Supporting information available

Thermotropic ionic liquid crystals by molecular-assembly and ion pairing of 4,4'-bipyridinium derivatives and tris(dodecyloxy)benzenesulfonats in a non-polar solvent

by

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The synthesis of compounds: \( \text{MV}^{2+}\text{I}_2, \text{V}^{2+}\text{Br}_3, \text{MV}^{6+}\text{I}_6 \) and \( \text{CsDOBS} \) are known and described in literature\(^1\text{-}^4\).

\(^1\text{H- and }^{13}\text{C- NMR Spectra, IR-Spectra, DSC-Analysis}\)
Experimental details corresponding to the synthesis and analytical data of compounds $\text{MV}^2\text{I}_2$, $\text{V}^3\text{Br}_3$, $\text{MV}^6\text{I}_6$ and CsDOBS

Materials and Measurements

4,4’-Bipyridine (99%+, Fluka), Magnesium sulfate, anhydrous (95%+, Alfa Aesar); acetonitrile (99.9%+, Sigma Aldrich), diethyl ether (99%+, Sigma Aldrich), methyliodide (99%+, Aldrich) 3,4,5-Trihydroxybenzene(99 %, Aldrich), 1-bromodecane (99 % Aldrich), sulfuric acid (95.97%, Merck), sodium hydroxide, sodium sulfite, hypochloric acid 0.1 M (ACS reagent), barium acetate (99%, Fluka), Amberlite IR 120 (Fluka), caesium carbonate (99%, Aldrich) were used like received. Ethanol, n-hexane, ethylacetate, toluene, tetrahydrofuran, isopropyl ether were all ACS reagents and used as received. Dichloromethane, diethylether, chloroform and N,N-Dimethylformamide was distillated before to use.

$\textit{NMR Analysis:}$ $^1\text{H}$-NMR (500 MHz) and $^{13}\text{C}$-NMR (125 MHz) spectra were recorded on Bruker AMX-500 spectrometer; chemical shift $\delta$ in ppm related to tetramethylsilane (TMS) as internal standard in deuterated chloroform or deuterated water at 20°C. $\textit{Elemental analyses}$ were made on VarioMICRO cube and IR Analysis on FT-IR Spektrophotometer Vertex 70. $\textit{DSC Analysis:}$ Differential scanning calorimetry (DSC) measurements were performed on samples of about 4-12 mg. Phase transitions were measured on a Netzsch DSC 204 ‘Phoenix’ differential scanning calorimeter. The heating and cooling rates were 10°C/min. Indium, tin and cyclohexane were used as calibration standards. $\textit{Thermo-optical Polarizing Microscopy:}$ a Zeiss AXIOPLAN 2 polarising microscope was used; equipped with a Mettler FP 80 hot stage d. Pictures were taken using a digital Zeiss AxioCam MRC4 camera with a resolution of 4 megapixels in combination with Zeiss AxioVision.
software. *Electrochemistry* Analysis: CVs were measured with the potentiostat PGSTAT 302N from AUTOLAB, controlled by PC running under GPES from Windows, version 4.9 (ECO Chemie B.V.). Glass slides (60 mm x 70 mm) coated with ITO (In-doped SnO$_2$, 20 Ω/cm$^2$) from BTE Bedampfungstechnik (Elsoff, Germany) was used for CV. The electroactive film with an area of 0.42 cm$^2$ and a thickness of 5 μm was obtained between two pieces of SnO$_2$ conducting glass and measured in two electrode system without electrolyte.

*Synthesis of 1,1´-dimethyl(4-pyridin-4-ylpyridinium) diiodide (MV$^{2+}$I$_2$)$^{1}$*

To a solution of 5 g (32 mmol) 4,4´-bipyridine dissolved in 30 ml MeCN, 4 ml (64 mmol) of methyl iodide was added. The mixture was stirred at 70°C for 30 h, the resulting precipitate was filtered off, and thoroughly washed with dry diethyl ether and toluene. The crystallization of the product proceeded slowly (48 h at 4°C) from an ethanol-ether mixture (1:1.5 vol %). The resulting orange-red powder was dried for 12 h in an oil pump vacuum to yield 4.93 g (11.2 mmol) product as iodide, yield 35%. $^1$H-NMR (500 MHz, D$_2$O, 20°C, TMS, δ/ppm): 9.07 (d, 4H, J=5.0 Hz), 8.55 (d, 4H, J=7.0 Hz) 4.53 (s, 6H). $^{13}$C-NMR (125 MHz, D$_2$O, 20 °C, TMS, δ/ppm): 149.93 (s), 146.41 (d), 126.84 (d), 48.57 (q). IR (ATR, cm$^{-1}$) 3085(m), 2990(s), 1633(s), 1555(m), 1500(m), 1434(m), 1348(m), 1267(m), 1227(w), 1175(s), 1108(w), 965(w), 811(s), 700(w). Elemental analysis: calculated for C$_{12}$H$_{14}$I$_2$N$_2$ (wt %), C 32.75, H 3.21, N 6.37; found, C 32.77, H 3.55, N 6.50.

*Synthesis of 1,1´,1´´-[benzene-1,3,5-triyltris(methylene)tris](4-pyridin-4-ylpyridinium) tribromide (V$^{3+}$Br$_3$)$^{2}$*

14 g (89 mmol) 4,4´-Bipyridine were dissolved in 80 mL of warm MeCN, and a solution of 5 g (5,8 mmol) 1,3,5-tris(bromomethyl)benzene$^3$ in 50 mL MeCN was
added within 7 h at a rate of 0.118 mL/minute. The mixture was stirred at 70°C for 30 h under reflux. Subsequently the reaction mixture was cooled to 20°C, filtered and washed for three times with 45 mL of CH₂Cl₂. The filter cake was dissolved in water and extracted four times with 200 mL of CH₂Cl₂ each. The water was evaporated and the residue was dissolved in 30 ml methanol and then filtered. Diethyl ether was added drop wise to initiate the precipitation. A yellow powder was obtained and dried in an oil pump vacuum to yield 3.63 g (4.4 mmol) product as bromide, 76 %. TGA: decomposition beyond 215°C. ¹H-NMR (500 MHz, 20°C, TMS, δ/ppm): 6.09 (s, 6H), 7.54 (s, 3H), 7.91 (d, 6H, J=3.0 Hz), 8.50 (d, 6H, J=7.0 Hz), 8.79 (d, 6H, J=3.0 Hz), 9.11 (d, 6H, J=6.5 Hz). ¹³C-NMR (125 MHz, D₂O, 20 °C, TMS, δ/ppm): 63.2 (t), 122.3 (d), 126.2 (d), 129.2 (d) 136.0 (s), 142.0 (s), 145.4 (d) 150.1 (d), 154.4 (s). IR (ATR, cm⁻¹) 3346(br), 3022(m), 2966(m), 1633(vs), 1597(m), 1542(m), 1521(m), 1490(m), 1490(m), 1405(s), 1350(m), 1216(m), 1157(m), 1069(w), 993(w), 870(w), 813(s), 748(m), 714(w). Elemental analysis: calculated for C₃₉H₃₃Br₃N₆ (wt %), C 56.75, H 4.03, N 10.18; found, C 55.92, H 4.22, N 8.62.

_Synthesis of 1,1',1''- [benzene-1,3,5-triytris(methylene)tris](1'methyl 4-pyridin-4-ylpiridinium) hexaiodide (MV₆⁺I₆)_.

To a solution of 0.5 g (0.5 mmol) 1,1',1''- [benzene-1,3,5-triytris(methylene)tris](4-pyridin-4-ylpyridinium) trihexafluorophosphate (V³⁺(PF₆)₃) dissolved in 8 mL MeCN was added 1 ml (16 mmol) of methyl iodide. After a few minutes from start the solution become red-dark and a precipitate was obtained. The mixture was stirred at 70 °C for 48 h. The resulting precipitate was filtered and thoroughly washed with MeCN. The resulting red powder was dried in an oil pump vacuum at 50°C for 12 h to result 0.300 g (0.4 mmol) as iodide, yield 44 %. ¹H NMR (500 MHz, D₂O, 20 °C, TMS, δ/ppm): 9.51(d, 6 H, J (H,H) = 6.5 Hz ), 9.29 (d, 6 H, J (H,H) = 6.5 Hz ), 8.85 (d,
6 H, J (H,H) = 6.5 Hz ), 8.78 (d, 6 H, J (H,H) = 6.5 Hz), 7.89 (s, 3H), 6.05 (s, 6H),
4.46 (s, 9H).   \(^{13}\text{C}\text{ NMR (125 MHz, D}_2\text{O, 20 °C, TMS, } \delta/\text{ppm)}: \delta = 48.10 (q), 62.23 (t),
126.18(d), 127.01(d), 130.36(d), 135.37(s), 145.91 (d), 146.51(d), 147.89(s),
148.98(s). Elemental analysis: calculated for C\(_{42}\)H\(_{77}\)N\(_6\) (wt %), C 36.23, H 3.04, N
6.04; found, C 36.10, H 3.46, N 6.26;0

Caesium 3,4,5-tris(dodecyloxy)benzenesulfonate (CsDOBS)\(^4\)

5.0 g (7.03 mmol) 3,4,5-Trihydroxybenzenesulfonic acid and 23.8 g (73.05 mmol) Cs\(_2\)CO\(_3\) were mixed with 60 ml of dried DMF under a nitrogen atmosphere. At 100 °C, 10 ml (41.6 mmol) of 1-bromododecane were added dropwise. The reaction mixture was stirred for 48 h at 100 °C and subsequently slowly poured into 50 ml of ice water. The precipitate was isolated by filtration and recrystalised twice from 100 ml of methanol to give a white powder. Yield: 1.8 g (2.1 mmol) 29.8%. M.p. 116.9 °C (by DSC). TLC (KG-60, CHCl\(_3\): methanol = 6 vol : 1 vol): R\(_f\) = 0.46. \(^1\text{H NMR (500 MHz,CDCl}_3\text{, 20 °C, TMS; } \delta/\text{ppm))}: 7.02 (s, 2H, aromatic), 3.95-3.91 (m, 6H, OCH\(_2\)),
1.71-1.70 (m, 6H, OCH\(_2\)CH\(_2\)), 1.45-1.41 (m, 6H, O(CH\(_2\))\(_2\)CH\(_2\)), 1.26 (overlapped peaks, 48H, O(CH\(_2\))\(_3\)(CH\(_2\))\(_8\)), 0.88 (t, 9H, CH\(_3\), J = 5.0 Hz). \(^{13}\text{C}\text{ NMR (125 MHz, CDCl}_3\text{, 20 °C, TMS; } \delta/\text{ppm):} 153.25(s), 140.19(s), 140.06(s), 104.59(d), 73.68(t),
69.65(t), 32.17(t), 30.64(t), 29.92(t), 29.73(t), 26.50(t), 22.91(t), 14.30(q). Elemental
analysis: calculated for C\(_{42}\)H\(_{77}\)CsO\(_6\)S (wt %), C 59.84, H 9.21; found, C 59.51, H
9.11.
References


$^{1}$H-NMR

Caesium 3,4,5-tris(dodecyloxy)benzene sulfonate (DOBS)

1,1'-Dimethyl (4-pyrid-4-ylpyridinium) diiodide (MV$^{2+}$I$_2$)
1,1',1"-[Benzene-1,3,5-triyltris(methylene)]tris (4-pyridin-4-ylpyridinium) tribromide

(V^3+Br_3)

1,1',1"-[benzene-1,3,5-triyltris(methylene)]tris([methyl] 4-pyridin-4-ylpyridinium])

hexaiodide (MV^6+I_6)
$\text{MV}^{6+}(\text{DOBS})_6$

\[ \text{Caesium 3,4,5-tris(dodecyloxy)benzene sulfonate (DOBS)} \]
1,1'-Dimethyl (4-pyridin-4-ylpyridinium) diiodide (MV$^{2+}$I$_2$)

1,1',1''-[Benzene-1,3,5-triyltris(methylene)]tris (4-pyridin-4-ylpyridinium) tribromide (V$^{3+}$Br$_3$)
1,1',1''-[benzene-1,3,5-triyltris(methylene)]tris[(methyl) 4-pyridin-4-ylpyridinium)] hexaiodide ($\text{MV}^6\text{I}_6$)

$\text{MV}^2\text{O}(\text{DOBS})_2$
\[ \text{V}^{3+}(\text{DOBS})_3 \]

\[ \text{MV}^{6+}(\text{DOBS})_6 \]
MV^{2+}(DOBS)_2

V^{3+}(DOBS)_3
**MV^{6+}(DOBS)_6**

![Graph showing infrared spectrum with wavenumber cm⁻¹ ranging from 3500 to 500.]

**MV^{2+}(DOBS)_2**

![Graph showing DSC and flow rate measurements with temperature in °C ranging from -60 to 100.]

The graph depicts endothermic and exothermic events at specific temperatures.
$V^3+(DOBS)_3$

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**Electronic Supplementary Material (ESI) for Journal of Materials Chemistry**

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**MV^6+(DOBS)_6**