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# *Ionic Liquid Crystals of Imidazolium Salts with A Pendant Hydroxyl Group*

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## Experimental Section

**General Information.** All the solvents used were reagent grade and were used as received. Imidazole was purchased from R. D. H. product. Racemic epoxides were obtained from TCI and Aldrich. Alkyl halides were obtained from TCI. The $^1$H NMR spectra was recorded on a Bruker Avance $DPX_{300}$ spectrometer in $CDCl_3$. Elemental microanalyses were performed by Taiwan Instrumentation Center. Optical characterization was performed by using covered microscope slides on a Zeiss Axioplan 2 polarizing microscope equipped with a Mettler Toledo FP82 hot stage and Mettler Toledo FP90 central processor. Phase transition temperatures were determined by differential scanning calorimetry at a scan rate of 10 $^{o}$C/min using a Mettler Toledo DSC822$^{e}$ calorimeter calibrated with indium and tin standards. The IR spectra were recorded on a JASCO FT/IR 410. The powder X-ray diffraction data were collected from the Wiggler-A beamline of the National Synchrotron Radiation Research Center (NSRRC). Diffraction patterns were recorded in θ/2θ geometry with step scans normally

0.02 degree in 2θ = 1-10 degree $step^{-1}s^{-1}$ and 0.5 degree in 2θ = 1-25 degree $step^{-1}s^{-1}$ and a gas flow heater was used to control the temperature. The powder samples were charged in Lindemann capillary tubes (80 mm long and 0.01 mm thick) from Charles Supper Co. with an inner diameter of 0.10 or 0.15 mm.

Single crystal X-ray diffraction data were collected on a Bruker SMART diffractometer equipped with a CCD array detector with graphite monochromatized Mo-$K_\alpha$ radiation (λ = 0.71073 Å) in $\phi$ and $\omega$ scan modes. Details of crystal parameters, data collection and structure refinements are summarized in Table 1. The structure was solved by the heavy atom method and refined (based on $F^2$ using all independent data) by full matrix least squares methods (Bruker SHELXTL 97). The non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in idealized positions with their coordinates and thermal parameters riding on the attached atoms.

Although $imC_n$(2-OH) of n = 10, 12, 14, 16 and 18 have been reported,[24a,b,c] characterization data of these compounds were not given except for n = 10.[24c] Therefore detailed preparation and characterization of these compounds were presented. (See the main text for the details of references)

**Preparation of 1-(2-hydroxyoctadecyl)imidazole, $C_{18}$(2-OH)-im.** Imidazole (0.3 g, 4.41 mmol) and 1,2-epoxyoctadecane (1.0 g, 3.72 mmol) were mixed in a 50 mL round bottom flask without solvent. The mixture was reacted neat for 12 h at 100 $^oC$ with stirring. After cooling, the residue was dissolved in $CH_2Cl_2$ (30 mL) and washed two times with water (70 mL). The volume of the $CH_2Cl_2$ solution was then reduced to 15 mL by rotary evaporator. To this solution, hexane was then added to obtain the product white solid in a yield of 87%. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^3J$ = 7 Hz, 3H, $CH_3$),

1.25-1.48 (m, 30H, $CH_2$), 3.88 (m, 2H, α-$CH_2$), 4.00 (m, 1H, β-CH), 6.95 (s, 1H, CH), 6.99 (s, 1H, CH), 7.66 (s, 1H, CH). Anal. Calcd. for $C_{21}H_{40}N_2O$: C, 74.94; H, 11.98; N, 8.32 %; Found: C, 74.83; H, 11.97; N, 8.16 %.

The following $C_n$(2-OH)-im compounds (n = 16, 14, 12 and 10) were prepared as for n = 18.

**1-(2-hydroxyhexadecyl)imidazole, $C_{16}$(2-OH)-im.** White solid, yield 85 %. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, $^3J$ = 7 Hz, 3H, $CH_3$), 1.26-1.48 (m, 26H, $CH_2$), 3.86 (m, 2H, α-$CH_2$), 3.99 (m, 1H, β-CH), 6.97 (s, 1H, CH), 7.01 (s, 1H, CH), 7.59 (s, 1H, CH). Anal. Calcd. for $C_{19}H_{36}N_2O$: C, 73.97; H, 11.76; N, 9.08 %. Found: C, 74.04; H, 11.76; N, 8.95 %.

**1-(2-hydroxytetradecyl)imidazole, $C_{14}$(2-OH)-im.** White solid, yield 84 %. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^3J$ = 7 Hz, 3H, $CH_3$), 1.26-1.48 (m, 22H, $CH_2$), 3.87 (m, 2H, α-$CH_2$), 3.99 (m, 1H, β-CH), 6.95 (s, 1H, CH), 7.02 (s, 1H, CH), 7.54 (s, 1H, CH). $^{13}$C NMR (74 MHz, $CDCl_3$): 13.03, 22.31, 25,18, 28.98, 29.23, 29.29, 31.64, 47.62 (-$NCH_2$), 120.09, 127.07, 137.57 (-C2). Anal. Calcd. for $C_{17}H_{32}N_2O$: C, 72.81; H, 11.50; N, 9.99 %. Found: C, 72.55; H, 11.50; N, 9.54 %.

**1-(2-hydroxydodecyl)imidazole, $C_{12}$(2-OH)-im.** White solid, yield 80 %. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^3J$ = 7 Hz, 3H, $CH_3$), 1.25-1.48 (m, 18H, $CH_2$), 3.83 (m, 2H, α-$CH_2$), 3.97 (m, 1H, β-CH), 6.93 (s, 1H, CH), 6.96 (s, 1H, CH), 7.45 (s, 1H, CH). Anal. Calcd. for $C_{15}H_{28}N_2O$: C, 71.38; H, 11.18; N, 11.10 %. Found: C, 71.28; H, 11.14; N, 11.07 %.

**1-(2-hydroxydecyl)imidazole, $C_{10}$(2-OH)-im.** White solid, yield 80 %. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^3J$ = 7 Hz, 3H, $CH_3$), 1.26-1.48 (m, 14H, $CH_2$), 3.83 (m, 2H, α-

$CH_2$), 3.97 (m, 1H, β-CH), 6.92 (s, 1H, CH), 6.95 (s, 1H, CH), 7.45 (s, 1H, CH). Anal. Calcd. for $C_{13}H_{24}N_2O$: C, 69.60; H, 10.78; N, 12.49 %. Found: C, 69.64; H, 10.79; N, 12.47 %.

**1-(2-hydroxyhexyl)imidazole, $C_6$(2-OH)-im.** Yellow liquid, yield 70 %. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, $^3J$ = 7 Hz, 3H, $CH_3$), 1.33-1.48 (m, 6H, $CH_2$), 3.83 (m, 2H, α-$CH_2$), 3.99 (m, 1H, β-CH), 6.93 (s, 1H, CH), 6.94 (s, 1H, CH), 7.54 (s, 1H, CH). Anal. Calcd. for $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.65 %. Found: C, 64.59; H, 9.67; N, 16.37 %.

**Preparation of 1-(2-hydroxyhexyl)-3-octadecyl-imidazole bromide, [$C_{18}$,$C_6$(2-OH)-im]Br.** 1-(2-hydroxyhecyl)imidazole (1 g, 5.94 mmol) and 1-bromooctadecane (2 g, 6.00 mmol) in a round bottom flask was heated neat at 100 $^o$C with stirring for 12 h under nitrogen environment. After cooling, the viscous material was recrystallined from $CH_2Cl_2$/Hexane. The waxy product was isolated and was dried under vacuum for ~12h. The yield was about 80% yield. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^3J$ = 7 Hz, 6H, $CH_3$), 1.10~1.55 (m, 36H, -$CH_2$), 1.90 (m, 2H, β-$CH_2$), 3.98 (m, 1H, β-CH), 4.25 (m, 2H, α-$CH_2$), 4.41 (m, 2H, α-$CH_2$), 7.30 (s, 1H, CH), 7.47 (s, 1H, CH), 9.70 (s, 1H, CH). Anal. Calcd. For $C_{27}H_{53}N_2OBr$: C, 64.65; H, 10.65; N, 5.58 %. Found: C, 64.59; H, 10.66; N, 5.65 %.

The other [$C_n$,$C_6$(2-OH)-im]Br compounds were prepared in 70-80% yield as for n = 18.

**1-(2-hydroxyhexyl)-3-hexadecyl-imidazole bromide, [$C_{16}$,$C_6$(2-OH)-im]Br.** Pale yellow gelly like material. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^3J$ = 7 Hz, 6H, $CH_3$), 1.10~1.60 (m, 32H, -$CH_2$), 1.93 (m, 2H, β-$CH_2$), 4.00 (m, 1H, β-CH), 4.25 (m, 2H, α-

$CH_2$), 4.40 (m, 2H, α-$CH_2$), 7.21 (s, 1H, CH), 7.32 (s, 1H, CH), 9.82 (s, 1H, CH). Anal. Calcd. For $C_{25}H_{51}N_2OBr$: C, 61.08; H, 10.46; N, 5.70 %. Found: C, 61.35; H, 10.44; N, 5.65 %.

**1-(2-hydroxyhexyl)-3-tetradecyl-imidazole bromide, [$C_{14}$,$C_6$(2-OH)-im]Br.** Colorless viscous liquid. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^3J$ = 7 Hz, 6H, $CH_3$), 1.20~1.54 (m, 28H, -$CH_2$), 1.93 (m, 2H, β-$CH_2$), 4.00 (m, 1H, β-CH), 4.26 (m, 2H, α-$CH_2$), 4.35 (m, 2H, α-$CH_2$), 7.22 (s, 1H, CH), 7.34 (s, 1H, CH), 9.82 (s, 1H, CH). Anal. Calcd. For $C_{23}H_{47}N_2OBr$: C, 59.60; H, 10.22; N, 6.04 %. Found: C, 59.61; H, 10.19; N, 6.05 %.

**1-(2-hydroxyhexyl)-3-dodecyl-imidazole bromide, [$C_{12}$,$C_6$(2-OH)-im]Br.** Colorless viscous liquid. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, $^3J$ = 7 Hz, 6H, $CH_3$), 1.10~1.53 (m, 24H, -$CH_2$), 1.92 (m, 2H, β-$CH_2$), 4.00 (m, 1H, β-CH), 4.26 (m, 2H, α-$CH_2$), 4.41 (m, 2H, α-$CH_2$), 7.25 (s, 1H, CH), 7.39 (s, 1H, CH), 9.79 (s, 1H, CH). Anal. Calcd. For $C_{21}H_{43}N_2OBr$: C, 57.92; H, 9.95; N, 6.43 %. Found: C, 58.13; H, 9.88; N, 6.46 %.

**1-(2-hydroxyhexyl)-3-decyl-imidazole bromide, [$C_{10}$,$C_6$(2-OH)-im]Br.** Colorless viscous liquid. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, $^3J$ = 7 Hz, 6H, $CH_3$), 1.10~1.51 (m, 20H, -$CH_2$), 1.90 (m, 2H, β-$CH_2$), 3.99 (m, 1H, β-CH), 4.25 (m, 2H, α-$CH_2$), 4.42 (m, 2H, α-$CH_2$), 7.32 (s, 1H, CH), 7.43 (s, 1H, CH), 9.79 (s, 1H, CH). Anal. Calcd. For $C_{19}H_{39}N_2OBr$: C, 56.01; H, 9.65; N, 6.88 %. Found: C, 56.55; H, 9.71; N, 6.97 %.

The following [$C_n$,$C_n$(2-OH)-im]Br compounds were prepared as for [$C_{18}$,$C_6$(2-OH)-im]Br in high yield.

**1-(2-hydroxyoctadecyl)-3-octadecyl-imidazole bromide, [$C_{18}$,$C_{18}$(2-OH)-im]Br.** White solid, yield > 95%. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^3J$ = 7 Hz, 6H, $CH_3$), 1.25-1.57 (m, 60H, $CH_2$), 1.93 (m, 2H, β-$CH_2$), 3.98 (m, 1H, β-CH), 4.23 (m, 2H, α-$CH_2$),

4.41 (m, 2H, α-$CH_2$), 7.17 (s, 1H, CH), 7.25 (s, 1H, CH), 9.85 (s, 1H, CH). Anal. Calcd. for $C_{39}H_{77}N_2OBr$: C, 69.92; H, 11.58; N, 4.18 %. Found: C, 69.58; H, 11.54; N, 4.21 %.

**1-(2-hydroxyhexadecyl)-3-hexadecyl-imidazole bromide, [$C_{16}$,$C_{16}$(2-OH)-im]Br.** White solid, yield > 95%. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^3J$ = 7 Hz, 6H, $CH_3$), 1.24-1.57 (m, 52H, $CH_2$), 1.92 (m, 2H, β-$CH_2$), 3.99 (m, 1H, β-CH), 4.23 (m, 2H, α-$CH_2$), 4.40 (m, 2H, α-$CH_2$), 7.18 (s, 1H, CH), 7.28 (s, 1H, CH), 10.04 (s, 1H, CH). Anal. Calcd. for $C_{35}H_{69}N_2OBr$: C, 68.48; H, 11.33; N, 4.56 %. Found: C, 68.25; H,11.29; N, 4.57 %.

**1-(2-hydroxytetradecyl)-3-tetradecyl-imidazole bromide, [$C_{14}$,$C_{14}$(2-OH)-im]Br.** White solid, yield > 95%. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, $^3J$ = 7 Hz, 6H, $CH_3$), 1.13-1.57 (m, 44H, $CH_2$), 1.89 (m, 2H, β-$CH_2$), 3.97 (m, 1H, β-CH), 4.24 (m, 2H, α-$CH_2$), 4.41 (m, 2H, α-$CH_2$), 7.14 (s, 1H, CH), 7.32 (s, 1H, CH), 9.84 (s, 1H, CH). Anal. Calcd. for $C_{31}H_{61}N_2OBr$: C, 66.76; H, 11.02; N, 5.02 %. Found: C, 66.61; H, 11.09; N, 5.10 %.

**1-(2-hydroxydodecyl)-3-dodecyl-imidazole bromide, [$C_{12}$,$C_{12}$(2-OH)-im]Br.** Colorless gelly like material, yield > 90%. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^3J$ = 7 Hz, 6H, $CH_3$), 1.17-1.56 (m, 36H, $CH_2$), 1.90 (m, 2H, β-$CH_2$), 3.97 (m, 1H, β-CH), 4.24 (m, 2H, α-$CH_2$), 4.40 (m, 2H, α-$CH_2$), 7.24 (s, 1H, CH), 7.38 (s, 1H, CH), 9.77 (s, 1H, CH). Anal. Calcd. for $C_{27}H_{53}N_2OBr$: C, 64.65; H, 10.65; N, 5.58 %. Found: C, 64.89; H, 10.75; N, 5.69 %.

**1-(2-hydroxydecyl)-3-decyl-imidazole bromide, [$C_{10}$,$C_{10}$(2-OH)-im]Br.** Colorless gelly like material, yield > 90%. $^1$H-NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, $^3J$ = 7 Hz, 6H, $CH_3$), 1.19-1.54 (m, 28H, $CH_2$), 1.90 (m, 2H, β-$CH_2$), 3.97 (m, 1H, β-CH), 4.26 (m, 2H, α-$CH_2$), 4.40 (m, 2H, α-$CH_2$), 7.19 (s, 1H, CH), 7.26 (s, 1H, CH), 9.79 (s, 1H, CH). Anal.

Calcd. for $C_{23}H_{45}N_2OBr$: C, 62.01; H, 10.18; N, 6.29 %. Found: C, 61.59; H, 10.30; N, 6.24 %.

**Table S1.** Crystal data and structure refinement for $[C_{14},C_{14}(2\text{-OH})\text{-im}]Br$

| | |
|---|---|
| Formula | $C_{31}H_{61}BrN_2O$ |
| Formula weight | 557.73 |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| a / Å | 27.0966(12) |
| b / Å | 9.2018(4) |
| c / Å | 13.7101(5) |
| $\alpha$, deg | 90 |
| $\beta$, deg | 95.859(2) |
| $\gamma$, deg | 90 |
| Cell volume Å$^3$ | 3400.6(2) |
| Z | 4 |
| 1$D_{calcd}$, Mg/m$^3$ | 1.089 |
| T / K | 294(2) |
| $\mu$/mm$^{-1}$ | 1.231 |
| F(000) | 1216 |
| Crystal size, nm | 0.10 x 0.03 x 0.03 |
| $\theta_{min}$, $\theta_{max}$, deg | 0.76, 25.06 |
| Reflections collected | 26836 |
| Independent reflections | 6028 [R(int) = 0.0684] |
| no. of refined parameters | 316 |
| goodness-of-fit on $F^2$ [a] | 0.795 |
| Final R indices[b] [$I > 2\sigma(I)$] | |
| R1 = | 0.0448 |
| *w*R2 | 0.1079 |
| R indices (all data) | |
| R1 | 0.1252 |
| *w*R2 | 0.1290 |

[a]GOF = $[\Sigma w(F_o^2\text{-}F_c^2)^2/(n\text{-}p)]^{1/2}$, where $n$ is the number of reflections and $p$ is the number of parameters refined. [b]R1 = $\Sigma(||F_o|\text{-}|F_c||)/\Sigma|Fo|$; *w*R2 = $[\Sigma w(F_o^2\text{-}F_c^2)^2/\Sigma wFo^4]^{1/2}$.

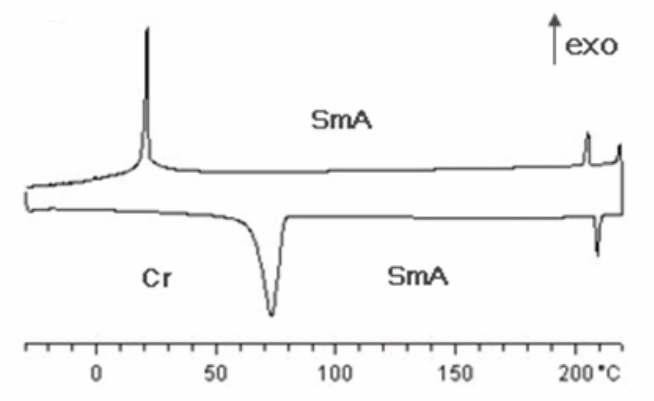


**Figure S1.** The heating and cooling DSC thermogram of [$C_{14}$,$C_{14}$(2-OH)-im]Br at a scan rate of 10 $^{o}$C/min.