Electronic Supporting Information

Mesomorphic and electrooptical properties of viologens based on nonsymmetric alkyl/polyfluoroalkyl functionalization and on oxadiazolyl-extended bent core

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DSC and POM





Figure S1. DSC trace of 1.2bp14: heating run is the lower trace, cooling run the upper trace.



Figure S2. POM textures of 1.2bp14 on cooling from the melt. a) 53 °C; b) 40 °C





Figure S3. DSC trace of 6.2bp8: heating run is the lower trace, cooling run the upper trace.



Figure S4. POM microphotographs obtained on cooling from the isotropic liquid of **6.2bp8** at a) 155 °C; and b) 48 °C. The bar corresponds to 100 μ m.





Figure S5. DSC trace of 8.2bp7: heating run is the lower trace, cooling run the upper trace.



Figure S6. POM microphotographs obtained on cooling from the isotropic liquid of **8.2bp7**. a) 186 °C; b) 151 °C; c) 47 °C. The white bar is 100 μ m.





Figure S7. DSC trace of 8.3bp8: heating run is the lower trace, cooling run the upper trace.



Figure S8. Mosaic textures of **8.3bp8** acquired on cooling from the isotropic liquid state at a) 191 °C; b) 85 °C and c) 42 °C. The bar corresponds to 100 μ m.





Figure S9. DSC trace of 8.2bp12: heating run is the lower trace, cooling run the upper trace.



Figure S10 Microphotographs at POM of compound **8.2bp12** on cooling from the Iso state at: a) 225 °C; b) 184 °C; c) 155 °C; d) 120 °C and e) 57 °C. The bar is 100 μ m.





Figure S11. DSC trace of 8.2bp14: heating run is the lower trace, cooling run the upper trace.



Figure S12. POM Microphotographs of compound **8.2bp14** from the isotropic liquid state at: a) 230 °C; b) 180 °C; c) 56 °C. The bar is 100 μm.





Figure S13. DCS traces of 10.2bp14. (Top) full run; (Bottom) zoom of the clearing peak.



Figure S14. POM textures of **10.2bp14** on cooling from the melt at: a) 240 °C; b) 220 °C; c) 170 °C; d) 140 °C. The blue bar is 100 μ m.





Figure S15. (top) DSC trace of **10.2bp16**: heating run is the lower trace, cooling run the upper trace. (bottom) zoom of the clearing point.





Figure S16. POM textures of **10.2bp16** observed o cooling from the melt at: a) 250 °C; b) 245 °C; d) 236 °C; 190 °C; 126 °C. Photographs a), b) d) and c), e) are taken with a different camera/microscope apparatus. The blue bar is 100 μm.





Figure S17. DSC trace of 10obp10 heating run is the lower trace, cooling run the upper trace.



Figure S18. POM Microphotographs of compound **10obp10** from the isotropic liquid state at: a) 150 °C; b) 50 °C. The white bar is 100 μm.





Figure S19. DSC trace of 12obp12 heating run is the lower trace, cooling run the upper trace.



Figure S20. POM Microphotographs of compound **12obp12** from the isotropic liquid state at: a) 149 °C; b) 113 °C and c) 45 °C. The white bar is 40 μ m.



Figure S21. DSC trace of 14obp14 heating run is the lower trace, cooling run the upper trace.

Temperature (°C)

Exo Up



Universal V4.5A TA Instruments

Figure S22. POM Microphotographs of compound **14obp14** from the isotropic liquid state at: a) 205 °C; b) 137 °C; c) 49 °C.

Cyclovoltammetry



Figure S23. Reduction waves for representative viologen compounds: **M.2bpL** (with M= 1-10 and L= 14-16) **8.3bp8** and **8bp8** (0.5mM). Conditions: working electrode: glassy carbon; reference electrode: Ag/AgCl; counter-electrode: Pt. Scan rate: 100mV/s; solvent: acetonitrile; support electrolyte: Bu₄NClO₄ 0.1M. Potentials vs Ag/AgCl.



Figure S24. First reduction waves for representative viologen compounds: **M.2bpL** (with M= 1-10 and L= 14-16) **8.3bp8** and **8bp8** (0.5mM). Conditions: working electrode: glassy carbon; reference electrode: Ag/AgCl; counter-electrode: Pt. Scan rate: 100mV/s; solvent: acetonitrile; support electrolyte: Bu_4NCIO_4 0.1M. Potentials vs Ag/AgCl.



Figure S25. First reduction waves for the oxadiazolylbipyridinium compounds: **LobpL** (L=10, 12, 14), and **8.2obp2.8** (5mM). Conditions: working electrode: glassy carbon; reference electrode: Ag/AgCl; counter-electrode: Pt. Scan rate: 100mV/s; solvent: DMF; support electrolyte: Bu₄NClO₄ 0.1M. Potentials vs Ag/AgCl.



Figure S26. Reduction waves for the oxadiazolylbipyridinium compounds: **LobpL** (L=10, 12, 14), and **8.2obp2.8** (5mM). Conditions: working electrode: glassy carbon; reference electrode: Ag/AgCl; counter-electrode: Pt. Scan rate: 100mV/s; solvent: DMF; support electrolyte: Bu₄NClO₄ 0.1M. Potentials vs Ag/AgCl.

	E _{pc} (I) ^a	E _{pa} (I) ^b	E _{1/2} (I) ^c	$\Delta E(I)^{d}$	E _{pc} (II) ^e	$E_{pa}(II)^{f}$	E _{1/2} (II) ^g	$\Delta E(II)^{h}$
#	(V)	(V)	(V)	(mV)	(V)	(V)	(V)	(mV)
8bp8	-0.431	-0.353	-0.392	78	-0.845	-0.784	-0.815	61
1.2bp14	-0.360	-0.283	-0.322	77	-0.941	-0.775	-0.858	166
6.2bp8	-0.357	-0.278	-0.318	79	-0.889	-0.742	-0.816	147
8.2bp7	-0.360	-0.280	-0.320	80	-0.935	-0.765	-0.850	170
8.3bp8	-0.389	-0.310	-0.350	79	-0.782	-0.682	-0.732	100
8.2bp12	-0.359	-0.280	-0.320	79	-0.986	-0.766	-0.876	220
8.2bp14	-0.371	-0.270	-0.321	101	-0.992	-0.763	-0.878	229
10.2bp14	-0.356	-0.275	-0.316	81	-1.080	-0.754	-0.917	326
10.2bp16	-0.352	-0.275	-0.314	77	-1.080	-0.744	-0.912	336
10obp10	-0.473	-0.379	-0.426	94	-0.743	-0.677	-0.710	66
12obp12	-0.467	-0.385	-0.426	82	-0.881	-0.798	-0.840	83
14obp14	-0.480	-0.370	-0.425	110	-0.827	-0.716	-0.772	111
8.2obp2.8	-0.412	-0.328	-0.370	84	-0.786	-0.713	-0.750	73

Table S1. Voltammetric data of all samples.

^aE pc(I): first cathodic peak, ^bE pa(I): first anodic peak, ^cE_{1/2}(I): half potential of the first electronic transition, ^d Δ E(I): Epa(I)-Epc(I), ^eE pc(II): second cathodic peak, ^fE pa(II): second anodic peak, ^gE_{1/2}(II): half potential of the second electronic transition, ^h Δ E(II): Epa(II)-Epc(II). Cyclic voltammetry data were collected using a glassy carbon working electrode, a Ag/AgCl reference electrode and a Pt counter electrode. The samples (0.5mM) were dissolved in acetonitrile (viologens) or DMF (oxadiazoylbipiridiniums) containing Bu₄NClO₄ 0.1M as support electrolyte. A scan rate of 100mV/s was applied in all cases. For all samples the counteranion is bistriflimide.

Spectroelectrochemistry





Figure S27. Vis-NIR spectroelectrochemistry of the fluorinated viologens of the series **M.NbpL** and of the oxadiazolylviologen derivative **8.2obp2.8**. The potentials are referenced to AgCl/Ag.



Figure S28. Vis-NIR bulk spectroelectrochemistry of the fluorinated viologen derivative **8.2obp14** acquired at 214 °C in the smectic phase. Cell gap = 5 μ m.

Synthesis

Procedure for the synthesis of compound 1-octyl-[4,4'-bipyridin]-1-ium bromide [bp8][Br]

This procedure, where the alkylation is the first step, was attempted for two of the compounds discussed in the paper, though the majority of the samples were prepared following Scheme 1 as reported in the main text.

A fivefold excess of 4,4'-bipyridine (5 g, 32 mmol) was dissolved in CH₃CN (25 ml) in a ACE pressure tube and 1-bromoctane (1 mL, 6.4 mmol) was added. The solution was refluxed under stirring at 80 °C for 1 day. After cooling, the yellow precipitate was filtered and dissolved in 100 mL of hot DMF. 25 ml of Toluene where then added and from the cooled solution a pale yellow precipitate, corresponding to the mono-alkylated salt, was obtained. The suspension was filtered and washed several times with a total amount of 100 mL of Et₂O. The final product was dried under vacuum. Yellow solid, Yield 85%. ¹H NMR (200 MHz, D₂O) δ : 9.01 (d, *J* = 6.5 Hz, 2H), 8.82 (d, *J* = 6.5 Hz, 2H), 8.46 (d, *J* = 6.5 Hz, 2H), 7.96 (d, *J* = 6.5 Hz, 2H), 4.71 (t, *J*= 7.1 Hz, 2H), 2.11 (m, 2H), 1.40-1.31 (m, 10H), 0.89 (t, J = 6.2 Hz, 3H).

Procedure for the synthesis of the 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)-1'-octyl-[4,4'bipyridine]-1,1'-diium bromide iodide [6.2bp8] [I][Br]

A tenfold excess of 3,3,4,4,5,5,6,6,7,7,8,8,8 tridecafluorooctyl lodide (1.4 mL, 5.7 mmol) was mixed in 10 mL of CH₃CN in a ACE pressure tube with [bp8][Br] (200 mg, 0.57 mmol) and the solution was refluxed under stirring at 80 °C for 2 days. The orange precipitate was filtered and washed with 20 mL of CH₂Cl₂ and dried under vacuum. Orange solid, Yield=31 %. ¹H NMR (300 MHz, CD₃OD) δ : 9.37 (d, *J* = 6.4 Hz, 2H), 9.34 (d, *J* = 6.5 Hz, 2H), 8.93-8.71 (m, 4H), 5.09 (t, 7.1 Hz 2H), 4.76 (partially overlapped with the water signal), 2.45 (t, *J*= 8.4 Hz, 2H), 2.13 (m, 2H), 1.43-1.33 (m, 10H), 0.88 (t, J = 6.6 Hz, 3H).

HPLC-MS (exact mass): $[M^+] = 616.2133$ (theoretical 616.2118); $[M^{2+}] = 308.1072$ (theoretical 308.1056).

Procedure for the synthesis of the 1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)-1'-octyl-[4,4'-bipyridine]-1,1'-diium bromide iodide [8.3bp8] [I][Br]

A sixfold excess of 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl lodide (1 g, 1.7 mmol) were mixed in 10 mL of CH₃CN in a ACE pressure tube with [bp8][Br] (100 mg, 0.29 mmol) and the solution was refluxed under stirring at 80 °C for 1 day. The orange precipitate was filtered

and washed with 20 mL of CH_2Cl_2 and dried under vacuum. Yield=55 %. ¹H NMR (300 MHz, CD_3OD) δ : 9.33 (d, J = 6.3 Hz, 2H), 9.30 (d, J = 6.5 Hz, 2H), 8.71 (m, 4H), ca. 4.87-4.74 (overlapped with the water signal, 6H), 2.46 (t, J= 8.4 Hz, 2H), 2.13 (m, 2H), 1.43-1.33 (m, 10H), 0.89 (t, J = 6.7 Hz, 3H)

HPLC-MS (exact mass): $[M^+] = 730.2239$ (theoretical 730.2210); $[M^{2+}] = 365.1122$ (theoretical 365.1102).

Procedure for the synthesis of compound 1-(3,3,3-trifluoropropyl)-[4,4'-bipyridin]-1-ium iodide [1.2bp][I]

A tenfold excess of 4,4'-bipyridine (7,8 g, 50 mmol) was dissolved in CH₃CN (25 ml) in a ACE pressure tube and 1H,1H,2H,2H-trifluoro-1-iodopropane (0.60 mL, 5 mmol) was added. A reddish-brown solution started to form after 20 min and was refluxed under stirring at 80 °C for 2 days. The solution was cooled down a 4° C and a mixture of red-brownish and white precipitate, due to the excess of the 4,4'-bipyridine, was formed. The solvent was removed under vacuum and the precipitate was treated with 20 mL of CH₂Cl₂. The resulting suspension was filtered and washed several times with further CH₂Cl₂ amounts until all the 4,4'-bipyridine excess was removed (purity checked by ¹H NMR). The final red precipitate was dried under vacuum. Red solid, Yield = 85%. ¹H NMR (200 MHz, CD₃OD) δ : 9.21 (d, *J* = 6.4 Hz, 2H), 8.83 (d, *J* = 6.4 Hz, 2H), 8.58 (d, *J* = 6.4 Hz, 2H), 8.00 (d, *J* = 6.4 Hz, 2H), 5.02 (t, *J* = 7.1 Hz, 2H), 3.16 (2H, partially overlapped with the solvent signal).

Procedure for the synthesis of compound 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12henicosafluorododecyl)-[4,4'-bipyridin]-1-ium iodide [10.2bp][I]

A tenfold excess of 4,4'-bipyridine (2.2 g, 14.1 mmol) was dissolved in CH₃CN (20 ml) in a ACE pressure tube and 1H,1H,2H,2H-perfluorododecyl iodide (0.94 g, 1.4 mmol) was added. A yellow solution was quickly formed and was refluxed under stirring at 80 °C for 4 days. The solution was cooled down a 4° C and a mixture of red-brownish and white precipitate, due to the excess of the 4,4'-bipyridine, was formed. The solvent was removed under vacuum and the precipitate was washed several times with acetone until all the 4,4'-bipyridine excess was removed (purity checked by ¹H NMR). Red solid, Yield = 45%. ¹H NMR (200 MHz, CD₃OD) δ : 9.24 (d, *J* = 6.7 Hz, 2H), 8.85 (dd, *J* = 6.7, 1.9 Hz, 2H), 8.58 (d, *J* = 6.6 Hz, 2H), 8.00 (d, *J* = 6.6 Hz, 2H), 5.03 (7, J = 7.1 Hz 2H), 3.16 (2H, partially overlapped with the solvent signal).

Procedure for the synthesis of compound 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10heptadecafluorodecyl)-[4,4'-bipyridin]-1-ium bromide [8.2bp][Br] A sixfold excess of 4,4'-bipyridine (1.0 g, 6.402 mmol) was dissolved in CH_3CN (16 ml) in a ACE pressure tube and 1H,1H,2H,2H-heptadecafluoro-1-bromodecane (0.5 g, 1.1 mmol) was added. The yellow solution was refluxed under stirring at 80 °C for 4 days. The solution was cooled down a 4° C and a mixture of red-brownish and white precipitate, due to the excess of the 4,4'-bipyridine, was formed. The solvent was removed under vacuum and the precipitate was washed several times with ethyl acetate until all the 4,4'-bipyridine excess was removed (purity checked by ¹H NMR).

Alternatively, the mixture was reacted under microwave irradiations at 80 °C for 3 hours, following the same treatment for the work-up. Yield = 61%. (59% for MW-assisted reaction).

Yellow solid. m.p. = 252-253 °C. ¹H NMR (300 MHz, CD₃CN) δ: 9.02 (d, *J* = 6.9 Hz, 2H), 8.85 (d, *J* = 6.9 Hz, 2H), 8.70 (d, *J* = 6.6 Hz, 2H), 8.39 (d, *J* = 6.6 Hz, 2H), 5.10 – 4.91 (m, 2H), 3.12 – 3.04 (m, 2H).

General procedure for the synthesis of the [8.2bp][Br] based bipyridinium halides

[8.2bp][Br] (0.5 g, 0.732 mmol) was mixed with CH₃CN (16 ml) in a ACE pressure tube and alkyl halide (18 mmol) was added. The solution was refluxed under stirring at 80 °C for 7 days, after which the solvent was filtered under vacuum, washing the precipitate with cold chloroform. Alternatively, the mixture was reacted under microwave radiations at 80 °C for 5 hours, following the same treatment for the work-up.

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-1'-heptyl-[4,4'-bipyridine]-1,1'diium bromide iodide [8.2bp7] [I][Br]

Yield = 85.9% (63.7% for MW-assisted reaction). Orange solid. ¹H NMR (300 MHz, CD₃CN) δ : 9.16 (d, J = 6.9 Hz, 2H), 9.03 (d, J = 6.9 Hz, 2H), 8.57 (d, J = 6.6 Hz, 2H), 8.51 (d, J = 6.6 Hz, 2H), 5.08 (t, J = 9H, 2H), 4.68 (t, J = 9 Hz, 2H), 3.23 – 3.05 (m, 2H), 3.17 (p, J = 6.5 Hz, 2H), 1.49 – 1.38 (m, 8H), 0.93 (t, J = 6.5 Hz, 3H).

HPLC-MS (exact mass): $[M^+] = 702.1850$ (theoretical 702.1892); $[M^{2+}] = 351.0916$ (theoretical 351.0946).

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-1'-dodecyl-[4,4'-bipyridine]-1,1'diium bromide iodide [8.2bp12] [I][Br]

Yield = 76.6%. Orange solid. ¹H NMR (300 MHz, CD₃OD) δ: 9.44 (d, *J* = 6.9 Hz, 2H), 9.32 (d, *J* = 6.9 Hz, 2H), 8.78 (d, *J* = 6.6 Hz, 2H), 8.73 (d, *J* = 6.6 Hz, 2H), 5.20 (t, *J* = 6 Hz), 4.78 (t, *J* = 6 Hz, 2H), 3.73 – 3.55 (m, 2H), 2.12 – 1.98 (m, 2H), 1.45 – 1.37 (m, 18H), 0.94 (t, 3H, *J* = 6.5 Hz).

HPLC-MS (exact mass): [M⁺] = 772.2649 (theoretical 772.2674); [M²⁺] = 386.1324 (theoretical 386.1337).

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-1'-tetradecyl-[4,4'-bipyridine]-1,1'diium bromide [8.2bp14][Br]₂

Yield = 86.5%. Yellow solid. ¹H NMR (300 MHz, CD₃CN) δ: 8.97 (d, *J* = 6.9 Hz, 2H), 8.91 (d, *J* = 6.9 Hz, 2H), 8.40 (d, *J* = 6.6 Hz, 2H), 7.82 (d, *J* = 6.6 Hz, 2H), 4.98 (t, *J* = 9 Hz, 2H), 4.20 (t, *J* = 9 Hz, 2H), 3.76 – 3.52 (m, 2H), 2.11 – 1.98 (m, 2H), 1.45 – 1.37 (m, 22H), 0.91 (t, 3H, *J* = 6.5 Hz).

HPLC-MS (exact mass): $[M^+] = 800.2942$ (theoretical 800.2987); $[M^{2+}] = 400.1467$ (theoretical 400.1493).

Procedure for the synthesis of 1-(3,3,3-trifluoropropyl)-1'-tetradecyl- [4,4'-bipyridin]-1,1'-diium iodide bromide [1.2bp14][I][Br]

[1.2bp][I] (410 mg, 1 mmol) was mixed with CH₃CN (25 ml) in a ACE pressure tube and a tenfold excess of tetradecylbromide (3 ml, 10 mmol) was added. The solution was refluxed under stirring at 80 °C for 2 days. The solution was cooled down a 4° C and an orange precipitate was formed. The precipitate was filtered and recrystallized from 10 mL of a water/acetone mixture (2:100). The final product was filtered and dried under vacuum. Orange solid, Yield = 25%. ¹H NMR (200 MHz, CD₃OD) δ : 9.42 (d, *J* = 6.8 Hz, 2H), 9.30 (d, *J* = 6.8 Hz, 2H), 8.75 (d, *J* = 6.8 Hz, 2H, Ar), 8.70 (d, *J* = 6.8 Hz, 2H), 5.10 (t, J = 6.9 Hz, 2H), 4.76 (partially overlapped with the water signal) 3.19 (partially overlapped with the solvent signal). 2.15 (t, J = 6.8 Hz, 2H), 1.44-1.29 (m, 22 H), 0.95 (t, J=6.3, 3H).

HPLC-MS (exact mass): [M⁺] = 450.3238 (theoretical 450.3211); [M²⁺] = 225.1618 (theoretical 225.1605).

[10.2bp][I] (200 mg, 0.2 mmol) was mixed with CH_3CN (30 ml) in a ACE pressure tube and excess of tetradecylbromide (1.4 ml, 5 mmol) was added. The solution was refluxed under stirring at 80 °C for 3 days. The solution was cooled down a 4° C and an orange precipitate was formed. The precipitate was filtered, washed with cold chloroform (0 °C) and dried under vacuum. Yield = 20%.

Orange solid. ¹H NMR (200 MHz, CD₃OD) δ : 9.42 (d, *J* = 6.8 Hz, 2H), 9.30 (d, *J* = 6.8 Hz, 2H), 8.75 (d, *J* = 6.8 Hz, 2H), 8.69 (d, *J* = 6.8 Hz, 2H), 5.18 (t, J = 7.2 Hz, 2H), 4.73 (partially overlapped with the water signal) 3.19 (partially overlapped with the solvent signal), 2.10 (t, J = 6.9 Hz, 2H), 1.44-1.30 (m, 22 H), 0.90 (t, J=6.3, 3H)

HPLC-MS (exact mass): [M⁺] = 900.2988 (theoretical 900.2929); [M²⁺] = 450.1479 (theoretical 450.1462).

Synthesis of compound 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12,12 henicosafluorododecyl)-1'-hexadecyl-[4,4'-bipyridin]-1-diium iodide bromide [10.2bp16] [I][Br]

[10.2bp][I] (200 mg, 0.2 mmol) was mixed with CH_3CN (30 ml) in a ACE pressure tube and excess of hexadecylbromide (1.6 ml, 5 mmol) was added. The solution was refluxed under stirring at 80 °C for 3 days. The solution was cooled down a 4° C and an orange precipitate was formed. The precipitate was filtered, washed with cold chloroform (0 °C) and dried under vacuum. Yield = 15%.

Orange solid. ¹H NMR (200 MHz, CD₃OD) δ : 9.43 (d, *J* = 6.8 Hz, 2H), 9.31 (d, *J* = 6.8 Hz, 2H), 8.76 (d, *J* = 6.8 Hz, 2H, Ar), 8.70 (d, *J* = 6.8 Hz, 2H), 5.19 (t, 6.9 Hz, 2H), 4.73 (partially overlapped with the water signal), 3.25 (partially overlapped with the solvent signal), 2.13, 1.44-1.30 (m, 26 H), 0.90 (t, J=6.2, 3H)

HPLC-MS (exact mass): $[M^+] = 928.3291$ (theoretical 928.3242); $[M^{2+}] = 464.1655$ (theoretical 464.1618).

General procedure for the synthesis of the based bipyridinium bistriflimide salts

bipyridinediium halides (0.1 g) were dissolved in amounts of CH_3OH as small as possible to dissolve them (10-20 mL) in a glass tube and $LiTf_2N$ (2.5 mol eq.) was added. The mixture was stirred for 0.5 h at 35-40 °C and just after water was added dropwise, until permanent suspension was formed. After this the mixture was stirred for further 2 h and the solid was filtered under vacuum washing with water, until a negative assay with AgNO₃ was obtained.

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-1'-heptyl-[4,4'-bipyridine]-1,1'diium bis((trifluoromethyl)sulfonyl)amide [8.2bp7][Tf₂N]₂

Yield = 67.7%. White solid. ¹H NMR (300 MHz, CD₃CN) δ : 9.03 (d, *J* = 6.9 Hz, 2H), 8.93 (d, *J* = 6.9 Hz, 2H), 8.46 (d, *J* = 6.6 Hz, 2H), 8.41 (d, *J* = 6.6 Hz, 2H), 5.03 (t, *J* = 12 Hz, 2H), 4.64 (t, *J* = 9 Hz, 2H), 3.19 - 3.03 (m, 4H), 1.42 - 1.34 (m, 8H), 0.91 (t, J = 6.5 Hz, 3H).

HPLC-MS (exact mass): $[M^+] = 702.1894$ (theoretical 702.1892); $[M^{2+}] = 351.0947$ (theoretical 351.0946); $[M^-] = 279,9125$ (theoretical 279,9178).

$\label{eq:1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-1'-dodecyl-[4,4'-bipyridine]-1,1'-diium bis((trifluoromethyl)sulfonyl)amide [8.2bp12][Tf_2N]_2$

Yield = 49.5%. White solid. ¹H NMR (300 MHz, CD₃CN) δ: 9.07 (d, *J* = 3 Hz, 2H), 9.05 (d, *J* = 9 Hz, 2H), 9.01 (d, *J* = 6 Hz, 2H), 8.95 (d, *J* = 6 Hz, 2H), 5.05 (t, *J* = 9 Hz, 2H), 4.65 (t, *J* = 9 Hz, 2H), 3.19 – 3.02 (m, 2H), 2.08 – 2.00 (m, 2H), 1.39 – 1.29 (m, 18H), 0.93 (t, *J* = 6.5 Hz, 3H).

HPLC-MS (exact mass): [M⁺] = 772.2682 (theoretical 772.2674); [M²⁺] = 386.1339 (theoretical 386.1337); [M⁻] = 279,9136 (theoretical 279,9178).

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-1'-tetradecyl-[4,4'-bipyridine]-1,1'-diium bis((trifluoromethyl)sulfonyl)amide [8.2bp14][Tf₂N]₂

Yield = 60.0%. White solid. ¹H NMR (300 MHz, CD₃CN) δ : 9.03 (d, *J* = 6.9 Hz, 2H), 8.93 (d, *J* = 6.9 Hz, 2H), 8.47 (d, *J* = 6.6 Hz, 2H), 8.42 (d, *J* = 6.6 Hz, 2H), 5.03 (t, *J* = 9 Hz, 2H), 4.64 (t, *J* = 9 Hz), 3.19 - 3.00 (m, 2H), 2.07 - 1.98 (m, 2H), 1.38 - 1.31 (m, 22H), 0.95 (t, *J* = 6.5 Hz, 3H).

HPLC-MS (exact mass): $[M^+] = 800.2982$ (theoretical 800.2987); $[M^{2+}] = 400.1490$ (theoretical 400.1493), $[M^-] = 279,9158$ (theoretical 279,9178).

1-(3,3,3-trifluoropropyl)-1'-tetradecyl-[4,4'-bipyridin]-1,1'-diium bis((trifluoromethyl)sulfonyl) amide [1.2bp14][Tf₂N]₂

Yield = 50%. White solid, ¹H NMR (300 MHz, CD₃CN) δ: 8.97 (d, *J* = 6.7 Hz, 2H), 8.89 (d, *J* = 6.7 Hz, 2H), 8.42 (d, *J* = 6.8 Hz, 2H, Ar), 8.37 (d, *J* = 6.8 Hz, 2H), 4.92 (t, J = 7.1 Hz, 2H), 4.61 (t, J = 7.4 Hz, 2H), 3.06 (m, 2H). 2.09 (m, 2H), 1.43-1.20 (m, 22 H), 0.88 (t, J=6.8, 3H).

HPLC-MS (exact mass): [M⁺] = 450.3221 (theoretical 450.3211); [M²⁺] = 225.1615 (theoretical 225.1605); [M⁻] = 279,9133 (theoretical 279,9178).

1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoroocty)-1'-octyl-[4,4'-bipyridine]-1,1'-diium bis

(trifluoromethyl)sulfonyl)amide [6.2bp8][Tf₂N]₂

Yield = 50%. White solid. ¹H NMR (300 MHz, CD₃CN) δ : 8.99 (d, *J* = 6.2 Hz, 2H), 8.89 (d, *J* = 6,2 Hz, 2H), 8.47-8.32 (m, 4H), 5.00 (br t, 6.3 Hz, 2H), 4.61 (br t, 6.6 Hz, 2H), 3.06 (m, 2H), 2.09 (m, 2H, partially overlapped with the water signal), 1.43-1.22 (m, 10 H), 0.89 (m, 3H).

HPLC-MS (exact mass): $[M^+] = 616.2128$ (theoretical 616.2118); $[M^{2+}] = 308.1068$ (theoretical 308.1056); $[M^-] = 279,9145$ (theoretical 279,9178).

$1-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)-1'-octyl-[4,4'-bipyridine]-1,1'-diium bis((trifluoromethyl)sulfonyl)amide [8.3bp8][Tf_2N]_2$

Yield =40%. White solid. ¹H NMR (300 MHz, CD₃CN) δ : 8.91 (d, *J* = 6.2 Hz, 2H), 8.89 (d, *J* = 6,2 Hz, 2H), 8.39 (d, *J* = 6,6 Hz, 2H), 8.36 (d, *J* = 6,6 Hz, 2H), 4.69 (br t, J = 7.2 Hz, 2H), 4.61 (t, 7.5 Hz, 2H), 2.50-2.27 (m, 4H), 2.02 (m, 2H, partially overlapped with the solvent signal), 1.43-1.23 (m, 10 H), 0.89 (t, J = 6.8 Hz, 3H).

HPLC-MS (exact mass): [M⁺] = 730.2218 (theoretical 730.2210); [M²⁺] = 365.1104 (theoretical 365.1102); [M⁻] = 279,9166 (theoretical 279,9178).

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)-1'-hexadecyl-[4,4'bipyridin]-1-diium bis((trifluoromethyl)sulfonyl)amide [10.2bp14][Tf₂N]₂

Yield = 50%. White solid. ¹H NMR (200 MHz, CD₃CN) δ : 8.99 (d, *J* = 6.5 Hz, 2H), 8.90 (d, *J* = 6,5 Hz, 2H), 8.44-8.41 (4H), 8.38 (d, *J* = 6.8 Hz, 2H), 5.01 (t, 7.2 Hz, 2H), 4.62 (t, 7.5 Hz, 2H), 2.10 (partially overlapped with the water signal), 1.37-1.29 (22 H), 0.89 (t, J=5.8, 3H).

HPLC-MS (exact mass): $[M^+] = 900.2952$ (theoretical 900.2929); $[M^{2+}] = 450.1473$ (theoretical 450.1462); $[M^-] = 279,9162$ (theoretical 279,9178).

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)-1'-hexadecyl-[4,4'bipyridin]-1-diium bistriflimides [10.2bp16][Tf₂N]₂

Yield = 50%. White solid. ¹H NMR (200 MHz, CD₃CN) δ : 8.99 (d, *J* = 6.5 Hz, 2H), 8.90 (d, *J* = 6,5 Hz, 2H), 8.44-8.41 (4H), 8.38 (d, *J* = 6.8 Hz, 2H), 5.01 (t, 7.2 Hz, 2H), 4.62 (t, 7.5 Hz, 2H), 2.10 (partially overlapped with the water signal), 1.37-1.29 (26 H), 0.89 (t, J=5.8, 3H).

HPLC-MS (exact mass): $[M^+] = 928.3283$ (theoretical 928.3242); $[M^{2+}] = 464.1639$ (theoretical 464.1618); $[M^-] = 279,9154$ (theoretical 279,9178).

Procedure for the synthesis of N'-hydroxyisonicotinimidamide

Isonicotinonitrile (3.0 g; 28.820 mmol) was dissolved in EtOH (100 mL) in a 250 mL round-bottomed flask. Separately NaOH (1.5 g) was dissolved in an amount of water as small as possible in another flask, using ice to help the dissolution, and NH₂OH⁺HCl (2.5 g) was added. The solutions were blended together and heated under reflux for 8 h and the reaction was monitored by TLC (petroleum ether and ethyl acetate 5:1). Ethanol was removed under vacuum, water (100 mL) was added and the precipitate was filtered under vacuum, washing with cold water. Yield = 71.7% White solid. ¹H NMR (300 MHz, (CD₃)₂SO) δ : 10.11 (s, 1H), 8.63 (m, 2H), 7.70 (m, 2H), 7.11 (s, 2H).

Procedures for the synthesis of 3,5-Di(pyridin-4-yl)-1,2,4-oxadiazole

N'- hydroxyisonicotinimidamide (1.0 g, 7.292 mmol) and Isonicotinonitrile (3 mol eq.) were placed in a ACE pressure tube and heated to 150 °C for 7 h and the reaction was monitored by TLC (petroleum ether and ethyl acetate 50:1). The oxadiazole was isolated by chromatography using petroleum ether/ethyl acetate 20:1 as eluents. Yield = 72.3%. White solid. m.p. = 163.9 - 165.5 °C. ¹H NMR (300 MHz, CDCl₃) δ : 8.93 (d, *J* = 5,5 Hz, 2H), 8.85 (d, *J* = 5,4 Hz, 2H,), 8.11 – 8.02 (m, 4H).

General procedure for the synthesis of the oxadiazole bis-pirydinium halides

The dipyrinidyl oxadiazole (0.5 g, 2.230 mmol) was dissolved with CH₃CN (16 ml) in ACE pressure tube and alkyl or polyfluoroalkyl halide (40 mol eq.) was added. The solution was refluxed under stirring at 80 °C for 5 days, after which the solvent was filtered under vacuum, washing with cold chloroform.

4,4'-(1,2,4-oxadiazole-3,5-diyl)bis(1-decylpyridin-1-ium) iodide [10obp10][I]2

Yield = 52.9%. Red solid. ¹H NMR (300 MHz, (CD₃)₂SO) δ : 9.44 (d, *J* = 6.9 Hz, 2H), 9.38 (d, *J* = 6.9 Hz, 2H), 8.90 (d, *J* = 6.6 Hz, 2H), 8.79 (d, *J* = 6.6 Hz, 2H), 4.75 (t, J = 9 Hz, 2H), 4.73 (t, *J* = 9 Hz, 2H), 2.08 – 1.90 (m, 4H), 1.34 – 1.25 (m, 28H), 0.85 (t, *J* = 6.5 Hz, 6H). HPLC-MS (exact mass): [M⁺] = 506.3997 (theoretical 506.3975); [M²⁺] = 253.1945 (theoretical 253.1987).

4,4'-(1,2,4-oxadiazole-3,5-diyl)bis(1-dodecylpyridin-1-ium) iodide [12obp12][I]2

Yield = 50.6%. Red solid. ¹H NMR (300 MHz, (CD₃)₂SO) δ : 9.45 (d, *J* = 6.9 Hz, 2H), 9.38 (d, *J* = 6.9 Hz, 2H), 8.90 (d, *J* = 6.6 Hz, 2H), 8.79 (d, *J* = 6.6 Hz, 2H), 4.76 (t, J = 9 Hz, 2H), 4.74 (t, *J* = 9 Hz, 2H), 2.06 – 1.91 (m, 4H), 1.34 – 1.26 (m, 36H), 0.85 (t, *J* = 6.5 Hz, 6H). HPLC-MS (exact mass): [M⁺] = 562.8886 (theoretical 562,8870); [M²⁺] = 281,4490 (theoretical 281,4435).

4,4'-(1,2,4-oxadiazole-3,5-diyl)bis(1-tetradecylpyridin-1-ium) bromide [14obp14][Br] 2

Yield = 75.2%. Pale yellow solid. ¹H NMR (300 MHz, $(CD_3)_2SO$) δ : 9.44 (d, J = 6.9 Hz, 2H), 9.38 (d, J = 6.9 Hz, 2H), 8.89 (d, J = 6.6 Hz, 2H), 8.78 (d, J = 6.6 Hz, 2H), 4.75 (t, J = 9 Hz, 2H), 4.73 (t, J = 9 Hz, 2H), 2.03 – 1.89 (m, 4H), 1.32 – 1.23 (m, 44H), 0.84 (t, J = 6.5 Hz, 6H). HPLC-MS (exact mass): [M⁺] = 618,9945 (theoretical 618,9950); [M²⁺] = 309,4925 (theoretical 309,4975).

4,4'-(1,2,4-oxadiazole-3,5-diyl)bis(1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)

pyridin-1-ium) iodide [8.2obp2.8][I]2

Yield = 75.8%. Red solid. ¹H NMR (300 MHz, (CD₃)₂SO) δ : 9.55 (d, *J* = 6.9 Hz, 2H), 9.49 (d, *J* = 6.9 Hz, 2H), 8.96 (d, *J* = 6.6 Hz, 2H), 8.85 (d, *J* = 6.6 Hz, 2H), 5.17 (t, J = 9 Hz, 2H), 5.14 (t, *J* = 9 Hz, 2H), 2.90 – 2.71 (m, 4H). HPLC-MS (exact mass): [M⁺] = 1118,4321 (theoretical 1118,4390); [M²⁺] = 559,2109 (theoretical 559,2195).

General procedure for the synthesis of the oxadiazole bis-pirydinium bistriflimides

The oxadiazole bispirydinium halides (0.1 g) were dissolved in amounts of MeOH as small as possible to dissolve them (10-20 mL) in a glass tube and LiTf₂N (2.5 mol eq.) was added. The mixture was stirred for 0.5 h at 35 °C and just after water was added dropwise, until permanent suspension was

formed. After this the mixture was stirred for further 2 h and the solid was filtered under vacuum washing with water, until a negative assay with AgNO₃ was obtained.

4,4'-(1,2,4-oxadiazole-3,5-diyl)bis(1-decylpyridin-1-ium) bis((trifluoromethyl)sulfonyl)amide [10obp10][Tf₂N]₂

Yield = 85.5%. White solid. ¹H NMR (300 MHz, (CD₃)₂SO) δ : 9.41 (d, *J* = 6.9 Hz, 2H), 9.35 (d, *J* = 6.9 Hz, 2H), 8.88 (d, *J* = 6.6 Hz, 2H), 8.78 (d, *J* = 6.6 Hz, 2H), 4.74 (t, J = 9 Hz, 2H), 4.72 (t, *J* = 9 Hz, 2H), 2.07 – 1.89 (m, 4H), 1.31 – 1.25 (m, 28H), 0.85 (t, *J* = 6.5 Hz, 6H). HPLC-MS (exact mass): [M⁺] = 506.3974 (theoretical 506.3979); [M²⁺] = 253.2054 (theoretical 253.1987); [M⁻] = 279,9152 (theoretical 279,9178).

4,4'-(1,2,4-oxadiazole-3,5-diyl)bis(1-dodecylpyridin-1-ium) bis((trifluoromethyl)sulfonyl)amide

[12obp12][Tf₂N]₂

Yield = 51.1%. White solid. ¹H NMR (300 MHz, (CD₃)₂SO) δ : 9.42 (d, *J* = 6.9 Hz, 2H), 9.38 (d, *J* = 6.9 Hz, 2H), 8.90 (d, *J* = 6.6 Hz, 2H), 8.79 (d, *J* = 6.6 Hz, 2H), 4.74 (t, J = 9 Hz, 2H), 4.72 (t, *J* = 9 Hz, 2H), 2.06 – 1.91 (m, 4H), 1.34 – 1.26 (m, 36H), 0.85 (t, *J* = 6.5 Hz, 6H). HPLC-MS (exact mass): [M⁺] = 562.8861 (theoretical 562.8870); [M²⁺] = 281.4445 (theoretical 281.4435); [M⁻] = 279,9174 (theoretical 279,9178).

4,4'-(1,2,4-oxadiazole-3,5-diyl)bis(1-tetradecylpyridin-1-ium) bis((trifluoromethyl)sulfonyl)amide [14obp14][Tf₂N]₂

Yield = 46.5%. White solid. ¹H NMR (300 MHz, (CD₃)₂SO) δ : 9.42 (d, *J* = 6.9 Hz, 2H), 9.38 (d, *J* = 6.9 Hz, 2H), 8.90 (d, *J* = 6.6 Hz, 2H), 8.79 (d, *J* = 6.6 Hz, 2H), 4.74 (t, J = 9 Hz, 2H), 4.72 (t, *J* = 9 Hz, 2H), 2.06 – 1.91 (m, 4H), 1.34 – 1.26 (m, 44H), 0.85 (t, *J* = 6.5 Hz, 6H). HPLC-MS (exact mass): [M⁺] = 618.9981 (theoretical 618.9950); [M²⁺] = 309.4921 (theoretical 309.4975); [M⁻] = 279,9171 (theoretical 279,9178).

4,4'-(1,2,4-oxadiazole-3,5-diyl)bis(1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)

pyridin-1-ium) bis((trifluoromethyl)sulfonyl)amide [8.2obp2.8][Tf₂N]₂

Yield = 85.5%. White solid. ¹H NMR (300 MHz, (CD₃)₂SO) δ : 9.54 (d, *J* = 6.9 Hz, 2H), 9.48 (d, *J* = 6.9 Hz, 2H), 8.96 (d, *J* = 6.6 Hz, 2H), 8.85 (d, *J* = 6.6 Hz, 2H), 5.16 (t, J = 9 Hz, 2H), 5.13 (t, *J* = 9 Hz, 2H), 2.99 – 2.75 (m, 4H). HPLC-MS (exact mass): [M⁺] = 1118,4338 (theoretical 1118.4390); [M²⁺] = 559,2159 (theoretical 559.2195) [M⁻] = 279,9116 (theoretical 279,9178).

Materials and methods

<u>Flash chromatography</u> was performed using silica gel (200-400 mesh) and mixtures of ethyl acetate and light petroleum (fraction boiling in the range 40-60°C) in various ratios as eluents. All other starting materials and solvents were purchased from standard commercial sources and were used without further purification.

<u>Microwave assisted synthesis</u> were carried out by a Start Synth Microvawe Lab station (Milestone Microvawe Laboratory Systems).

<u>Solution-state NMR</u> spectra were recorded on *i*) a Bruker AVANCE DMX 300 spectrometer operating at 300 MHz (¹H) and *ii*) a Bruker DXP 200 equipped with a 5mm QNP probe. Solutions were prepared in CDCl₃, CD₃CN, CD₃OD or (CD₃)₂SO and TMS was used as a reference.

Mass spectra were recorded on a Agilent Technologies 1260 Infinity.

Polarised optical microscopy was performed with

i) a Zeiss Axiovision microscope using a Linkam LTS420 hot-stage controlled by a Linkam PE95/T95 central processor. Photomicrographs were captured via an Axiocam ICc 1 digital camera mounted atop the microscope. Images were recorded at a magnification of 100x, and 200x during heating and cooling of the samples which were placed between two cover slips. Heating and cooling rates were 0.1-10 °C min⁻¹.

ii) a Leica DM4000M polarized light microscope. The samples were placed between a glass slide and a cover slip. A Mettler FP82HT hot stage was used to control the temperature. The samples were heated at 10 °C/min beyond the melting temperature determined by DSC experiments, and subsequently cooled at 10 °C/min to room temperature. The photomicrographs were taken between crossed-polarizers with a Leica DFC280 digital camera.

iii) POM images and videos were acquired with a Leitz Laborlux 12 POL polarizing optical microscope connected to a Lumix Panasonic DMC-FS42 photocamera.

Differential scanning calorimetry parameters were determined with

i) a TA Instrument Q20 thermal analyser calibrated before use against an indium standard. Pure samples (2-4 mg) were prepared in 40 μ L aluminium light crucibles and analysis were carried out with a rate of 10 °C min⁻¹ for each sample under a N₂ flux of 50 cm³ min⁻¹.

ii) a TA Instruments mod. 2920 calorimeter operating under N2 atmosphere. Samples weighing about 5 mg closed in aluminium pans were used throughout the experiments. Indium of high purity was used for calibrating the DSC temperature and enthalpy scales. Four ramps were included in the temperature program: one heating from room temperature to 160 °C at 10 °C/min, followed by a cooling step to room temperature at 10 °C/min and by another analogous heating/cooling cycle. The repetition of two similar heating/cooling ramps was done to assess the repeatability of the phase transitions.

Cyclic Voltammetry

A BAS C3 Cell stand instrument was used to collect cyclic voltammetry data. This was equipped with a glassy carbon working electrode, an Ag/AgCl reference electrode and a Pt counter electrode. The samples (0.5mM) were dissolved in acetonitrile (viologens) or DMF (oxazolidines) containing Bu₄NClO₄ 0.1M as support electrolyte. A scan rate of 100mV/s was applied in all cases. Potentials were calculated vs NHE.

Spectroelectrochemical measurements in solution and in bulk.

Spectroelectrochemical experiments were performed with an electrolytic cell (BAS Inc.) composed of a 1 mm path length cuvette, where a platinum gauze thin layer and a platinum wire were used as the working electrode and the auxiliary electrode, respectively. A pseudo-reference electrode consisting of an Ag wire was calibrated against the Fc⁺/Fc redox couple. The spectroelectrochemical cell was filled with acetonitrile solutions of each compound (in a range from 0.5 to 3 mM) and TBAPF₆ (0.1 M). UV-vis-NIR spectra were recorded using a Vertex 80 (Bruker) spectrophotometer. The potential was supplied by means of an Amel 2049 model potentiostat. Measurements were performed at 25 °C.

Bulk electrochemical and optical material properties were investigated in a liquid crystal cell made by sandwitching two ITO glass electrodes with active area of about 2×2 cm². The cell gap was controlled by inserting cylindrical spacers with mean base diameter of 10×10⁻⁶ m. Cells were filled by capillary action with the compound in the isotropic liquid state. Spectroelectrochemical experiments were performed on the LC cell placed in a customized variable temperature controller hot plate (HPM200, CaLCTec S.r.l., Italy) equipped with electric contacts for voltage delivering, which was inserted into the probe of the Vertex 80 (Bruker) spectrophotometer.

DFT calculations.

Geometries of the model systems were optimized at the B3LYP/6-311+G(d,p) level of theory using the software package Gaussian09.¹ We selected the solvent acetonitrile with a dielectric constant of ε =35.688 and the PCM continuum model.² Frequency calculations using the minimized structures revealed no imaginary frequencies. Optimized geometries for the singlet (dicationic) and doublet (radical monocations) of the model systems investigated are reported below.

¹ Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

² J. Tomasi, B. Mennucci, and R. Cammi, "Quantum mechanical continuum solvation models," *Chem. Rev.*, **105** (2005) 2999-3093.

DFT calculations

 $[\mathsf{CF}_3\mathsf{CH}_2\mathbf{bp}\mathsf{CH}_2\mathsf{CH}_3]^{2+}$

dicationic polyfluoro viologen

$[CF_3CH_2bpCH_2CH_3]^+$ •

radical cation polyfluoro viologen



Map of electrostatic potential



Map of electrostatic potential



номо



SOMO



lumo



LUMO



Electron spin density

Figure 29. Electrostatic potential, HOMO-LUOMO and electron spin density of 1.1bp2

$[CH_3CH_2 \textbf{b} \textbf{p} CH_2 CH_3]^{2+}$

dicationic alkyl viologen

$[CH_3CH_2bpCH_2CH_3]^+$ •

radical cation alkyl viologen



Electron spin density

Figure 30. Electrostatic potential, HOMO-LUOMO and electron spin density of 2bp2

$[\mathsf{CH}_3\mathsf{CH}_2\textbf{obp}\mathsf{CH}_2\mathsf{CH}_3]^{2+}$

dicationic oxadiazolyl bipyridinium



Map of electrostatic potential

$[CH_3CH_2obpCH_2CH_3]^+$

radical cation oxadiazolyl bipyridinium



Map of electrostatic potential



номо



SOMO

LUMO



LUMO



Electron spin density

Figure 31. Electrostatic potential, HOMO-LUOMO and electron spin density of 10bp1

10k	pp1²⁺ singlet,	DFT Energy	: -836.001790
Ν	-0.290356	0.000444	-0.190745
С	-0.197662	-0.007933	1.104382
0	1.075851	-0.009489	1.537493
Ν	1.880860	-0.001267	0.411742
С	1.024502	0.004351	-0.583564
С	1.447110	0.013829	-1.989669
С	-1.281239	-0.015565	2.085618
С	2.802228	0.018257	-2.341181
С	3.153616	0.026986	-3.672256
Ν	2.208424	0.031312	-4.640903
С	0.897922	0.027240	-4.323270
С	0.488849	0.018494	-3.004263
Н	3.580331	0.014938	-1.591236
Н	4.183049	0.030719	-4.001653
С	2.635940	0.041001	-6.061061
Н	0.197233	0.031075	-5.145240
Н	-0.567596	0.015331	-2.777580
С	-1.020466	-0.025054	3.459554
С	-2.078712	-0.032244	4.342932
Ν	-3.354761	-0.030150	3.897089
С	-3.625074	-0.020920	2.574709
С	-2.605932	-0.013511	1.644324
Н	-0.012149	-0.027019	3.848060
Н	-1.938716	-0.039719	5.414648
С	-4.461241	-0.037420	4.885982
Н	-4.666787	-0.019762	2.290040
Н	-2.847438	-0.006307	0.591079
Н	1.753788	0.040250	-6.693771
Н	3.224439	0.937838	-6.244613
Н	3.232797	-0.848228	-6.254263
Н	-5.407673	-0.040901	4.354330
Н	-4.375875	-0.931558	5.500242
Н	-4.384316	0.854980	5.503946

10	bp1 + doublet	, DFT Energy	: -836.154501
С	-2.813953	-1.183574	-0.007218
С	-2.412933	0.187789	-0.010135
С	-3.460165	1.160518	-0.017179
С	-4.765488	0.769517	-0.019367
Ν	-5.122189	-0.557688	-0.022009
С	-4.133411	-1.517727	-0.009162
С	-1.047388	0.547845	-0.006762
Ν	0.025920	-0.235044	-0.005266
С	1.052576	0.647924	-0.001236
Ν	0.712441	1.924683	-0.000423
0	-0.694297	1.875768	-0.004333
С	2.458526	0.232515	0.001356
С	3.498173	1.174028	0.020959
С	4.804825	0.744156	0.021677
Ν	5.104569	-0.576265	0.003898
С	4.120102	-1.501467	-0.014336
С	2.793523	-1.124712	-0.016062
С	6.526418	-0.991681	0.005319
С	-6.530440	-0.957704	0.055173
Н	3.291461	2.234544	0.035651
Н	5.642238	1.427551	0.036257
Н	4.428133	-2.536697	-0.027918
Н	2.024827	-1.883823	-0.031196
Н	-3.235411	2.218073	-0.023236
Н	-5.580921	1.478838	-0.024734
Н	-4.472330	-2.544170	-0.004444
Н	-2.072667	-1.970757	-0.004387
Н	6.576369	-2.076132	-0.016600
Н	7.016133	-0.581342	-0.875900
Н	7.004023	-0.617648	0.909134
Н	-6.701297	-1.817199	-0.592604
Н	-6.797794	-1.219350	1.081960
Н	-7.155780	-0.132405	-0.278851

1.1	hn2 ²⁺ single	t DFT Energy	v = -951 499180
<u>с</u>	-2.359414	-1.070133	-0.426857
C	-1.751970	0.112544	0.008421
C	-2.560702	1.235003	0.217162
C	-3.919554	1.148574	-0.005080
N	-4.480587	-0.002959	-0.429558
С	-3.722637	-1.098837	-0.641342
С	-0.289287	0.177168	0.238600
С	0.449891	1.301034	-0.149643
С	1.807531	1.341714	0.079792
Ν	2.436094	0.305319	0.683648
С	1.745889	-0.793335	1.071751
С	0.387950	-0.880622	0.857034
С	3.894118	0.367826	0.909745
С	4.672746	-0.188634	-0.281687
С	-5.962545	-0.074967	-0.626434
С	-6.685748	-0.442844	0.664115
Н	-2.154540	2.173035	0.569321
Н	-4.584650	1.986420	0.146009
Н	-4.234772	-1.984338	-0.989419
Н	-1.786709	-1.964901	-0.628370
Н	-0.130746	-1.765217	1.199187
Η	2.307787	-1.576663	1.558407
Η	2.416986	2.186976	-0.203695
Н	-0.012069	2.143228	-0.645760
Н	4.187446	1.402818	1.071106
Н	4.143138	-0.211852	1.795903
Н	-6.135736	-0.812867	-1.407455
Н	-6.275057	0.898231	-1.002172
Н	-7.756105	-0.494268	0.456116
Н	-6.361425	-1.416332	1.036453
Н	-6.524445	0.306458	1.441269
F	5.988114	-0.110833	-0.030239
F	4.366369	-1.478244	-0.521338
F	4.420489	0.500833	-1.411644

1.1	bp2 ⁺, double	et DFT Energ	y = -951.663098
С	-2.502096	1.213314	0.096123
С	-1.731297	0.017708	-0.034644
С	-2.475326	-1.193602	0.106568
С	-3.819235	-1.179509	0.346965
Ν	-4.515992	-0.010995	0.466256
С	-3.845819	1.171566	0.334388
С	-0.322073	0.032221	-0.282532
С	0.440759	-1.164894	-0.468473
С	1.781138	-1.130824	-0.700042
Ν	2.469054	0.060183	-0.765269
С	1.774285	1.237451	-0.602511
С	0.432987	1.245097	-0.373605
С	3.909903	0.073412	-0.977036
С	4.696128	-0.032683	0.327347
С	-5.981847	-0.026809	0.668730
С	-6.753341	-0.051800	-0.648801
Н	-1.999998	-2.161041	0.038825
Н	-4.392026	-2.089113	0.461824
Н	-4.439683	2.069376	0.434084
Н	-2.050118	2.190392	0.009770
Н	-0.035527	2.211846	-0.261934
Н	2.352861	2.147120	-0.673202
Н	2.363879	-2.028073	-0.850585
Н	-0.023228	-2.139864	-0.442269
Н	4.199261	-0.762236	-1.613433
Н	4.200638	0.999079	-1.472238
Н	-6.234755	0.857227	1.254630
Н	-6.213327	-0.902267	1.275998
Н	-7.824816	-0.060845	-0.436804
Н	-6.531630	0.830721	-1.252951
Н	-6.512647	-0.943979	-1.231190
F	6.019112	0.001419	0.072838
F	4.416311	0.979009	1.175843
F	4.436209	-1.183376	0.984399

2hi	and the singlet		- 652 699222
20 	1 /0/555	1 209151	0 220067
C C	-1.494333	1.200151	0.239907
C C	-0.737349	0.073882	
C C	-1.413008	-1.001025	-0.538185
	-2.785892	-1.034497	-0.6/120/
N	-3.491/5/	0.072016	-0.358461
C	-2.865945	1.180037	0.091057
C	0./3/335	0.073850	0.074353
C	1.494644	1.208144	-0.240416
С	2.865971	1.180049	-0.091104
Ν	3.491668	0.072017	0.358603
С	2.785743	-1.034542	0.670931
С	1.412935	-1.061105	0.537479
С	4.983740	0.053246	0.465552
С	-4.983869	0.053299	-0.464887
Н	1.037097	2.111781	-0.618477
Н	3.490802	2.030677	-0.322830
Η	3.348582	-1.882877	1.032378
Η	0.886305	-1.961815	0.819995
Н	-0.886443	-1.961650	-0.820987
Н	-3.348894	-1.882813	-1.032448
Н	-3.490669	2.030680	0.323021
Н	-1.036935	2.111779	0.617956
С	-5.635138	-0.381271	0.843293
Н	-5.288935	1.057744	-0.754059
Н	-5.228970	-0.624938	-1.280671
Н	5.228525	-0.624935	1.281472
С	5.635476	-0.381271	-0.842411
Н	5.288704	1.057724	0.754713
Н	6.718336	-0.383387	-0.704447
Н	5.323912	-1.388454	-1.125778
Н	5.395772	0.306280	-1.655703
Н	-6.718043	-0.383528	0.705664
Н	-5.323363	-1.388441	1.126495
Н	-5.395326	0.306264	1.656571

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20	p2 ⁺ , doublet,	DFT Energy	= -653.845038
C	-1.4/8651	1.204222	-0.163992
С	-0.711042	0.000002	-0.077851
С	-1.478569	-1.204253	-0.163907
С	-2.834681	-1.177091	-0.309674
Ν	-3.528214	-0.000099	-0.387073
С	-2.834749	1.176977	-0.309740
С	0.711034	0.000088	0.077737
С	1.478540	1.204376	0.163653
С	2.834638	1.177260	0.309502
Ν	3.528185	0.000266	0.387145
С	2.834742	-1.176811	0.309901
С	1.478648	-1.204102	0.164054
С	5.003405	0.000290	0.475702
С	-5.003412	-0.000084	-0.475648
Н	1.010501	2.176904	0.119688
Н	3.423742	2.081293	0.377046
Н	3.423925	-2.080765	0.377806
Н	1.010699	-2.176687	0.120480
Н	-1.010556	-2.176803	-0.120195
Н	-3.423795	-2.081108	-0.377337
Н	-3.423955	2.080933	-0.377447
Н	-1.010668	2.176788	-0.120314
С	-5.673900	-0.000065	0.896408
Н	-5.291897	0.879617	-1.051948
Н	-5.291920	-0.879823	-1.051881
Н	5.291876	-0.878995	1.052658
С	5.673981	-0.000758	-0.896279
Н	5.291888	0.880432	1.051325
Н	6.758704	-0.001093	-0.766935
Н	5.397994	-0.888440	-1.470042
Н	5.398631	0.886430	-1.471107
Н	-6.758634	0.000573	0.767196
Н	-5.398612	-0.887802	1.470424
Н	-5.397628	0.887064	1.470893