]$ (Cl-12): colourless solid (87%). Elemental analysis: Found: C, 68.9; H, 8.9; N, 7.9%. $C_{21}H_{33}N_2OCl$ requires C, 69.1; H, 9.1; N, 7.7%. ν_{max}(KBr)/cm^{-1}: 3144, 3083 ν(NH), 1615 ν(C=C + C=N). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.27 (18 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.01 (2 H, t, *J* 6.7, OCH_2), 6.71 (1 H, d, *J* 2.8, H4), 7.02 (2 H, d, *J* 8.9, H_m), 7.90 (1 H, d, *J* 2.8, H5), 7.93 (2 H, d, *J* 8.9, H_o).

$[H_2pz^{R(14)}][Cl]$ (Cl-14): colourless solid (76%). Elemental analysis: Found: C, 69.9; H, 9.1; N, 7.2%. $C_{23}H_{37}N_2OCl$ requires C, 70.3; H, 9.4; N, 7.1%. ν_{max}(KBr)/cm^{-1}: 3145, 3082 ν(NH), 1615 ν(C=C + C=N). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (22 H, m, CH_2), 1.80 (2 H, m, CH_2), 4.01 (2 H, t, *J* 6.7, OCH_2), 6.71 (1 H, d, *J* 2.8, H4), 7.02 (2 H, d, *J* 8.9, H_m), 7.90 (1 H, d, *J* 2.8, H5), 7.93 (2 H, d, *J* 8.9, H_o).

$[H_2pz^{R(16)}][Cl]$ (Cl-16): colourless solid (82%). Elemental analysis: Found: C, 71.2; H, 9.5; N, 6.6%. $C_{25}H_{41}N_2OCl$ requires C, 71.3; H, 9.8; N, 6.6%. ν_{max}(KBr)/cm^{-1}: 3145, 3082 ν(NH), 1615 ν(C=C + C=N). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (26 H, m, CH_2), 1.80 (2 H, m, CH_2), 4.01 (2 H, t, *J* 6.7, OCH_2), 6.71 (1 H, d, *J* 2.8, H4), 7.02 (2 H, d, *J* 8.9, H_m), 7.90 (1 H, d, *J* 2.8, H5), 7.93 (2 H, d, *J* 8.9, H_o).

$[H_2pz^{R(18)}][Cl]$ (Cl-18): colourless solid (83%). Elemental analysis: Found: C, 71.8; H, 9.8; N, 6.2%. $C_{27}H_{45}N_2OCl$ requires C, 72.2; H, 10.1; N, 6.2%. ν_{max}(KBr)/cm^{-1}: 3145, 3083 ν(NH), 1616 ν(C=C + C=N). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (30 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.71 (1 H, d, *J* 2.8, H4), 7.02 (2 H, d, *J* 8.9, H_m), 7.90 (1 H, d, *J* 2.8, H5), 7.93 (2 H, d, *J* 8.9, H_o).

$[H_2pz^{R(8)}][BF_4]$ (BF_4-8): pale yellow solid (69%). Elemental analysis: Found: C, 57.0; H, 6.9; N, 7.8%. $C_{17}H_{25}N_2OBF_4$ requires C, 56.7; H, 7.0; N, 7.8%. ν_{max}(KBr)/cm^{-1}: 3385, 3241 ν(NH), 1615 ν(C=C + C=N), 1083 ν(B-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.89 (3 H, t, *J* 6.7, CH_3), 1.30 (10 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.81 (1 H, d, *J* 2.8, H4), 7.02 (2 H, d, *J* 8.9, H_m), 7.67 (2 H, d, *J* 8.9, H_o), 8.14 (1 H, d, *J* 2.8, H5), 12.83 (br s, NH), 13.27 (br s, NH).

$[H_2pz^{R(10)}][BF_4]$ (BF_4-10): pale yellow solid (73%). Elemental analysis: Found: C, 58.3; H, 7.3; N, 7.1%. $C_{19}H_{29}N_2OBF_4$ requires C, 58.8; H, 7.5; N, 7.2%. ν_{max}(KBr)/cm^{-1}: 3371, 3242 ν(NH), 1615 ν(C=C + C=N), 1083 ν(B-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.29 (14 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.01 (2 H, t, *J* 6.7, OCH_2), 6.81 (1 H, d, *J* 2.8, H4), 7.02 (2 H, d, *J* 8.9, H_m), 7.67 (2 H, d, *J* 8.9, H_o), 8.12 (1 H,

d, *J* 2.8, H5).

[$H_2pz^{R(12)}$][BF_4] (BF_4-12): pale yellow solid (79%). Elemental analysis: Found: C, 60.3; H, 7.7; N, 6.5%. $C_{21}H_{33}N_2OBF_4$ requires C, 60.6; H, 8.0; N, 6.7%. ν_{max}(KBr)/cm^{-1}: 3375, 3236 ν(NH), 1616 ν(C=C + C=N), 1083 ν(B-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.27 (18 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.81 (1 H, d, *J* 2.8, H4), 7.02 (2 H, d, *J* 8.9, H_m), 7.67 (2 H, d, *J* 8.9, H_o), 8.10 (1 H, d, *J* 2.8, H5).

[$H_2pz^{R(14)}$][BF_4] (BF_4-14): pale yellow solid (72%). Elemental analysis: Found: C, 61.9; H, 8.1; N, 6.2%. $C_{23}H_{37}N_2OBF_4$ requires C, 62.2; H, 8.4; N, 6.3%. ν_{max}(KBr)/cm^{-1}: 3388, 3250 ν(NH), 1616 ν(C=C + C=N), 1087 ν(B-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.27 (22 H, m, CH_2), 1.82 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.81 (1 H, d, *J* 2.8, H4), 7.03 (2 H, d, *J* 8.9, H_m), 7.67 (2 H, d, *J* 8.9, H_o), 8.07 (1 H, d, *J* 2.8, H5).

[$H_2pz^{R(16)}$][BF_4] (BF_4-16): pale yellow solid (75%). Elemental analysis: Found: C, 63.3; H, 8.4; N, 5.7%. $C_{25}H_{41}N_2OBF_4$ requires C, 63.6; H, 8.7; N, 5.9%. ν_{max}(KBr)/cm^{-1}: 3385, 3250 ν(NH), 1617 ν(C=C + C=N), 1083 ν(B-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (26 H, m, CH_2), 1.82 (2 H, m, CH_2), 4.03 (2 H, t, *J* 6.7, OCH_2), 6.82 (1 H, d, *J* 2.8, H4), 7.03 (2 H, d, *J* 8.9, H_m), 7.67 (2 H, d, *J* 8.9, H_o), 8.08 (1 H, d, *J* 2.8, H5).

[$H_2pz^{R(18)}$][BF_4] (BF_4-18): pale yellow solid (70%). Elemental analysis: Found: C, 65.2; H, 8.8; N, 5.6%. $C_{27}H_{45}N_2OBF_4$ requires C, 64.8; H, 9.1; N, 5.6%. ν_{max}(KBr)/cm^{-1}: 3383, 3249 ν(NH), 1619 ν(C=C + C=N), 1084 ν(B-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (30 H, m, CH_2), 1.82 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.82 (1 H, d, *J* 2.8, H4), 7.03 (2 H, d, *J* 8.9, H_m), 7.67 (2 H, d, *J* 8.9, H_o), 8.03 (1 H, d, *J* 2.8, H5).

[$H_2pz^{R(1)}$][ReO_4] (ReO_4-1): colourless solid (45%). Elemental analysis: Found: C, 27.9; H, 2.5; N, 6.4%. $C_{10}H_{11}N_2O_5Re$ requires C, 28.2; H, 2.6; N, 6.6%. ν_{max}(KBr)/cm^{-1}: 3138, 3121 ν(NH), 1617 ν(C=C + C=N), 896 ν(Re-O). δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.87 (3 H, s, CH_3), 6.83 (1 H, d, *J* 2.3, H4), 6.98 (2 H, d, *J* 8.7, H_m), 7.70 (2 H, d, *J* 8.7, H_o), 7.91 (1 H, d, *J* 2.3, H5).

[$H_2pz^{R(8)}$][ReO_4] (ReO_4-8): colourless solid (75%). Elemental analysis: Found: C, 38.7; H, 4.8; N, 5.4%. $C_{17}H_{25}N_2O_5Re$ requires C, 39.0; H, 4.8; N, 5.4%. ν_{max}(KBr)/cm^{-1}: 3144, 3124 ν(NH), 1616 ν(C=C + C=N), 908 ν(Re-O). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.89 (3 H, t, *J* 6.7, CH_3), 1.29 (10 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.79 (1 H, d, *J* 2.3, H4), 7.04 (2 H, d, *J* 8.7, H_m), 7.72 (2 H, d, *J* 8.7, H_o), 7.93 (1 H, d, *J* 2.3, H5).

[$H_2pz^{R(10)}$][ReO_4] (ReO_4-10): colourless solid (77%). Elemental analysis: Found: C, 41.4; H, 5.3; N, 5.3%. $C_{19}H_{29}N_2O_5Re$ requires C, 41.4; H, 5.3; N, 5.1%. ν_{max}(KBr)/cm^{-1}: 3144, 3124 ν(NH), 1617 ν(C=C + C=N), 906 ν(Re-O). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.28 (14 H, m, CH_2), 1.80 (2 H, m, CH_2), 4.00 (2 H, t, *J* 6.7, OCH_2), 6.74 (1 H, d, *J* 2.3, H4), 7.00 (2 H, d, *J* 8.7, H_m), 7.70 (2 H, d, *J* 8.7, H_o), 7.92 (1 H, d, *J* 2.3, H5).

[$H_2pz^{R(12)}$][ReO_4] (ReO_4-12): colourless solid (76%). Elemental analysis: Found: C, 43.0; H, 5.5; N, 4.8%. $C_{21}H_{33}N_2O_5Re$ requires C, 43.5; H, 5.7; N, 4.8%. ν_{max}(KBr)/cm^{-1}: 3145, 3125 ν(NH), 1617 ν(C=C + C=N), 904 ν(Re-O). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.27 (18 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.80 (1 H, d, *J* 2.3, H4), 7.02 (2 H, d, *J* 8.7, H_m), 7.72 (2 H, d, *J* 8.7, H_o), 7.93 (1 H, d, *J* 2.3, H5).

[$H_2pz^{R(14)}$][ReO_4] (ReO_4-14): colourless solid (70%). Elemental analysis: Found: C, 45.9; H, 6.1; N, 4.8%. $C_{23}H_{37}N_2O_5Re$ requires C, 45.5; H, 6.1; N, 4.6%. ν_{max}(KBr)/cm^{-1}: 3146, 3126 ν(NH), 1616 ν(C=C + C=N), 905 ν(Re-O). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (22 H, m, CH_2), 1.79 (2 H, m, CH_2), 3.99 (2 H, t, *J* 6.7, OCH_2), 6.84 (1 H, d, *J* 2.3, H4), 6.96 (2 H, d, *J* 8.7, H_m), 7.68 (2 H, d, *J* 8.7, H_o), 7.92 (1 H, d, *J* 2.3, H5).

[$H_2pz^{R(16)}$][ReO_4] (ReO_4-16): colourless solid (62%). Elemental analysis: Found: C, 47.3; H, 6.5; N, 4.4%. $C_{25}H_{41}N_2O_5Re$ requires C, 47.2; H, 6.5; N, 4.4%. ν_{max}(KBr)/cm^{-1}: 3148, 3128 ν(NH), 1618 ν(C=C + C=N), 906 ν(Re-O). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (26 H, m, CH_2), 1.80 (2 H, m, CH_2), 3.99 (2 H, t, *J* 6.7, OCH_2), 6.83 (1 H, d, *J* 2.3, H4), 6.96 (2 H, d, *J* 8.7, H_m), 7.66 (2 H, d, *J* 8.7, H_o), 7.92 (1 H, d, *J* 2.3, H5).

[$H_2pz^{R(18)}$][ReO_4] (ReO_4-18): colourless solid (65%). Elemental analysis: Found: C, 48.8; H, 6.7; N, 4.0%. $C_{27}H_{45}N_2O_5Re$ requires C, 48.8; H, 6.8; N, 4.2%. ν_{max}(KBr)/cm^{-1}: 3147, 3127 ν(NH), 1617 ν(C=C + C=N), 904 ν(Re-O). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (30 H, m, CH_2), 1.80 (2 H, m, CH_2), 3.99 (2 H, t, *J* 6.7, OCH_2), 6.83 (1 H, d, *J* 2.3, H4), 6.96 (2 H, d, *J* 8.7, H_m), 7.67 (2 H, d, *J* 8.7, H_o), 7.92 (1 H, d, *J* 2.3, H5).

[$H_2pz^{R(8)}$][SbF_6] (SbF_6-8): colourless solid (49%). Elemental analysis: Found: C, 40.5; H, 4.9; N, 5.6%. $C_{17}H_{25}N_2OSbF_6$ requires C, 40.1; H, 5.0; N, 5.5%. ν_{max}(KBr)/cm^{-1}: 3336, 3167 ν(NH), 1616 ν(C=C + C=N), 665 ν(Sb-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.90 (3 H, t, *J* 6.7, CH_3), 1.30 (10 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.01 (2 H, t, *J* 6.7, OCH_2), 6.74 (1 H, d, *J* 2.4, H4), 7.01 (2 H, d, *J* 8.3, H_m), 7.63 (2 H, d, *J* 8.3, H_o), 7.87 (1 H, d, *J* 2.4, H5).

[$H_2pz^{R(10)}$][SbF_6] (SbF_6-10): colourless solid (62%). Elemental analysis: Found: C, 42.7; H, 5.3; N, 5.3%. $C_{19}H_{29}N_2OSbF_6$ requires C, 42.5; H, 5.4; N, 5.2%. ν_{max}(KBr)/cm^{-1}: 3341, 3168 ν(NH), 1615 ν(C=C + C=N), 666 ν(Sb-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.28 (14 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.01 (2 H, t, *J* 6.7, OCH_2), 6.70 (1 H, d, *J* 2.4, H4), 6.99 (2 H, d, *J* 8.3, H_m), 7.63 (2 H, d, *J* 8.3, H_o), 7.80 (1 H, d, *J* 2.4, H5).

[$H_2pz^{R(12)}$][SbF_6] (SbF_6-12): colourless solid (59%). Elemental analysis: Found: C, 44.2; H, 5.6; N, 4.9%. $C_{21}H_{33}N_2OSbF_6$ requires C, 44.6; H, 5.9; N, 5.0%. ν_{max}(KBr)/cm^{-1}: 3338, 3168 ν(NH), 1614 ν(C=C + C=N), 665 ν(Sb-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (18 H, m, CH_2), 1.82 (2 H, m, CH_2), 4.04 (2 H, t, *J* 6.7, OCH_2), 6.82 (1 H, d, *J* 2.4, H4), 7.07 (2 H, d, *J* 8.3, H_m), 7.64 (2 H, d, *J* 8.3, H_o), 7.89 (1 H, d, *J* 2.4, H5).

[$H_2pz^{R(14)}$][SbF_6] (SbF_6-14): colourless solid (62%). Elemental analysis: Found: C, 46.5; H, 5.9; N, 4.7%. $C_{23}H_{37}N_2OSbF_6$ requires C, 46.6; H, 6.2; N, 4.7%. ν_{max}(KBr)/cm^{-1}: 3338, 3170 ν(NH), 1614 ν(C=C + C=N), 666 ν(Sb-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (22 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.03 (2 H, t, *J* 6.7, OCH_2), 6.85 (1 H, d, *J* 2.4, H4), 7.05 (2 H, d, *J* 8.3, H_m), 7.65 (2 H, d, *J* 8.3, H_o), 7.92 (1 H, d, *J* 2.4, H5).

[$H_2pz^{R(16)}$][SbF_6] (SbF_6-16): colourless solid (43%). Elemental analysis: Found: C, 47.9; H, 6.6; N, 4.5%. $C_{25}H_{41}N_2OSbF_6$ requires C, 48.3; H, 6.6; N, 4.5%. ν_{max}(KBr)/cm^{-1}: 3340, 3170 ν(NH), 1616 ν(C=C + C=N), 653 ν(Sb-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (26 H, m, CH_2), 1.80 (2 H, m, CH_2), 3.99 (2 H, t, *J* 6.7, OCH_2), 6.80 (1 H, d, *J* 2.4, H4), 6.96 (2 H, d, *J* 8.3, H_m), 7.65 (2 H, d, *J* 8.3, H_o), 7.86 (1 H, d, *J* 2.4, H5)

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[$H_2pz^{R(18)}$][SbF_6] (SbF_6-18): colourless solid (55%). Elemental analysis: Found: C, 50.0; H, 6.7; N, 4.4%. $C_{27}H_{45}N_2OSbF_6$ requires C, 49.9; H, 7.0; N, 4.3%. ν_{max}(KBr)/cm^{-1}: 3338, 3170 ν(NH), 1616 ν(C=C + C=N), 651 ν(Sb-F). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (30 H, m, CH_2), 1.80 (2 H, m, CH_2), 3.99 (2 H, t, *J* 6.7, OCH_2), 6.79 (1 H, d, *J* 2.4, H4), 6.96 (2 H, d, *J* 8.3, H_m), 7.67 (2 H, d, *J* 8.3, H_o), 7.87 (1 H, d, *J* 2.4, H5).

[$H_2pz^{R(1)}$][OTf] (OTf-1): colourless solid (67%). Elemental analysis: Found: C, 41.1; H, 3.5; N, 8.7; S, 9.7%. $C_{11}H_{11}N_2SO_4F_3$ requires C, 40.7; H, 3.4; N, 8.6; S, 9.9%. ν_{max}(KBr)/cm^{-1}: 3145 ν(NH), 1615 ν(C=C + C=N), 1260, 1026 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 3.88 (3 H, s, CH_3), 6.78 (1 H, d, *J* 2.8, H4), 7.04 (2 H, d, *J* 8.8, H_m), 7.71 (2 H, d, *J* 8.8, H_o), 8.08 (1 H, d, *J* 2.8, H5).

[$H_2pz^{R(8)}$][OTf] (OTf-8): colourless solid (75%). Elemental analysis: Found: C, 50.9; H, 5.8; N, 6.6; S, 7.6%. $C_{18}H_{25}N_2SO_4F_3$ requires C, 51.2; H, 6.0; N, 6.6; S, 7.6%. ν_{max}(KBr)/cm^{-1}: 3136 ν(NH), 1618 ν(C=C + C=N), 1257, 1032 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.90 (3 H, t, *J* 6.7, CH_3), 1.30 (10 H, m, CH_2), 1.82 (2 H, m, CH_2), 4.03 (2 H, t, *J* 6.7, OCH_2), 6.79 (1 H, d, *J* 2.8, H4), 7.03 (2 H, d, *J* 8.8, H_m), 7.70 (2 H, d, *J* 8.8, H_o), 8.11 (1 H, d, *J* 2.8, H5), 13.67 (br s, NH), 14.51 (br s, NH).

[$H_2pz^{R(10)}$][OTf] (OTf-10): colourless solid (77%). Elemental analysis: Found: C, 53.1; H, 6.3; N, 6.2; S, 7.1%. $C_{20}H_{29}N_2SO_4F_3$ requires C, 53.3; H, 6.5; N, 6.2; S, 7.1%. ν_{max}(KBr)/cm^{-1}: 3137 ν(NH), 1619 ν(C=C + C=N), 1257, 1031 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.29 (14 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.78 (1 H, d, *J* 2.8, H4), 7.03 (2 H, d, *J* 8.8, H_m), 7.70 (2 H, d, *J* 8.8, H_o), 8.10 (1 H, d, *J* 2.8, H5).

[$H_2pz^{R(12)}$][OTf] (OTf-12): colourless solid (81%). Elemental analysis: Found: C, 54.8; H, 6.6; N, 5.8; S,

6.5%. $C_{22}H_{33}N_2SO_4F_3$ requires C, 55.2; H, 6.9; N, 5.8; S, 6.7%. ν_{max}(KBr)/cm^{-1}: 3137 ν(NH), 1618 ν(C=C + C=N), 1257, 1031 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.27 (18 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.78 (1 H, d, *J* 2.8, H4), 7.03 (2 H, d, *J* 8.8, H_m), 7.70 (2 H, d, *J* 8.8, H_o), 8.08 (1 H, d, *J* 2.8, H5).

[$H_2pz^{R(14)}$][OTf] (OTf-14): colourless solid (80%). Elemental analysis: Found: C, 57.2; H, 7.4; N, 5.7; S, 6.6%. $C_{24}H_{37}N_2SO_4F_3$ requires C, 56.9; H, 7.4; N, 5.5; S, 6.3%. ν_{max}(KBr)/cm^{-1}: 3138 ν(NH), 1618 ν(C=C + C=N), 1257, 1032 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.27 (22 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.78 (1 H, d, *J* 2.8, H4), 7.03 (2 H, d, *J* 8.8, H_m), 7.72 (2 H, d, *J* 8.8, H_o), 8.10 (1 H, d, *J* 2.8, H5).

[$H_2pz^{R(16)}$][OTf] (OTf-16): colourless solid (72%). Elemental analysis: Found: C, 58.4; H, 7.5; N, 5.2; S, 5.9%. $C_{26}H_{41}N_2SO_4F_3$ requires C, 58.4; H, 7.7; N, 5.3; S, 6.0%. ν_{max}(KBr)/cm^{-1}: 3137 ν(NH), 1618 ν(C=C + C=N), 1258, 1031 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (26 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.79 (1 H, d, *J* 2.8, H4), 7.03 (2 H, d, *J* 8.8, H_m), 7.69 (2 H, d, *J* 8.8, H_o), 8.07 (1 H, d, *J* 2.8, H5).

[$H_2pz^{R(18)}$][OTf] (OTf-18): colourless solid (69%). Elemental analysis: Found: C, 60.2; H, 7.8; N, 5.0; S, 5.3%. $C_{28}H_{45}N_2SO_4F_3$ requires C, 59.8; H, 8.1; N, 5.0; S, 5.7%. ν_{max}(KBr)/cm^{-1}: 3137 ν(NH), 1619 ν(C=C + C=N), 1256, 1032 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (30 H, m, CH_2), 1.81 (2 H, m, CH_2), 4.02 (2 H, t, *J* 6.7, OCH_2), 6.80 (1 H, d, *J* 2.8, H4), 7.03 (2 H, d, *J* 8.8, H_m), 7.73 (2 H, d, *J* 8.8, H_o), 8.07 (1 H, d, *J* 2.8, H5).

[$H_2pz^{R(1)}$][PTS] (PTS-1): colourless solid (68%). Elemental analysis: Found: C, 58.7; H, 5.2; N, 8.0; S, 9.2%. $C_{14}H_{18}N_2SO_4$ requires C, 58.9; H, 5.2; N, 8.1; S, 9.3%. ν_{max}(KBr)/cm^{-1}: 3196, 3135 ν(NH), 1615 ν(C=C + C=N), 1186, 1030 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 2.36 (3 H, s, CH_3(PTS)), 3.85 (3 H, s, CH_3), 6.70 (1 H, d, *J* 2.7, H4), 6.97 (2 H, d, *J* 8.7, H_m), 7.19 (2 H, d, *J* 8.1, H_o(PTS)), 7.75 (2 H, d, *J* 8.7, H_o), 7.85 (2 H, d, *J* 8.1, H_m(PTS)), 8.09 (1 H, d, *J* 2.7, H5).

[$H_2pz^{R(8)}$][PTS] (PTS-8): colourless solid (85%). Elemental analysis: Found: C, 64.7; H, 7.1; N, 6.3; S, 7.1%. $C_{24}H_{32}N_2SO_4$ requires C, 64.8; H, 7.2; N, 6.3; S, 7.2%. ν_{max}(KBr)/cm^{-1}: 3218, 3136 ν(NH), 1617 ν(C=C + C=N), 1186, 1021 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.89 (3 H, t, *J* 6.7, CH_3), 1.29 (10 H, m, CH_2), 1.80 (2 H, m, CH_2), 2.36 (3 H, s, CH_3(PTS)), 3.99 (2 H, t, *J* 6.7, OCH_2), 6.70 (1 H, d, *J* 2.7, H4), 6.97 (2 H, d, *J* 8.7, H_m), 7.20 (2 H, d, *J* 8.1, H_o(PTS)), 7.73 (2 H, d, *J* 8.7, H_o), 7.84 (2 H, d, *J* 8.1, H_m(PTS)), 8.05 (1 H, d, *J* 2.7, H5).

[$H_2pz^{R(10)}$][PTS] (PTS-10): colourless solid (83%). Elemental analysis: Found: C, 66.3; H, 7.5; N, 5.9; S, 6.8%. $C_{26}H_{36}N_2SO_4$ requires C, 66.1; H, 7.7; N, 5.9; S, 6.8%. ν_{max}(KBr)/cm^{-1}: 3221, 3139 ν(NH), 1616 ν(C=C + C=N), 1176, 1027 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.27 (14 H, m, CH_2), 1.79 (2 H, m, CH_2), 2.36 (3 H, s, CH_3(PTS)), 3.99 (2 H, t, *J* 6.7, OCH_2), 6.70 (1 H, d, *J* 2.7, H4), 6.95 (2 H, d, *J* 8.7, H_m), 7.20 (2 H, d, *J* 8.1, H_o(PTS)), 7.73 (2 H, d, *J* 8.7, H_o), 7.84 (2 H, d, *J* 8.1, H_m(PTS)), 8.03 (1 H, d, *J* 2.7, H5).

[$H_2pz^{R(12)}$][PTS] (PTS-12): colourless solid (86%). Elemental analysis: Found: C, 67.2; H, 7.7; N, 5.6; S, 6.4%. $C_{28}H_{40}N_2SO_4$ requires C, 67.2; H, 8.0; N, 5.6; S, 6.4%. ν_{max}(KBr)/cm^{-1}: 3220, 3139 ν(NH), 1616 ν(C=C + C=N), 1176, 1028 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.27 (18 H, m, CH_2), 1.80 (2 H, m, CH_2), 2.36 (3 H, s, CH_3(PTS)), 3.99 (2 H, t, *J* 6.7, OCH_2), 6.69 (1 H, d, *J* 2.7, H4), 6.96 (2 H, d, *J* 8.7, H_m), 7.19 (2 H, d, *J* 8.1, H_o(PTS)), 7.73 (2 H, d, *J* 8.7, H_o), 7.84 (2 H, d, *J* 8.1, H_m(PTS)), 8.07 (1 H, d, *J* 2.7, H5).

[$H_2pz^{R(14)}$][PTS] (PTS-14): colourless solid (78%). Elemental analysis: Found: C, 67.9; H, 8.2; N, 5.4; S, 6.1%. $C_{30}H_{44}N_2SO_4$ requires C, 68.2; H, 8.4; N, 5.3; S, 6.1%. ν_{max}(KBr)/cm^{-1}: 3222, 3140 ν(NH), 1616 ν(C=C + C=N), 1176, 1028 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (22 H, m, CH_2), 1.79 (2 H, m, CH_2), 2.36 (3 H, s, CH_3(PTS)), 3.98 (2 H, t, *J* 6.7, OCH_2), 6.68 (1 H, d, *J* 2.7, H4), 6.96 (2 H, d, *J* 8.7, H_m), 7.19 (2 H, d, *J* 8.1, H_o(PTS)), 7.73 (2 H, d, *J* 8.7, H_o), 7.84 (2 H, d, *J* 8.1, H_m(PTS)), 8.09 (1 H, d, *J* 2.7, H5).

[$H_2pz^{R(16)}$][PTS] (PTS-16): colourless solid (76%). Elemental analysis: Found: C, 68.7; H, 8.4; N, 5.1; S, 5.6%. $C_{32}H_{48}N_2SO_4$ requires C, 69.0; H, 8.7; N, 5.0; S, 5.7%. ν_{max}(KBr)/cm^{-1}: 3220, 3140 ν(NH), 1616 ν(C=C + C=N), 1176, 1028 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (26 H, m, CH_2), 1.79 (2 H, m, CH_2), 2.36 (3 H, s, CH_3(PTS)), 3.98 (2 H, t, *J* 6.7, OCH_2), 6.68 (1 H, d, *J* 2.7, H4), 6.96 (2 H, d, *J* 8.7, H_m), 7.19 (2 H, d, *J* 8.1, H_o(PTS)), 7.73 (2 H, d, *J* 8.7, H_o), 7.84 (2 H, d, *J* 8.1, H_m(PTS)), 8.10 (1 H, d, *J* 2.7,

H5).

[$H_2pz^{R(18)}$][PTS] (PTS-18): colourless solid (79%). Elemental analysis: Found: C, 69.9; H, 8.8; N, 4.9; S, 5.3%. $C_{34}H_{52}N_2SO_4$ requires C, 69.8; H, 9.0; N, 4.8; S, 5.5%. ν_{max}(KBr)/cm^{-1}: 3220, 3140 ν(NH), 1616 ν(C=C + C=N), 1176, 1028 ν(SO). δ_H (300 MHz; $CDCl_3$; Me_4Si): 0.88 (3 H, t, *J* 6.7, CH_3), 1.26 (30 H, m, CH_2), 1.79 (2 H, m, CH_2), 2.36 (3 H, s, CH_3(PTS)), 3.99 (2 H, t, *J* 6.7, OCH_2), 6.68 (1 H, d, *J* 2.7, H4), 6.96 (2 H, d, *J* 8.7, H_m), 7.19 (2 H, d, *J* 8.1, H_o(PTS)), 7.71 (2 H, d, *J* 8.7, H_o), 7.85 (2 H, d, *J* 8.1, H_m(PTS)), 8.02 (1 H, d, *J* 2.7, H5).

Table S1 Selected bond distances (Å) and angles (º) for **BF_4-10**

N1–N2	1.353(3)	N1–N2–C3	108.3(3)
N1–C5	1.348(4)	N2–N1–C5	109.2(3)
N2–C3	1.313(4)	N2–C3–C4	109.3(3)
C3–C4	1.372(4)	N1–C5–C4	106.6(3)
C4–C5	1.384(4)	C3–C4–C5	106.5(3)
C3–C6	1.453(4)	N1–C5–C6	122.2(3)
B–F (mean)	1.35	C4–C5–C6	131.1(3)
		F–B–F (mean)	109.4

Table S2 Selected bond distances (Å) and angles (º) for **Cl-1**

N1–N2	1.348(3)	N1–N2–C3	110.2(2)
N1–C5	1.329(3)	N2–N1–C5	107.7(3)
N2–C3	1.336(3)	N2–C3–C4	106.2(3)
C3–C4	1.395(4)	N1–C5–C4	109.1(3)
C4–C5	1.365(4)	C3–C4–C5	106.7(3)
C3–C6	1.453(4)	N2–C3–C6	123.1(3)
		C4–C3–C6	130.7(3)

Table S3 Selected bond distances (Å) and angles (º) for **PTS-1**

N1–N2	1.333(5)	N1–N2–C3	109.1(5)
N1–C5	1.341(6)	N2–N1–C5	109.3(5)
N2–C3	1.331(6)	N2–C3–C4	107.7(6)
C3–C4	1.368(6)	N1–C5–C4	106.6(5)
C4–C5	1.381(7)	C3–C4–C5	107.3(5)
C5–C6	1.448(7)	N1–C5–C6	122.6(6)
N3–N4	1.347(5)	C4–C5–C6	130.8(5)
N3–C22	1.335(6)	N3–N4–C20	107.2(5)
N4–C20	1.351(6)	N4–N3–C22	111.1(5)
C20–C21	1.385(6)	N4–C20–C21	108.0(5)
C21–C22	1.384(7)	N3–C22–C21	106.5(5)
C22–C23	1.448(7)	C20–C21–C22	107.2(5)
N5–N6	1.326(6)	N3–C22–C23	123.3(6)
N5–C39	1.348(6)	C21–C22–C23	130.1(6)
N6–C37	1.325(6)	N5–N6–C37	109.8(5)
C37–C38	1.376(7)	N6–N5–C39	108.8(5)
C38–C39	1.388(7)	N6–C37–C38	108.2(6)
C39–C40	1.464(7)	N5–C39–C38	107.3(5)
S–O (mean)	1.45	C37–C38–C39	105.9(5)
		N5–C39–C40	122.0(6)
		C38–C39–C40	130.7(6)
		O–S–O (mean)	112.8

Table S4 Selected bond distances (Å) and angles (º) for **OTf-1**

N1–N2	1.350(5)	N1–N2–C3	108.6(4)
N1–C5	1.349(5)	N2–N1–C5	109.3(4)
N2–C3	1.327(5)	N2–C3–C4	108.5(4)
C3–C4	1.374(6)	N1–C5–C4	106.6(4)
C4–C5	1.387(6)	C3–C4–C5	107.0(4)
C5–C6	1.456(6)	N1–C5–C6	122.3(4)
S–O (mean)	1.43	C4–C5–C6	131.1(4)
		O–S–O (mean)	116.1

Table S5 Selected bond distances (Å) and angles (º) for **ReO_4-1**

N1–N2	1.348(6)	N1–N2–C3	110.3(4)
N1–C5	1.310(6)	N2–N1–C5	107.9(5)
N2–C3	1.341(6)	N2–C3–C4	106.1(4)
C3–C4	1.405(7)	N1–C5–C4	110.0(5)
C4–C5	1.377(8)	C3–C4–C5	105.6(5)
C3–C6	1.464(7)	N2–C3–C6	122.8(4)
Re–O (mean)	1.72	C4–C3–C6	131.1(5)
		O–Re–O (mean)	109.5

Table S6 Thermal data of compounds of the families **V** (**OTf-n**) and **VI** (**PTS-n**)

Compound	Transition	T / ºC	ΔH / kJmol^{-1}	Compound	Transition	T / ºC	ΔH / kJmol^{-1}
OTf-8	Cr → Cr’	72	13.0	**PTS-8**	Cr → Cr’	60	6.2
	Cr’ → I	155	27.1		Cr’ → Cr’’	110	4.4
OTf-10	Cr → Cr’	83	7.4		Cr’’→ I	161	27.8
	Cr’ → Cr’’	86	4.6	**PTS-10**	Cr → Cr’	64	7.6
	Cr’’ → Cr’’’	110	2.6		Cr’ → Cr’’	113	5.9
	Cr’’’→ I	146	17.4		Cr’’ → Cr’’’	125	2.6
OTf-12	Cr → Cr’	100	9.9		Cr’’’→ I	151	23.8
	Cr’ → Cr’’	106	5.8	**PTS-12**	Cr → Cr’	70	12.1
	Cr’’→ I	142	23.7		Cr’ → Cr’’	111	3.3
OTf-14	Cr → Cr’	81	3.1		Cr’’ → Cr’’’	117	11.9
	Cr’ → Cr’’	107	12.5		Cr’’’→ I	148	39.1
	Cr’’→ I	132	23.9	**PTS-14**	Cr → Cr’	77	17.1
OTf-16	Cr → Cr’	115	20.1		Cr’ → Cr’’	113	2.0
	Cr’ → I	135	40.3		Cr’’ → Cr’’’	123	10.0
OTf-18	Cr → Cr’	89	4.8		Cr’’’→ I	147	17.3
	Cr’ → Cr’’	116	16.9	**PTS-16**	Cr → Cr’	87	22.7
	Cr’’→ I	127	18.5		Cr’ → Cr’’	124	16.9
					Cr’’→ I	149	25.4
				PTS-18	Cr → Cr’	90	2.5
					Cr’ → Cr’’	94	22.2
					Cr’’ → Cr’’’	124	15.4
					Cr’’’→ I	144	14.6

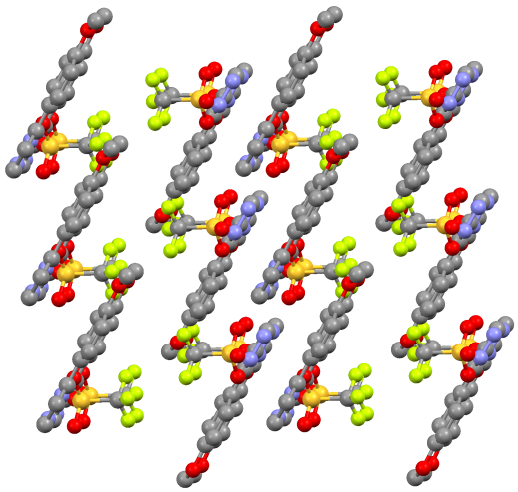

Fig. S1 Packing of **OTf-1** in the ac plane