Supporting information

First symmetrical banana compounds exhibiting $SmAP_R$ mesophase and unique transition between two orthogonal polar phases

Kinga Gomola[1], Lingfeng Guo [1], Ewa Gorecka[2], Damian Pociecha[2], Jozef Mieczkowski[2], Ken Ishikawa[1] and Hideo Takezoe[1]

[1]Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan
[2]Chemistry Department, Warsaw University, Al. Zwirki i Wigury 101, 02-089 Warsaw, Poland

Experimental

The molecular structures of synthesized compounds were confirmed by the following analytical methods. Infrared (IR) spectra were obtained using a JASCO FTIR-460 PLUS spectrometer. The carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Varian Unity Plus spectrometer operating at 75 MHz, whereas ^{1}H NMR spectra were recorded at 300 MHz. Tetramethylsilane was used as an internal standard. Chemical shifts were reported in ppm. Thin layer chromatography (TLC) analyses were performed on Merck 60 F254 silica gel aluminum plate. Column chromatography was carried out at atmospheric pressure using silica gel (100-200 mesh, Merck). Compositions of the synthesized compounds were determined by elemental analysis. Phase transition temperatures and associated enthalpies were determined by differential scanning calorimetry (Pyris Perkin – Elmer 7 and Pyris Diamond) at the rate of 10 °C/min under cooling and heating runs. Texture observation and the identification of the mesophases were done using a polarizing optical microscope (Olympus, BX50) equipped with a hot stage and temperature-controller (Mettler Toledo FP 82). Electrooptical switching behaviour was observed using a function generator connected with a high voltage amplifier. The polarization reversal current was measured by standard triangular wave technique. The current was measured across a 1 MΩ resistance and the spontaneous polarization value was obtained by integrating the area under the curve.

Spectral characterization od studied compounds

AP-16-NN-16

NMR: δ^1H (300 MHz, $CDCl_3$) 8.15 (d, J = 8.4 Hz, 4H, Ar), 8.02 (d, J = 2.4 Hz, 2H, Ar), 7.66 (dd, J_1 = 2.1 Hz, J_2 = 8.7 Hz, 2H, Ar), 7.63-7.52 (m, 5H, Ar), 7.25-7.06 (m, 8H, Ar), 4.13 (t, J = 6.3 Hz, 4H, $OC\underline{H}_2CH_2$), 2.49 (s, 3H, $COC\underline{H}_3$), 1.89-1.80 (m, 4H, $OCH_2C\underline{H}_2$), 1.51-1.08 (m, 52H, $C\underline{H}_2$), 0.88 (t, J = 6.3 Hz, 6H, $CH_2C\underline{H}_3$); ^{13}C NMR: δ^{13}C (75 MHz, $CDCl_3$) 198.42, 164.17, 152.29, 148.02, 142.22, 140.13, 132.05, 130.87, 129.20, 129.11, 127.82, 127.61, 126.63, 123.45, 120.62, 114.72, 69.93, 31.92, 31.38, 29.69, 29.64, 29.57, 29.50, 29.35, 29.26, 28.91, 25.82, 22.67, 14.10; IR (KBr): ν_{max}/cm^{-1}, 2920, 2851, 1734, 1603, 1531, 1457, 1263, 1223, 1176, 1084; Elemental analysis calcd (%) for $C_{70}H_{90}N_2O_{11}$ (1135.47): C, 74.04, H 7.99, N, 2.47, found C, 74.06, H, 7.94, N, 2.52;

AP-18-NN-18

NMR: δ^1H (300 MHz, $CDCl_3$) 8.15 (d, J = 8.4 Hz, 4H, Ar), 8.02 (d, J = 2.1 Hz, 2H, Ar), 7.67 (dd, J_1 = 2.1 Hz, J_2 = 8.7 Hz, 2H, Ar), 7.63-7.52 (m, 5H, Ar), 7.23-7.06 (m, 8H, $C\underline{H}$=$C\underline{H}$, Ar), 4.13 (t, J = 6.3 Hz, 4H, $OC\underline{H}_2CH_2$), 2.49 (s, 3H, $COC\underline{H}_3$), 1.88-1.83 (m, 4H, $OCH_2C\underline{H}_2$), 1.51-1.23 (m, 60H, $C\underline{H}_2$), 0.88 (t, J = 6.3 Hz, 6H, $CH_2C\underline{H}_3$); ^{13}C NMR: δ^{13}C (75 MHz, $CDCl_3$) 198,41, 164.20, 152.30, 148.03, 142.32, 140.08, 132.09, 130.88, 129.10, 129.84, 127.62, 126.64, 123.49, 120.62, 114.69, 69.90, 31.92, 31.41, 29.70, 29.58, 29.50, 29.36, 29.26, 28.92, 25.82, 22.69, 14.12; IR (KBr): ν_{max}/cm^{-1}, 2921, 2851, 1734, 1603, 1532, 14.57, 1351, 1267, 1223, 1178, 1084; Elemental analysis calcd (%) for $C_{74}H_{98}N_2O_{11}$ (1191.58): C, 74.59, H 8.29, N, 2.35, found C, 74.62, H, 8.27, N, 2.36;

AP-20-NN-20

NMR: δ^1H (300 MHz, $CDCl_3$) 8.15 (d, J = 8.4 Hz, 4H, Ar), 8.01 (d, J = 2.1 Hz, 2H, Ar), 7.66 (dd, J_1 = 2.1 Hz, J_2 = 8.7 Hz, 2H, Ar), 7.62 - 7.52 (m, 5H, Ar), 7.25 - 7.06 (m, 8H, $C\underline{H}$=$C\underline{H}$, Ar), 4.13 (t, J = 6.6 Hz, 4H, $OC\underline{H}_2CH_2$), 2.49 (s, 3H, $COC\underline{H}_3$), 1.89-1.80 (m, 4H, $OCH_2C\underline{H}_2$), 1.55 - 1.23 (m, 68H, $C\underline{H}_2$), 0.88 (t, J = 6.3 Hz, 6H, $CH_2C\underline{H}_3$); ^{13}C NMR: δ^{13}C (75 MHz, $CDCl_3$) 198.34, 164.19, 152.29, 148.04, 142.32, 140.12, 132.05, 130.86, 129.19, 129.10, 127.84, 127.64, 126.63, 123.46, 120.61, 114.72, 69.92, 31.91, 31.38,

29.68, 29.64, 29.57, 29.49, 29.35, 29.26, 28.92, 25.81, 22.67, 14.10; IR (KBr): ν_{max}/cm^{-1}, 2919, 2850, 1736, 1603, 1532, 1267, 1223, 1178, 1082, 408; Elemental analysis calcd (%) for $C_{78}H_{106}N_2O_{11}$ (1247.68): C, 75.09, H 8.56, N, 2.25, found C, 74.74, H, 8.47, N, 2.27;

AP-14-NCl-14

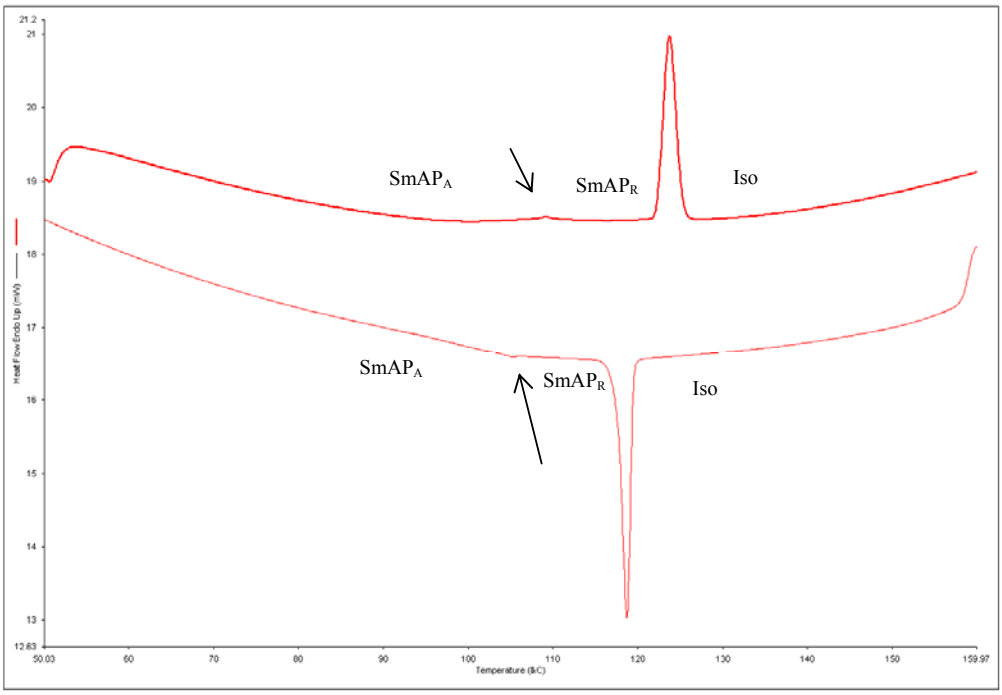
NMR: δ^1H (300 MHz, $CDCl_3$) 8.17-8.12 (m, 4H, Ar), 8.02 (d, J = 2.1 Hz, 1H, Ar), 7.67 (dd, J1 = 2.1 Hz, J2 = 8.7 Hz, 1H, Ar), 7.63 - 7.52 (m, 6H, Ar), 7.36 (dd, J_1 = 2.1 Hz, J_2 = 8.7 Hz, 1H, Ar), 7.25 - 6.98 (m, 7H, C<u>H</u>=C<u>H</u>, Ar), 6.91 (d, J = 8.7 Hz, 1H, Ar), 4.13 (t, J = 6.6 Hz, 2H, OC<u>H</u>$_2$CH$_2$), 4.06 (t, J = 6.6 Hz, 2H, OC<u>H</u>$_2$CH$_2$), 2.49 (s, 3H, COC<u>H</u>$_3$), 1.87 - 1.83 (m, 4H, OCH$_2$C<u>H</u>$_2$), 1.55-1.26 (m, 44H, C<u>H</u>$_2$), 0.88 (t, J = 6.9 Hz, 6H, CH$_2$C<u>H</u>$_3$); ^{13}C NMR: $\delta^{13}C$ (75 MHz, $CDCl_3$) 198.41, 164.27, 167.21, 154.74, 152.29, 148.08, 147.99, 142.96, 142.29, 132.09, 130.87, 130.82, 130.35, 129.98, 129.16, 129.07, 128.20, 127.84, 127.64, 127.10, 126.62, 126.44, 126.21, 123.47, 123.41, 114.68, 113.19, 69.90, 69.27, 31.92, 31.40, 29.64, 29.57, 29.54, 29.49, 29.35, 29.31, 29.27, 29.03, 28.91, 25.92, 25.81, 22.69, 14.12; IR (KBr): ν_{max}/cm^{-1}, 2921, 2851, 1741, 1603, 1531, 1499, 1458, 1263, 1253, 1225, 1177, 1080; Elemental analysis calcd (%) for $C_{66}H_{82}ClNO_9$ (1068.81): C, 74.17, H 7.73, N, 1.31, Cl, 3.32 found C, 74.21, H, 7.68, N, 1.36, Cl, 3.27;

AP-14-ClCl-14

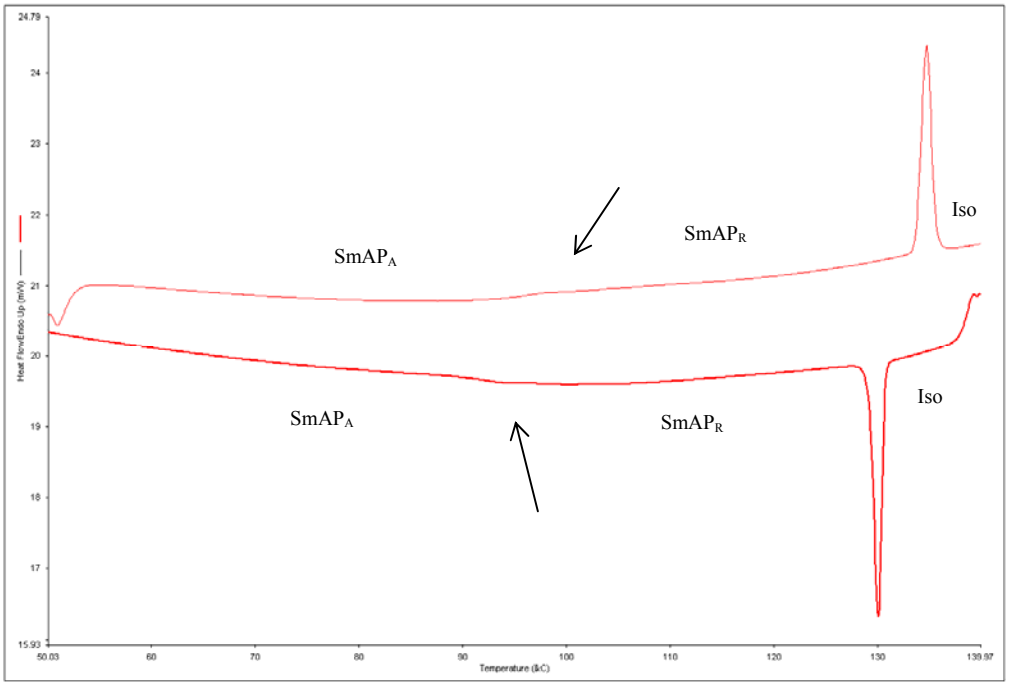
NMR: δ^1H (300 MHz, $CDCl_3$) 8.11 (d, J = 8.1 Hz, 4H, Ar), 7.58 - 7.51 (m, 7H, Ar), 7.35 – 7.32 (m, 2H, Ar), 7.22 (d, J = 7.8 Hz, 2H, Ar),7.12 (d, J =16.5 Hz, 2H, C<u>H</u>=CH), 6.99 (d, J = 16.2 Hz, 2H, CH=C<u>H</u>), 6.90 (d, J = 8.4 Hz, 2H, Ar), 4.04 (t, J= 6.6 Hz, 4H, OC<u>H</u>$_2$CH$_2$), 2.49 (s, 3H, COC<u>H</u>$_3$), 1.90-1.80 (m, 4H, OCH$_2$C<u>H</u>$_2$), 1.56-1.21 (m, 44H, C<u>H</u>$_2$), 0.88 (t, J = 6.9 Hz, 6H, CH$_2$C<u>H</u>$_3$); ^{13}C NMR: $\delta^{13}C$ (75 MHz, $CDCl_3$) 198.28, 164.23, 154.75, 148.05, 142.92, 130.77, 130.31, 130.02, 128.44, 128.21, 127.16, 126.56, 126.41, 126.23, 123.43, 120.54, 113.22, 69.27, 31.89, 31.35, 29.65, 29.63, 29.55, 29.52, 29.33, 29.31, 29.04, 25.91, 22.65, 14.08; IR (KBr): ν_{max}/cm^{-1}, 2922, 2851, 1733, 1593, 1507, 1498, 1466, 1456, 1263, 1249, 1222, 1176, 1078, 1064; Elemental analysis calcd (%) for $C_{66}H_{82}Cl_2O_7$ (1058.26): C, 74.91, H 7.81, Cl, 6.70 found C, 74.96, H, 7.58, Cl, 6.76;

DSC thermograms for studied compounds

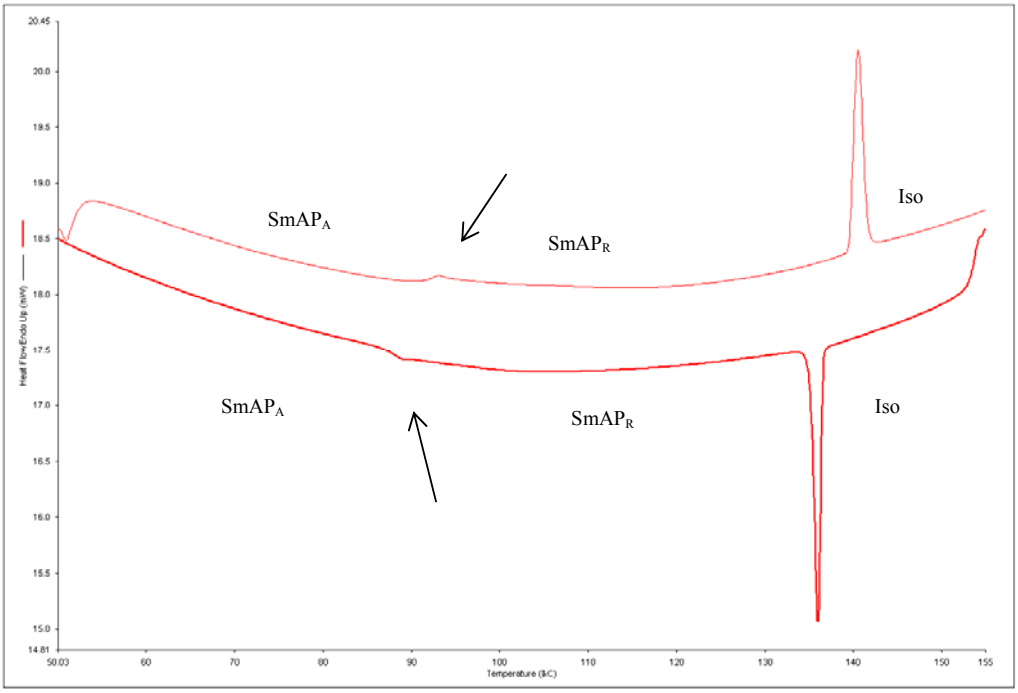
AP-14-NN-14



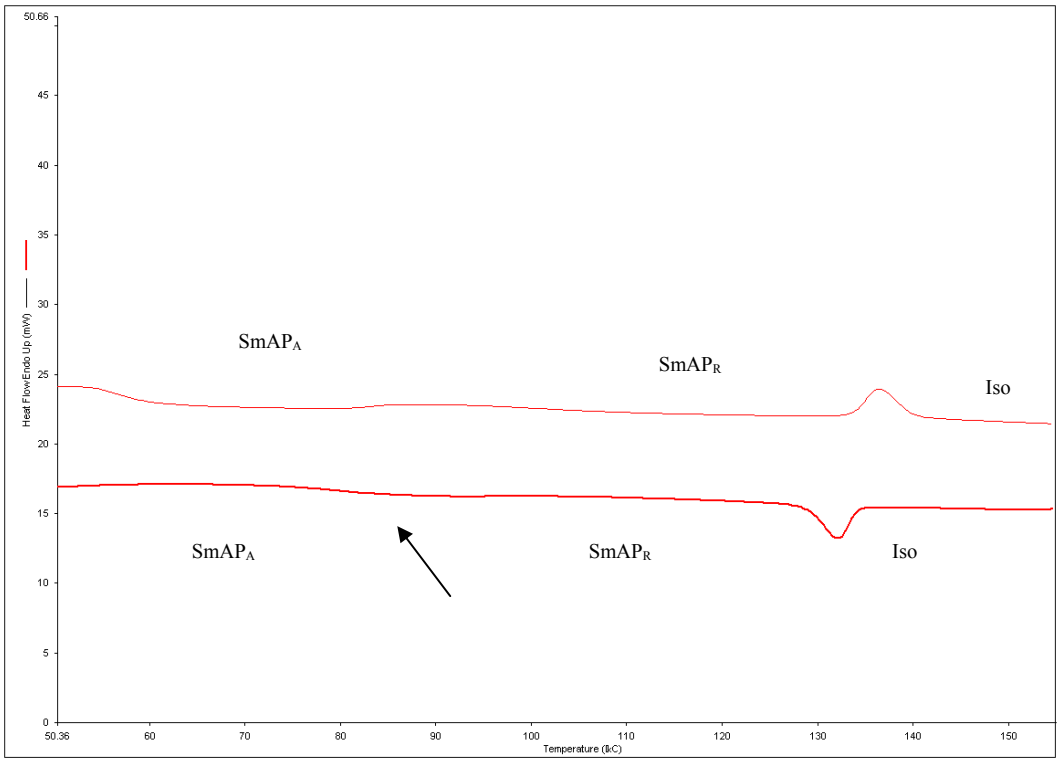
AP-16-NN-16



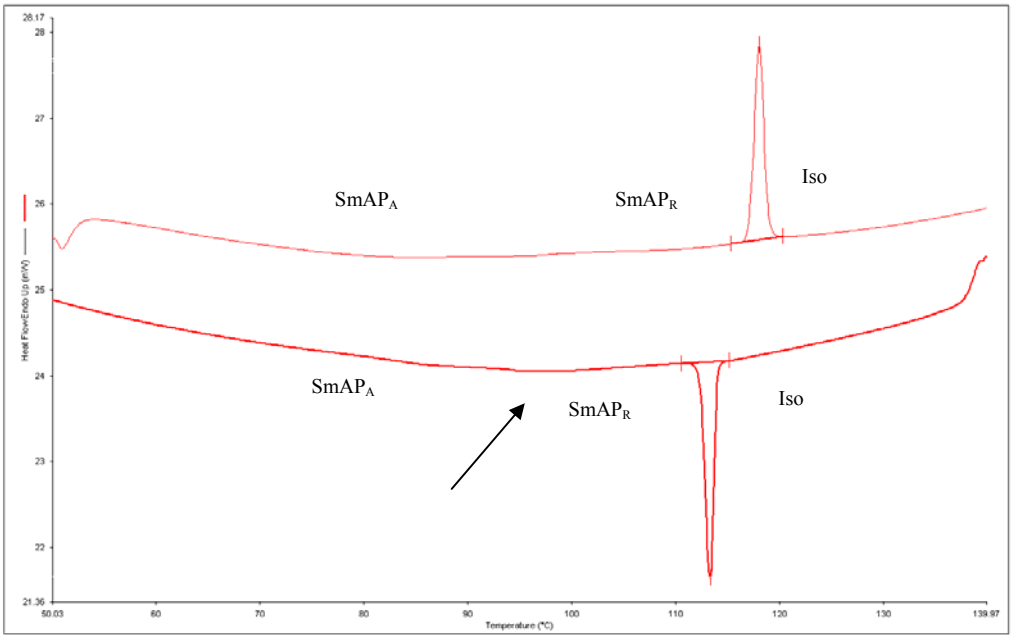
AP-18-NN-18



AP-20-NN-20



AP-14-NCl-14



14-ClCl-14