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Supplementary Material

Ionic liquids with solvatochromatic and charge-transfer functionalities incorporating the viologen moiety

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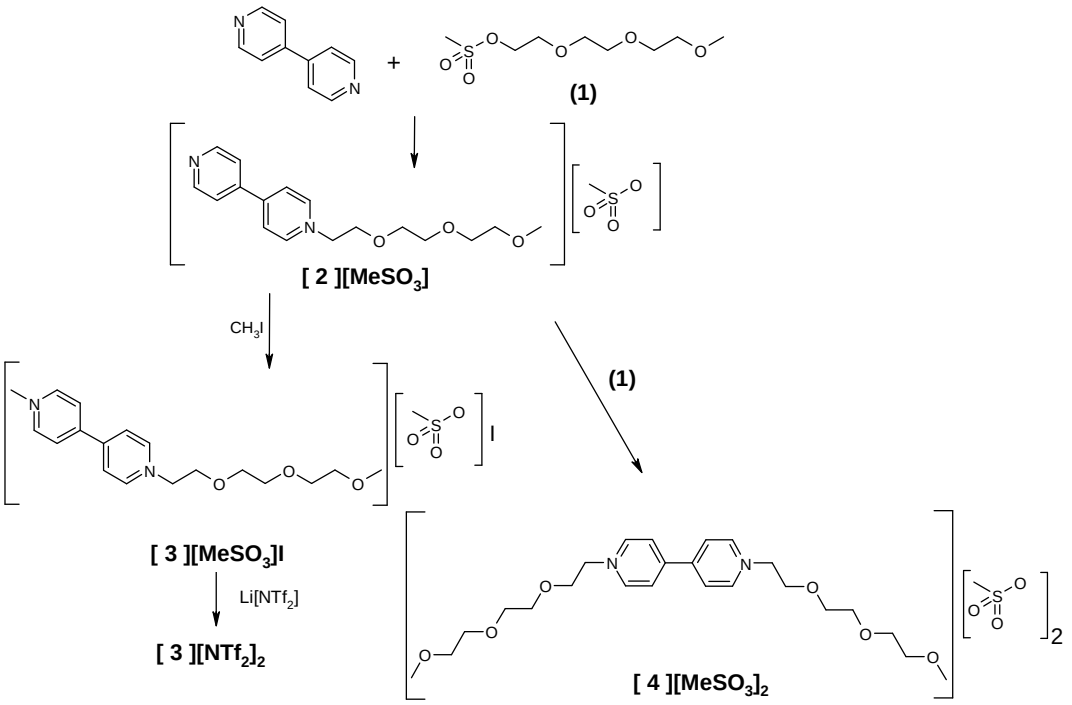
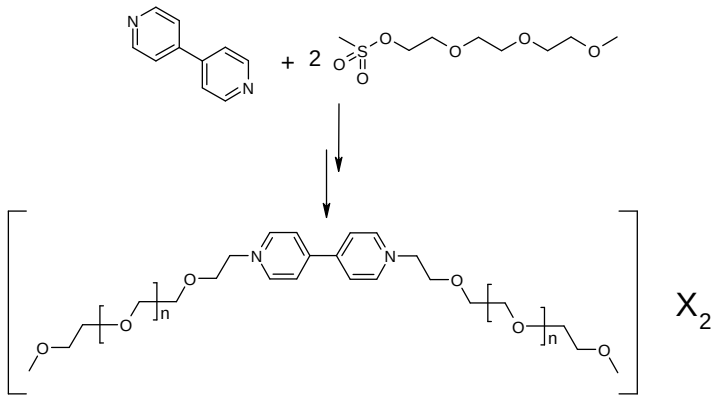
General procedure for the synthesis of 4,4'-dialkylbipyridine and 4-alkylbipyridine ionic liquids (as shown in the scheme below).



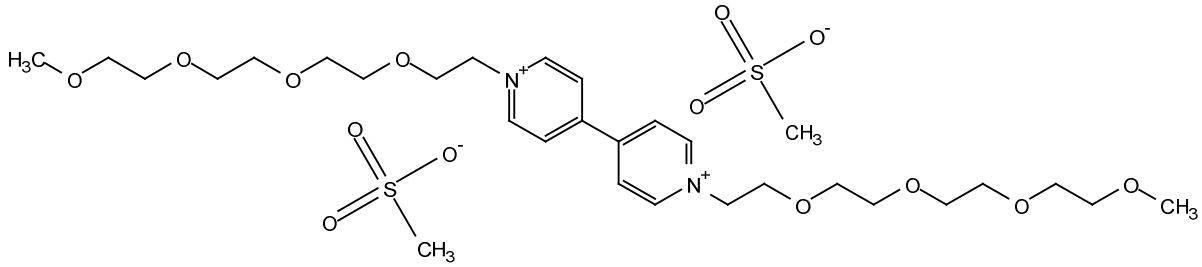
Alternatively:



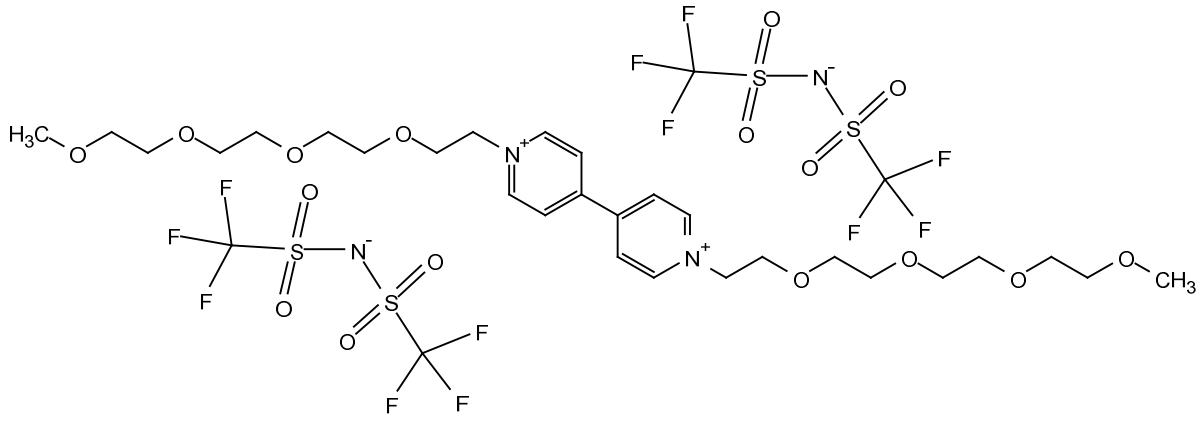
n = 1,2,3 and X=$MeSO_3^-$ or NTf_2

4,4'-bipyridine (4mM) was placed in a screw-cap pressure tube with 8.1 mM of the corresponding alkylsulfonate in acetonitrile (1 cm^3) and heated at 100 ^oC for 48h. After removing acetonitrile under vacuum, the residue was washed twice with ether and all solvents were removed under high vacuum. Metathesis of the methanesulfonate anion to the bistriflimide (NTf_2) anion was carried out by treating an aqueous solution of lithium bis(trifluoromethanesulphonyl)imide (2.5 eq) with 4,4'-dialkylbipyridine dimethylsulfonate (1 eq) and extracting the product with dichloromethane (20 cm^3 for 1 mM of the product).

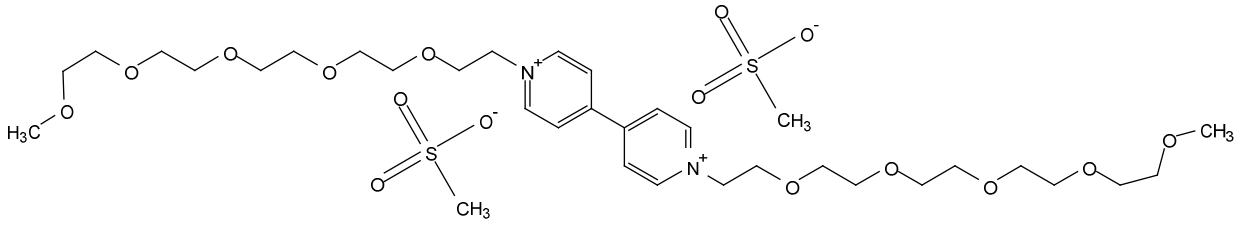
The dichloromethane layer was washed three times with water, filtered through silicone coated filter paper and the solvent was removed under high vacuum to yield the product.



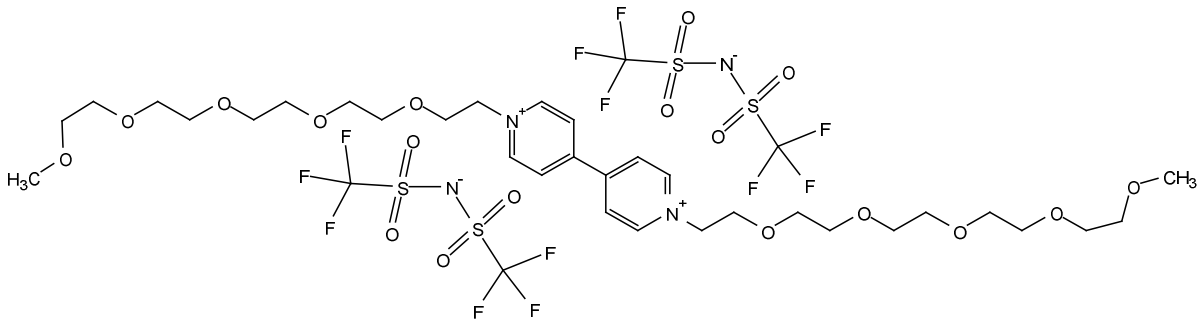
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.37 (d, 4H, Ar), 8.77 (d, 4H, Ar), 5.04 (t, 4H), 4.06 (m, 8H), 3.65 (m, 16H), 3.38 (m, 4H), 3.30 (s, 6H), 2.73 (s, 6H); HRMS (ESMS) *m/z* calcd for $C_{29}H_{49}N_2O_{11}S$ $[M - OMs]^+$ 633.3057, found 633.3057, calcd for CH_3O_3S $[OMs]^-$ 95.098, found 94.980.



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21 (d, 4H, Ar), 8.53 (d, 4H, Ar), 4.84 (t, 4H), 4.03 (t, 4H), 3.65 (m, 20H), 3.38 (m, 4H), 3.26 (s, 3H); HRMS (ESMS) *m/z* calcd for $C_{30}H_{46}N_3O_{12}F_6S_2$ $[M\text{-}NTf_2]^+$ 818.2427, found, 818.2470.



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, 4H, Ar), 8.83 (d, 4H, Ar), 5.05 (t, 4H), 4.08 (t, 4H), 3.64 (m, 32H), 3.30 (s, 6H) 2.74 (s, 6H); HRMS (ESMS) *m/z* calcd for $C_{33}H_{57}N_2O_{13}S$ $[M - OMs]^+$ 721.3581, found 721.3616.

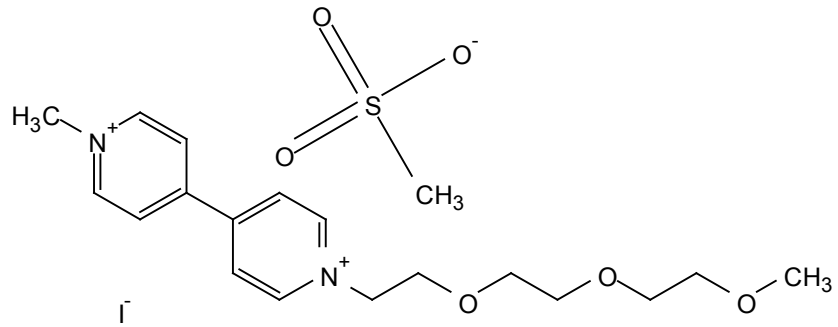


^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (d, 4H, Ar), 8.59 (d, 4H, Ar), 4.86 (t, 4H), 4.047 (t, 4H), 3.66 (m, 28H), 3.38 (m, 4H), 3.25 (s, 6H); HRMS (ESMS) *m/z* calcd for $C_{34}H_{54}N_3O_{14}F_6S_2$ $[M\text{-}NTf_2]^+$ 906.2951, found 906.2961.

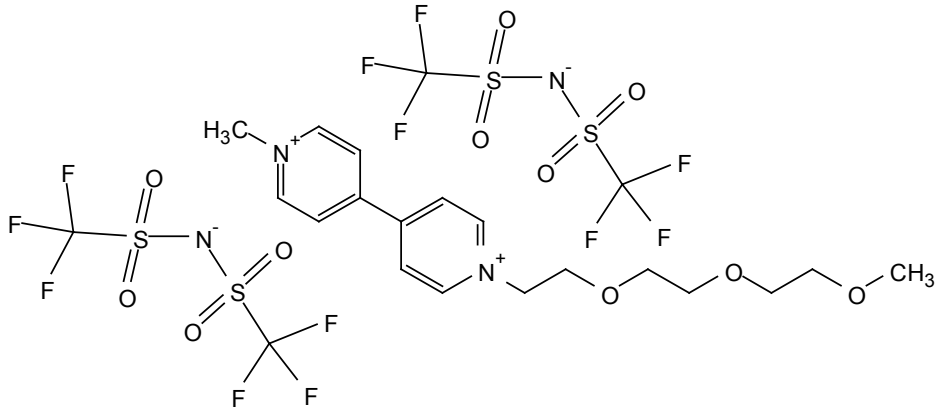
Synthesis of 4-methyl-4'-(3,6,9-trioxa-decyl)bipyridine iodide methanesulfonate

(a) 4,4'-bipyridine (4mM) and 3,6,9-trioxa-methylsulfonate(4 mM) was dissolved in acetonitrile (1 cm^3) and heated at 100°C for 48 h. After removal of the solvent, the residue was chromatographed on silica and eluted with 10% MeOH / dichloromethane to obtain the mono-quarternised bipyridine.

(b) This mono-quarternised bipyridine (2 mM scale) was used to synthesise the following two compounds via quarternisation with an excess of methyl iodide (4 mM) and the subsequent metathesis with lithium bis(trifluoromethanesulphonyl)imide.

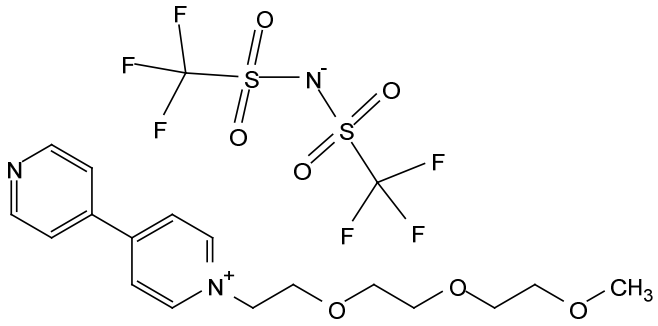


^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28-9.21 (dd, 4H, Ar), 8.73-8.68 (dd, 4H, Ar), 4.99 (m, 2H), 4.53 (s, 3H), 4.06 (m, 2H), 3.64 (m, 2H), 3.55-3.53 (m, 4H), 3.44 (m, 2H), 3.23 (s, 3H), 2.56 (s, 3H). HRMS (ESMS) *m/z* calcd for $C_{18}H_{26}N_2O_3$ $[M]^+$ 318.1943, found 318.1931, calcd. for I^- $[I]^-$ 126.905, found 126.9045, calcd for CH_3O_3S $[OMs]^-$ 95.098, found 94.9803.



^{1}H NMR (400 MHz, CD_3CN): δ 8.78 (d, 2H, Ar), 8.69 (d, 2H, Ar), 8.22 (d, 4H, Ar), 4.52-4.49 (t, 2H), 4.1 (s, 3H), 3.65 (t, 2H), 3.29-3.27 (m, 2H), 3.19-3.16 (m, 4H), 3.12-3.10 (m, 2H), 2.29 (s, 3H). HRMS (ESMS) m/z calcd for $C_{20}H_{26}N_3O_7F_6S_2$ $[M\text{-}NTf_2]^+$ 598.1116, found 598.1112.

4-(3,6,9-trioxa-decyl)bipyridine methanesulfonate



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (d, 2H, Ar), 8.89 (d, 2H, Ar), 8.23 (d, 2H, Ar), 7.68 (m, 2H, Ar), 4.80 (t, 2H), 4.00 (t, 2H), 3.68 (m, 2H), 3.60 (m, 4H), 3.55 (m, 2H), 3.35 (s, 3H). HRMS (ESMS) *m/z* calcd for $C_{17}H_{23}N_2O_3$ $[M]^+$ 303.1709, found 303.1903, calcd for $C_2F_6NO_4S_2$ $[NTf_2]^-$ 280.1466, found 279.9173.