

Supporting Information

Fluorescent Mesomorphic Pyrazinacenes

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Contents

1.0 General experimental and synthesis	S2
2.0 ¹ H-NMR and ¹³ C-NMR spectra of compounds 1 – 9	S7
3.0 Differential scanning calorimetry data for selected compounds	S16
4.0 Thermogravimetric analyses of compounds 1 – 9	S20

1.0 General experimental and synthesis

Starting materials were purchased from TCI Chemicals, Aldrich Chemical Co., Wako Chemical Co. and Nacalai Tesque. All reagents were used as received. Reactions were performed under a dry nitrogen atmosphere. Electronic absorption spectra were obtained using a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer. Fluorescence spectra were similarly obtained using a JASCO FP-6500 spectrofluorometer. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured using a JEOL AL300BX NMR spectrometer operating at 300 MHz and 75 MHz, respectively. Infrared absorption spectra were obtained using a Thermo-Nicolet Nexus 670 FT-IR spectrometer from samples prepared as KBr pellets. LDI-TOF-MS and MALDI-TOF-MS spectra were measured using a Shimadzu-Kratos Axima CR+ spectrometer. Differential scanning calorimetry was performed on samples sealed in aluminium pans using an MAC MTR 1000S/3000S system equipped with a Taitec VA-800F cooling unit. Thermogravimetric analyses were performed using a Seiko Instrument SII TGA analyzer. Samples (2–5 mg) were heated in aluminium pans under an atmosphere of nitrogen gas from room temperature to 550 °C. X-Ray diffraction of powdered samples (XRD) was performed using a Rigaku Ultima III diffractometer (Cu K α radiation) with samples mounted horizontally on a specially prepared glass plate. VT-pXRD was conducted at a scanning speed of 2-theta = 2degree/min using RINT1200 (RIGAKU) diffractometer with horizontal sample mounting utilizing Ni-filtered Cu(K α) radiation (λ = 1.5418 Å). The sample plate was mounted on a temperature controlled hot plate mounted on the goniometer. The temperature at the specimen was calibrated by direct temperature measurement using an ultrafine thermocouple attached on the surface of the glass plate. 5,6-dicyano-3,4,7,8-tetraazaanthracene,^{S1} 3,4,5-tris(1-*n*-dodecyloxy)benzyl chloride,^{S2} 3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl chloride,^{S3} 6,13-dihydro-[a,c,l,n]-tetrabenzo-5,6,7,12,13,14-hexaazapentacene,^{S4} 6,13-bis(1-*n*-dodecyl)-[a,c,l,n]-tetrabenzo-5,6,7,12,13,14-hexaazapentacene (**2**)^{S4} and 6,13-bis(3,4,5-tris[1-*n*-dodecyloxy]benzyl)-[a,c,l,n]-tetrabenzo-5,6,7, 12,13,14-hexaazapentacene (**8**)^{S4} were prepared according to the literature procedures.

Synthesis

6,13-dihydro-5,6,7,12,13,14-hexaazapentacene (fluorubine). A mixture of 5,6-dicyano-3,4,7,8-tetraazaanthracene (0.80 g, 3.45×10^{-3} mol), *o*-phenylenediamine (0.48 g, 4.5×10^{-3} mol) and potassium carbonate (1.24 g, 9.0×10^{-3} mol) in DMSO (20 mL) was heated at 100 °C for 4 hours. The reaction mixture was allowed to cool to room temperature and acetic acid (2 mL) was added and the mixture stirred for a further 20 minutes before filtering. The residue was washed with DMSO (5 mL), THF (2 \times 20 mL), hot water (3 \times 20 mL) and again with THF (2 \times 20 mL) to give a green/yellow solid which was dried under reduced pressure and used in subsequent reactions without further purification. Yield: 0.80 g (81 %).

2-bromo-6,13-dihydro-5,6,7,12,13,14-hexaazapentacene. A mixture of 5,6-dicyano-3,4,7,8-tetraazaanthracene (0.9 g, 3.9×10^{-3} mol), 4-bromo-1,2-diaminobenzene (0.94 g, 5.0×10^{-3} mol) and potassium carbonate (1.40 g, 1.01×10^{-2} mol) in DMSO (22 mL) was heated at 100 °C for 4 hours. The reaction mixture was allowed to cool to room temperature and acetic acid (2 mL) was added and the mixture stirred for a further 20 minutes before filtering. The residue was washed with cold DMSO (5 mL), THF (2 \times 20 mL), hot water (3 \times 20 mL) then again with THF (2 \times 20 mL) to give a green/yellow solid which was dried under reduced pressure. Yield 0.90 g (63 %). UV/Vis (DMSO) λ_{max} = 501.5, 471.0, 414.0, 418.5, 396.0 nm. FTIR (KBr): ν = 3191 (s); 1597 (s, arom. C-C str.); 1544 (m); 1475 (s, C=C def.); 1410 (s); 1369 (m); 1311 (m); 1219 (w, C-N str.); 1069 (w, C-Br str.); 952 (w); 841 (m); 757 (m, C-H def.); 698 (m, C-H def) cm^{-1} . ^1H NMR (300 MHz, DMSO, 25 °C): δ = 11.60 (s, 2H, NH); 7.54 (d, J = 2.1 Hz, ArH); 7.42 (m, ArH); 7.32 (m, ArH) ppm. MALDI-TOF-MS (dithranol): calculated for $\text{C}_{16}\text{H}_9\text{BrN}_6$ m/z = 364.01; found = 363.81 M^+ . Elemental analyses, calculated % (found %): C 52.62 (52.28); H 2.48 (2.65); N 21.88 (22.58).

N-alkylation of 6,13-dihydro-5,6,7,12,13,14-hexaazapentacene. A mixture of 4,11-dihydro-3,4,5,10,11,12-hexaazapentacene (202 mg, 7.06×10^{-4} mol), 3,4,5-tris(1-*n*-dodecyloxy)benzyl chloride (0.62 g, 9.18×10^{-4} mol), 3,4,5-tris [2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl chloride (0.56 g, 9.18×10^{-4} mol) and sodium hydrogen

carbonate (154 mg, 1.84×10^{-3} mol) in DMSO (10 mL) was heated at 100 °C for 24 h. The mixture was allowed to cool to room temperature and was poured into water (300 mL) and stirred for 1 hour. The mixture was filtered and the residue washed with water (2×30 mL) and methanol (2×10 mL) and purified by column chromatography on silica gel with gradient elution (dichloromethane (100%) to dichloromethane/tetrahydrofuran 3:1) to give products **2** and **3**. The aqueous filtrate was extracted with chloroform (3×75 mL), the organic extracts combined and dried over sodium sulphate, filtered and concentrated to a yellow-green oil which was purified by column chromatography [silica gel, dichloromethane: tetrahydrofuran 1:1] to give **1**.

6,13-Bis(3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl)-5,6,7,12,13,14-hexaazapentacene (1). Yield 155 mg (15%). UV/Vis (CH_2Cl_2) λ_{max} ($\epsilon/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 439 (56.5), 414 (47.2), 392 (22.3), 373 (8.4), 276 (34.9), 253 (48.2) nm. FTIR (KBr): ν = 2876 (m, aliph. C-H str.); 1591 (w, arom. C-C str.); 1504 (m); 1454 (s); 1374 (s); 1355 (s); 1329 (m); 1234 (w, C-N str.); 1112 (s, C-O str.); 853 (w); 761 (m, C-H def.) cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.61 (AA'BB', $J_{AB'} = 9.0$ Hz, $J_{AB} = 2.4$ Hz, 4H, ArH); 7.37 (AA'BB', $J_{AB'} = 9.0$ Hz, $J_{AB} = 2.4$ Hz, 4H, ArH); 7.10 (s, 4H, ArH); 5.52 (s, 4H, CH_2); 4.08 (m, 12H, OCH_2); 3.74 (m, 12H, OCH_2); 3.63 (m, 36H, OCH_2); 3.50 (m, 12H, OCH_2); 3.33 (s, 18H, OCH_3) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 152.35; 140.64; 138.36; 132.05; 127.18; 126.41; 110.45; 72.32; 71.98; 70.78; 70.67; 70.51; 70.47; 69.77; 69.03; 58.83; 43.80 ppm. MALDI-TOF-MS (dithranol): calculated for $\text{C}_{72}\text{H}_{106}\text{N}_6\text{O}_{24}$ m/z = 1438.73; found = 1462.32 $[\text{M} + \text{Na}]^+$. Elemental analyses, calculated % (found %): C 60.07 (59.35); H 7.41 (7.61); N 5.84 (5.80).

6,13-Bis[tris(3,4,5-dodecyloxy)benzyl]-5,6,7,12,13,14-hexaazapentacene (2). Yield 170 mg (16%). UV/Vis (CH_2Cl_2) λ_{max} ($\epsilon/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 439 (55.2), 414 (46.4), 392 (22.0), 373 (8.1), 276 (35.0), 253 (49.8) nm. FTIR (KBr): ν = 3453 (w); 2919 and 2850 (m, aliph. C-H str.); 1592 (m, arom. C=C str.); 1502 (s); 1458 (s, C=C def.); 1437 (s); 1378 (s); 1356 (s); 1331 (s); 1234 (m, C-N str.); 1145 (m); 1122 (s, C-O str.); 753 (s, C-H def.); 740 (s, C-H def.); 609 (s) cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.62 (AA'BB', $J_{AB} = 9.6$ Hz, $J_{AB'} = 2.7$ Hz, 4H, ArH); 7.36 (AA'BB', $J_{AB} = 9.9$ Hz, $J_{AB'} = 2.7$ Hz, 4H, ArH); 7.12 (s, 4H, ArH); 5.52 (s, 4H, CH_2); 3.89 (m, 12H, OCH_2); 1.69 (m, 12H, CH_2); 1.42-1.10 (m, 108H, CH_2); 0.87 (m, 18H, CH_3) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 152.78; 140.82; 138.42; 138.11; 131.64; 127.13; 126.39; 109.54; 73.46; 69.22; 43.85; 31.97; 30.37; 29.74; 29.70; 29.67; 20.44; 29.40; 26.12; 22.71; 14.09 ppm. MALDI-TOF-MS (dithranol): calculated for $\text{C}_{102}\text{H}_{155}\text{N}_6\text{O}_6$ m/z = 1472.29; found = 1570.48 $[\text{M} - \text{H}]^+$. Elemental analyses, calculated % (found %): C 77.91 (77.89); H 10.64 (10.91); N 5.34 (5.01).

6-(3,4,5-Tris[1-n-dodecyloxy]benzyl)-13-(3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl)-5,6,7,12,13,14-hexaazapentacene (3). Yield 230 mg (22%). UV/Vis (CH_2Cl_2) λ_{max} ($\epsilon/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 439 (59.5), 414 (49.6), 373 (8.8), 276 (36.3), 253 (50.8) nm. FTIR (KBr): ν = 3477 (s); 2919 and 2850 (s, aliph. C-H str.); 1592 (w, arom. C=C str.); 1504 (m); 1455 (s, C=C def.); 1437 (m); 1378 (m, CH_3 def.); 1330 (m); 1235 (w, C-N str.); 1119 (s, C-O str.); 753 (w, C-H def.); 739 (w, C-H def.) cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.63 (AA'BB', $J_{AB} = 9.9$ Hz, $J_{AB'} = 2.4$ Hz, 4H, ArH); 7.37 (AA'BB', $J_{AB} = 9.9$ Hz, $J_{AB'} = 2.4$ Hz, 4H, ArH); 7.13 (s, 2H, ArH); 7.10 (s, 2H, ArH); 5.55 (s, 2H, CH_2); 5.53 (s, 2H, CH_2); 4.07 (m, 6H, OCH_2); 3.91 (m, 6H, OCH_2); 3.76 (m, 6H, OCH_2); 3.53-3.49 (m, 24H, OCH_2); 3.35 (s, 9H, OCH_3); 1.73 (m, 9H, CH_2); 1.50-1.27 (m, 54H, CH_2); 0.88 (m, 9H, CH_3) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 152.49; 152.07; 140.43; 138.15; 138.10; 137.77; 137.63; 131.92; 131.38; 127.00; 126.97; 126.24; 126.15; 109.85; 109.21; 73.22; 72.12; 71.78; 70.61; 70.51; 70.37; 70.33; 69.55; 68.86; 68.60; 58.82; 43.62; 43.49; 31.80; 30.17; 29.58; 29.54; 29.45; 29.26; 29.24; 29.04; 25.94; 22.55; 13.98 ppm. MALDI-TOF-MS (dithranol): calculated for $\text{C}_{87}\text{H}_{136}\text{N}_6\text{O}_{15}$ m/z = 1505.01; found = 1528.51 $[\text{M} + \text{Na}]^+$. Elemental analyses, calculated % (found %): C 69.38 (69.12); H 9.10 (9.25); N 5.58 (5.50).

N-Alkylation of 2-bromo-6,13-dihydro-5,6,7,12,13,14-hexaazapentacene.

A mixture of 7-bromo-4,11-dihydro-3,4,5,10,11,12-hexa azapentacene (350 mg, 9.62×10^{-4} mol), 3,4,5-tris(1-n-dodecyloxy)benzyl chloride (0.85 g, 1.26×10^{-3} mol), 3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl chloride (0.77 g, 1.26×10^{-3} mol) and sodium hydrogen carbonate (211 mg, 2.52×10^{-3} mol) in DMSO (14 mL)

was heated at 100 °C for 24 h. The mixture was allowed to cool to room temperature and the entire mixture poured into water (350 mL) and stirred for 1 hour. The mixture was filtered and the residue washed with water (2 × 30 mL) and methanol (2 × 10 mL) and purified by column chromatography on silica gel with gradient elution with dichloromethane (100%) to dichloromethane/ tetrahydrofuran (3:1) to give **5** and **6**. The aqueous filtrate was extracted with chloroform (3 × 75 ml), the organic extracts combined and dried over sodium sulphate, filtered and concentrated to a yellow-green oil which was purified by column chromatography [silica gel, dichloromethane : tetrahydrofuran 1:1] to give **4**.

2-bromo-6,13-Bis(3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl)-5,6,7,12,13,14-hexaazapentacene (4). Yield 205 mg (14%). UV/Vis (CH₂Cl₂) λ_{max} ($\epsilon/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 443 (67.7), 418 (57.3), 395 (26.8), 377 (10.7), 277 (43.5), 256 (57.9) nm. FTIR (KBr): ν = 3466 (s); 2876 (s, aliph. C-H str.); 1589 (w, arom. C=C str.); 1500 (m); 1454 (s); 1419 (m); 1354 (m); 1243 (m, C-N str.); 1111 (s, C-O str.); 947 (w); 852 (w) cm^{-1} . ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.64 (s, 1H, ArH); 7.50 (m, 2H, ArH); 7.30 (m, 4H, ArH); 6.95 (s, 4H, ArH); 5.35 (s, 4H, CH₂); 23.98 (m, 12H, OCH₂); 3.64 (m, 12H, OCH₂); 3.55-3.49 (m, 36H, OCH₂); 3.40 (m, 12H, OCH₂); 3.23 (s, 18H, OCH₃) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 152.08; 140.92; 140.55; 139.97; 139.92; 138.94; 138.18; 138.04; 137.98; 136.92; 131.40; 131.34; 130.05; 128.40; 127.32; 127.21; 127.15; 126.21; 120.00; 110.11; 72.06; 71.71; 70.51; 70.41; 70.24; 69.48; 68.79; 68.71; 58.61; 43.57 ppm. MALDI-TOF-MS (dithranol): calculated for C₇₂H₁₀₅BrN₆O₂₄ m/z = 1516.64; found = 1540.65 [M + Na]⁺. Elemental analyses, calculated % (found %): C 56.95 (56.72); H 6.97 (7.11); N 5.53 (5.57).

2-bromo-6,13-Bis(3,4,5-tris[1-n-dodecyloxy]benzyl)-5,6,7,12, 13,14-hexaazapentacene (5). Yield 300 mg (19%). UV/Vis (CH₂Cl₂) λ_{max} ($\epsilon/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 444 (70.3), 419 (58.2), 396 (27.1), 377 (10.5), 277 (42.8), 256 (57.9) nm. FTIR (KBr): ν = 3459 (w); 2920 and 2850 (s, aliph. C-H str.); 1592 (w, arom. C=C str.); 1504 (m); 1455 (s); 1438 (s); 1378 (m); 1356 (m); 1224 (m, C-N str.); 1119 (s, C-O str.); 753 (w, C-H def.); 741 (m, C-H def.) cm^{-1} . ¹H NMR (300 MHz, CDCl₃, 22 °C): δ = 7.77 (d, J = 3 Hz, 1H, ArH); 7.63 (m, 2H, ArH); 7.49 (m, 4H, ArH); 7.08 (s, 2H, ArH); 7.08 (s, 2H, ArH); 5.48 (s, 4H, CH₂); 3.89 (m, 12H, CH₂); 1.70 (m, 12H, CH₂); 1.39 (m, 12H, CH₂); 1.33-1.13 (m, 96H, CH₂); 0.88 (m, 18H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 152.66; 141.30; 140.96; 140.40; 140.35; 139.18; 138.30; 138.24; 137.85; 137.16; 131.27; 131.17; 130.21; 128.62; 127.42; 127.33; 127.30; 126.41; 126.38; 120.17; 109.21; 73.39; 69.06; 69.01; 43.84; 31.93; 30.28; 29.72; 29.67; 29.64; 29.63; 29.57; 29.40; 29.37; 29.35; 26.07; 26.03; 22.69; 22.67; 14.10; 14.08 ppm. MALDI-TOF-MS (dithranol): calculated for C₁₀₂H₁₆₅N₆O₆ m/z = 1650.20; found = 1650.62 M⁺. Elemental analyses, calculated % (found %): C 74.19 (74.60); H 10.07 (10.23); N 4.84 (4.82).

2(3)-bromo-6-(3,4,5-Tris[1-n-dodecyloxy]benzyl)-13-(3,4,5-tris [2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl)-5,6,7,12,13, 14-hexaazapentacene (6). Yield 220 mg (14%). UV/Vis (CH₂Cl₂) λ_{max} ($\epsilon/10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 444 (65.9), 418 (53.6), 396 (48.6), 377 (8.6), 277 (39.5), 256 (53.8) nm. FTIR (KBr): ν = 3460 (s); 2919 and 2850 (s, aliph. C-H str.); 1593 (m, arom. C=C str.); 1503 (s); 1454 (s, C=C def.); 1439 (s); 1377 (m); 1355 (m); 1330 (s); 1224 (m, C-N str.); 1120 (C-O str.); 755 and 742 (m, C-H def.) cm^{-1} . ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.77 (s, 1H, ArH); 7.61 (m, 2H, ArH); 7.38 (m, 4H, ArH); 7.04 (m, 4H, ArH); 5.50 (s, 2H, CH₂); 5.49 (s, 2H, CH₂); 4.07 (m, 6H, OCH₂); 3.88 (m, 6H, OCH₂); 3.75 (m, 6H, OCH₂); 3.63 (m, 18H, OCH₂); 3.57 (m, 6H, OCH₂); 3.32 (s, 6H, OCH₂); 1.83-1.24 (m, 30H, CH₂); 0.86 (t, J = 3.9 Hz, 9H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 152.73; 152.33; 152.31; 141.28; 140.90; 140.34; 140.29; 139.20; 138.29; 138.24; 137.16; 131.68; 131.22; 131.13; 130.22; 128.69; 128.62; 127.54; 127.41; 127.37; 126.51; 126.38; 120.22; 110.25; 109.59; 73.34; 72.29; 71.94; 70.75; 70.63; 70.47; 69.71; 69.25; 69.20; 69.01; 68.92; 58.83; 43.93; 43.80; 43.78; 31.84; 30.28; 29.63; 29.58; 29.50; 29.40; 29.34; 29.26; 26.03; 26.00; 22.58; 13.94 ppm. MALDI-TOF-MS (dithranol): calculated for C₈₇H₁₃₅BrN₆O₁₅ m/z = 1582.92; found 1606.27 [M + Na]⁺. Elemental analyses, calculated % (found %): C 65.93 (65.77); H 8.59 (8.74); N 5.30 (5.22).

6,13-Bis(3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl)-[a,c,l,n]-tetrabenzo-5,6,7,12,13,14-hexaazapentacene (7). A mixture of 6,13-dihydro-[a,c,l,n]-tetrabenzo-5,6,7,12,13,14-hexaazapentacene (150 mg, 3.1 ×

10⁻⁴ mol), 3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl chloride (0.47 g, 7.7 × 10⁻⁴ mol) and sodium hydrogen carbonate (100 mg, 1.2 × 10⁻³ mol) in DMSO (10 mL) was heated at 100 °C for 24 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with gradient elution with chloroform/tetrahydrofuran (4:1 to 1:1) to give the target compound as a yellow ochre waxy solid. Yield 280 mg (55%). UV/Vis (CH₂Cl₂) λ_{max} (ε/10⁻³ dm³ mol⁻¹ cm⁻¹) = 486 (80.4), 455 (58.9), 428 (26.8), 297 (45.4), 256 (113.7) nm. FTIR (KBr): ν = 3455 (s); 2873 (s, aliph. C-H str.); 1594 (w, arom. C=C str.); 1479 (s); 1456 (s, C=C def.); 1439 (s); 1373 (s, CH₃ def.); 1337 (m); 1278 (m, C-N str.); 1229 (s, C-N str.); 1116 (s, C-O str.); 759 and 725 (w, C-H def.) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 8.93 (d, *J* = 7.8 Hz, 4H, ArH); 8.41 (d, *J* = 7.8 Hz, ArH); 7.68 (t, *J* = 7.2 Hz, 4H, ArH); 7.57 (t, *J* = 7.8 Hz, ArH); 7.23 (s, 4H, ArH); 5.37 (s, 4H, CH₂); 3.95 (m, 8H, OCH₂); 3.67-3.42 (m, 60H, OCH₂); 3.32 (s, 18H, OCH₃) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 152.31; 140.63; 137.61; 133.04; 132.23; 129.92; 127.41; 127.10; 123.85; 122.73; 109.02; 72.15; 71.80; 70.52; 70.47; 70.36; 70.32; 69.38; 68.53; 58.89; 58.88 ppm. MALDI-TOF-MS (dithranol): calculated for C₈₈H₁₁₄N₆O₂₄ *m/z* = 1638.79; found = 1638.08 [M - H]⁺. Elemental analyses, calculated % (found %): C 64.45 (64.28); H 7.01 (7.24); N 5.12 (5.12).

6,13-Bis(3,4,5-tris[1-*n*-dodecyloxy]benzyl)-[a,c,l,n]-tetrabenzo-5,6,7,12,13,14-hexaazapentacene (8). This compound was prepared according to a literature method.²⁵ Yield: 146 mg (81%). Mp: 216 °C. UV/Vis (CH₂Cl₂) λ_{max} (ε/10⁻³ dm³ mol⁻¹ cm⁻¹) = 487 (85.0), 456 (60.7), 430 (26.3), 297 (45.6) 256 (110.7) nm. FTIR (KBr): ν = 3456 (w); 2920 (s, aliph. C-H str.); 1591 (m); 1502 (w); 1480 (s); 1454 (s); 1435 (s); 1373 (s); 1331 (m); 1274 (m); 1228 (s, C-N str.); 1119 (m, C-O str.); 756 (m); 745 (w); 725 (m); 620 (w) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 45 °C): δ = 8.91 (d, ³*J* = 8.1 Hz, 4H, ArH); 8.31 (d, ³*J* = 8.1 Hz, 4H, ArH); 7.62 (t, ³*J* = 7.5 Hz, 4H, ArH); 7.48 (t, ³*J* = 8.1 Hz, 4H, ArH); 7.12 (s, 4H, ArH); 5.22 (s, 4H, CH₂); 3.75 (t, ³*J* = 6.6 Hz, 4H, OCH₂); 3.68 (t, ³*J* = 6.6 Hz, 8H, OCH₂); 1.58 (quint., ³*J* = 6.6 Hz, 4H; OCH₂CH₂); 1.45 (quint., ³*J* = 6.9 Hz, 8H, OCH₂CH₂); 1.0-1.3 (m, 108H, CH₂); 0.85 (m, 18H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃, 45 °C): δ = 152.91; 140.90; 137.93; 133.13; 131.92; 130.05; 129.47; 127.23; 126.99; 124.07; 122.73; 108.74; 73.34; 69.01; 43.61; 31.94; 31.89; 30.30; 29.68; 29.64; 29.62; 29.52; 29.36; 29.31; 29.30; 29.28; 26.06; 25.82; 22.67; 22.63; 14.03; 13.99 ppm. MALDI-TOF-MS (dithranol): calculated for C₁₁₈H₁₇₄N₆O₆ *m/z* = 1772.35; found = 1773.12 [M + H]⁺. Elemental analyses, calculated % (found %): C 79.95 (80.11); H 9.89 (10.00); N 4.74 (4.76).

6-(3,4,5-Tris[1-*n*-dodecyloxy]benzyl)-13-(3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl)-[a,c,l,n]-tetrabenzo-5,6,7,12,13,14-hexaazapentacene (9). A mixture of 6,13-dihydro-[a,c,l,n]-tetrabenzo-5,6,7,12,13,14-hexaazapentacene (150 mg, 3.1 × 10⁻⁴ mol), 3,4,5-tris(1-*n*-dodecyloxy)benzyl chloride (0.26 g, 3.9 × 10⁻⁴ mol), 3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl chloride (0.24 g, 3.9 × 10⁻⁴ mol) and sodium hydrogen carbonate (100 mg, 1.2 × 10⁻³ mol) in DMSO (10 mL) was heated at 100 °C for 24 h. The mixture was allowed to cool to room temperature and the entire mixture poured into water (150 mL) and stirred for 1 hour. The mixture was filtered and the residue washed with water (2 × 20 mL) and methanol (2 × 10 mL) and purified by column chromatography on silica gel eluting first with chloroform then with chloroform/tetrahydrofuran, 3:1) to give the product as a yellow solid. Yield 95 mg (18%). UV/Vis (CH₂Cl₂) λ_{max} (ε/10⁻³ dm³ mol⁻¹ cm⁻¹) = 487 (75.5), 456 (55.1), 428 (26.8), 297 (43.5), 256 (105.9) nm. FTIR (KBr): ν = 3453 (s); 2920 and 2851 (s, aliph. C-H str.); 1591 (w, arom. C=C str.); 1479 (m); 1454 (m); 1433 (m); 1373 (m); 1331 and 1274 (w, C-N str.); 1228 (m, C-N str.); 1117 (m, C-O str.); 758 and 727 (w, C-H def.) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 8.89 (m, 4H, ArH); 8.29 (d, *J* = 8 Hz, 4H, ArH); 7.65 (m, 4H, ArH); 7.49 (m, 4H, ArH); 7.13 (s, 2H, ArH); 7.09 (s, 2H, ArH); 5.18 (s, 2H, CH₂); 5.15 (s, 2H, CH₂); 3.94 (m, 6H, OCH₂); 3.88 (m, 6H, OCH₂); 3.86 (m, 6H, OCH₂); 3.74-3.41 (m, 24H, OCH₂); 3.29 (s, 9H, OCH₃); 1.70-1.05 (m, 60H, CH₂); 0.85 (m, 9H, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 152.76; 152.30; 140.62; 137.63; 133.02; 132.94; 132.23; 131.79; 129.90; 129.25; 127.30; 127.04; 126.99; 123.93; 122.68; 109.06; 108.36; 76.58; 73.25; 72.15; 71.83; 71.81; 70.54; 70.49; 70.37; 70.33; 69.38; 68.78; 68.55; 58.89; 58.87; 31.89; 31.85; 30.20; 29.65; 29.50; 29.33; 29.28; 29.26; 29.18; 25.99; 25.75; 22.66; 22.61; 14.08; 14.03 ppm. MALDI-TOF-MS (dithranol): calculated for C₁₀₃H₁₄₄N₆O₁₅ *m/z* = 1706.07; found = 1705.01 [M - H]⁺. UV/Vis (CH₂Cl₂) λ_{max} = 486.5; 472.5; 456.0; 444.0; 429.5; 406.0 nm. Elemental analyses, calculated % (found %): C 72.50 (72.43); H 8.51 (8.68); N 4.93 (4.86).

References

- S1** J. Nishida, Naraso, S. Murai, E. Fujiwara, H. Tada, M. Tomura, and Y. Yamashita, *Org. Lett.*, 2004, **6**, 2007.
- S2** M. Yoshio, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2004, **126**, 994.
- S3** M. A. Oar, J. A. Serin, W. R. Dichtel, J. M. J. Fréchet, T. Y. Ohulchanskyy and P. N. Prasad, *Chem. Mater.*, 2005, **17**, 2267.
- S4** G. J. Richards, J. P. Hill, J. Labuta, Y. Wakayama, M. Akada and K. Ariga, *Phys. Chem. Chem. Phys.*, 2011, **13**, 4868.

2.0 NMR Spectra

6,13-Bis(3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl)-5,6,7,12,13,14-hexaazapentacene (1)

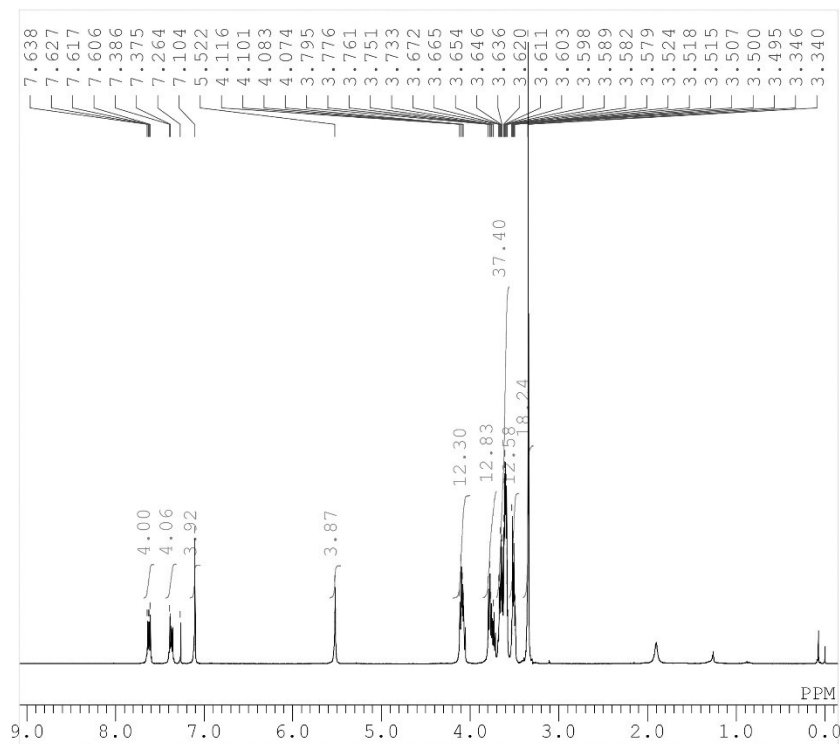


Figure S1. Proton NMR spectrum of 1.

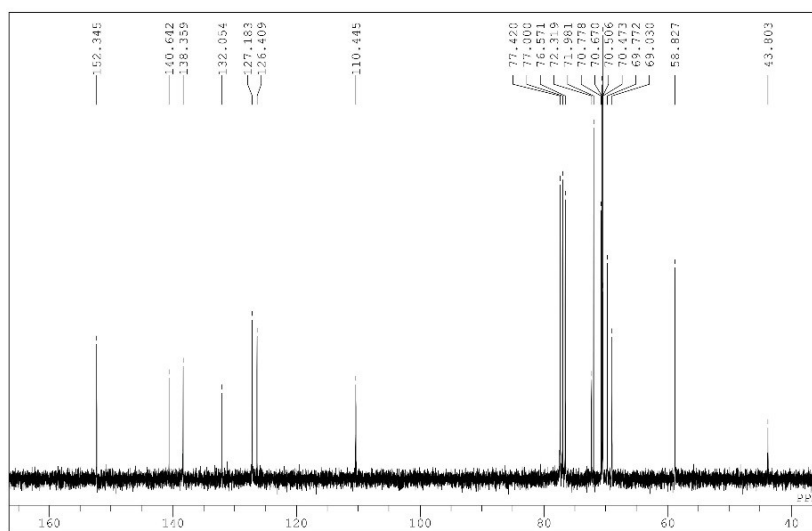


Figure S2. ¹³C NMR spectrum of 1.

6,13-Bis[tris(3,4,5-dodecyloxy)benzyl]-5,6,7,12,13,14-hexaazapentacene (**2**).

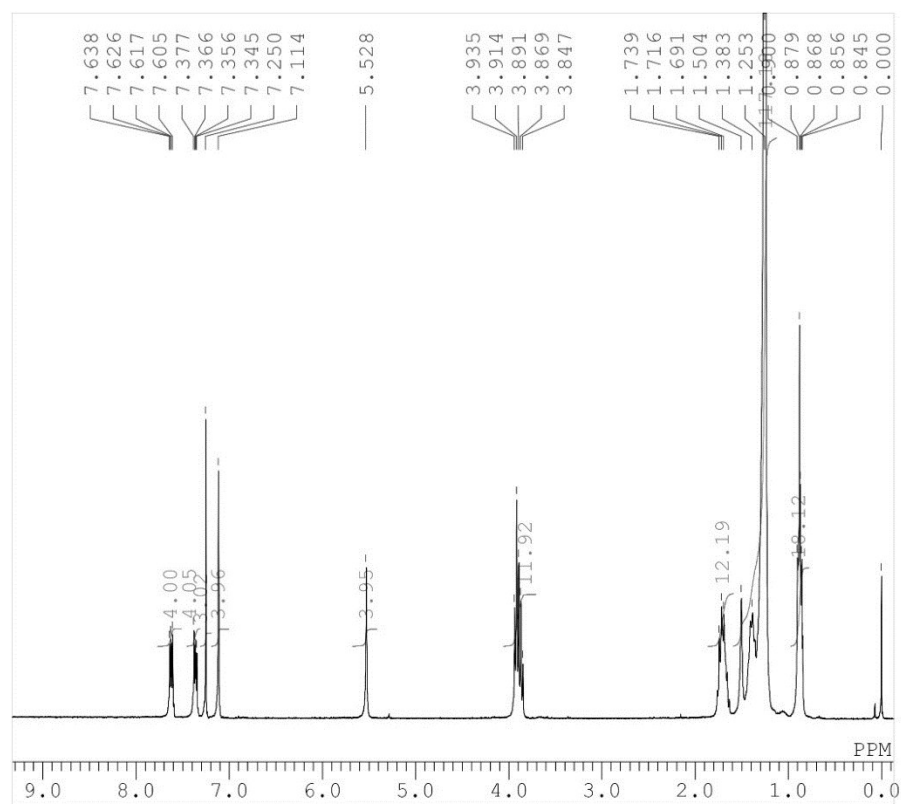


Figure S3. Proton NMR spectrum of **2**.

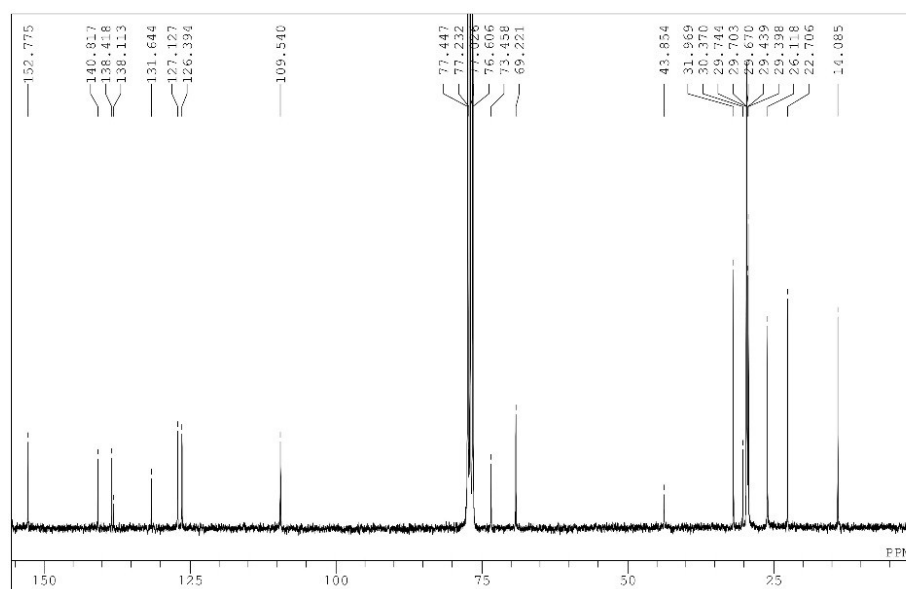


Figure S4. ^{13}C NMR spectrum of **2**.

6-(3,4,5-*Tris*[1-*n*-dodecyloxy]benzyl)-13-(3,4,5-*tris*[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl)-5,6,7,12,13,14-hexaazapentacene (3).

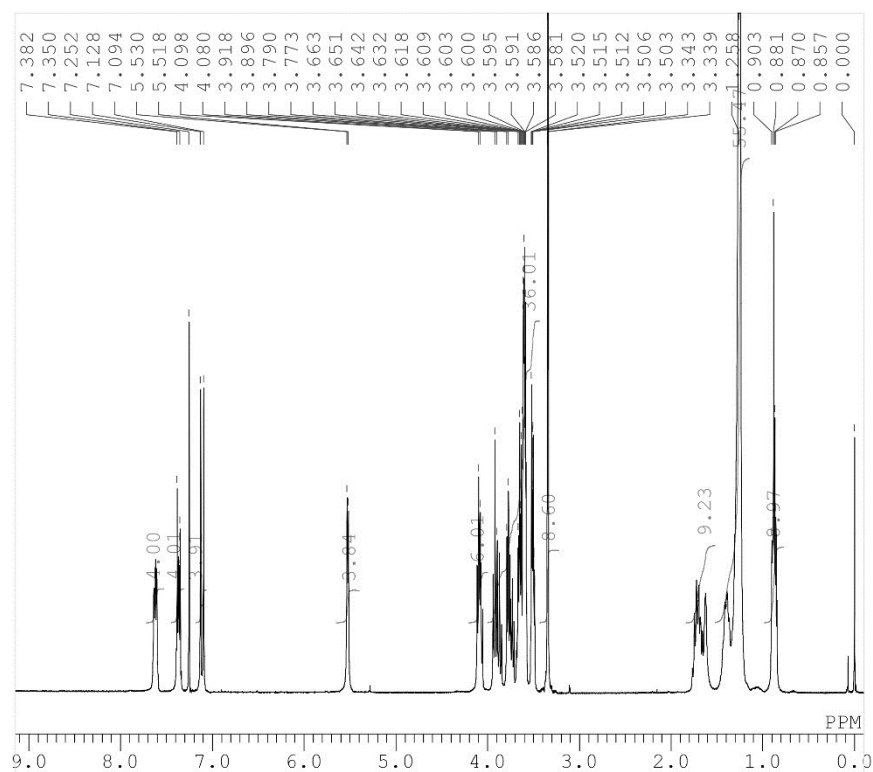


Figure S5. Proton NMR spectrum of 3.

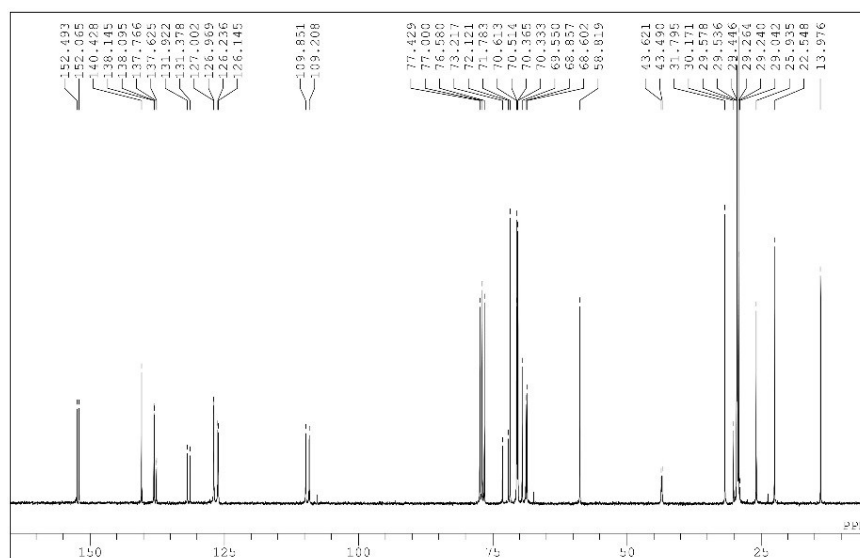


Figure S6. ^{13}C NMR spectrum of 3.

2-Bromo-6,13-bis(3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl)-5,6,7,12,13,14-hexaazapentacene (4).

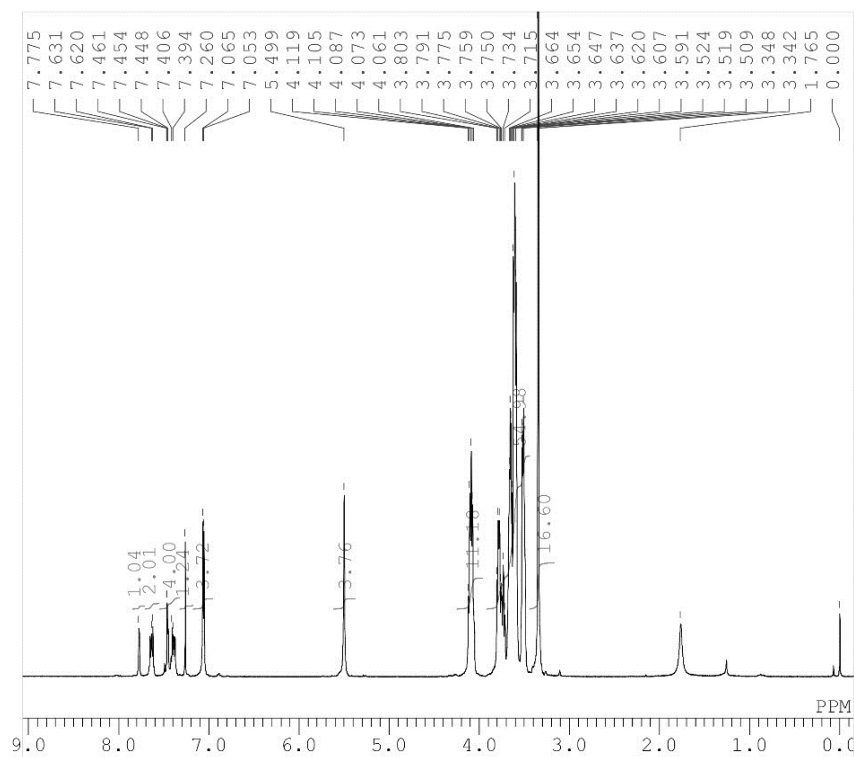


Figure S7. Proton NMR spectrum of **4**.

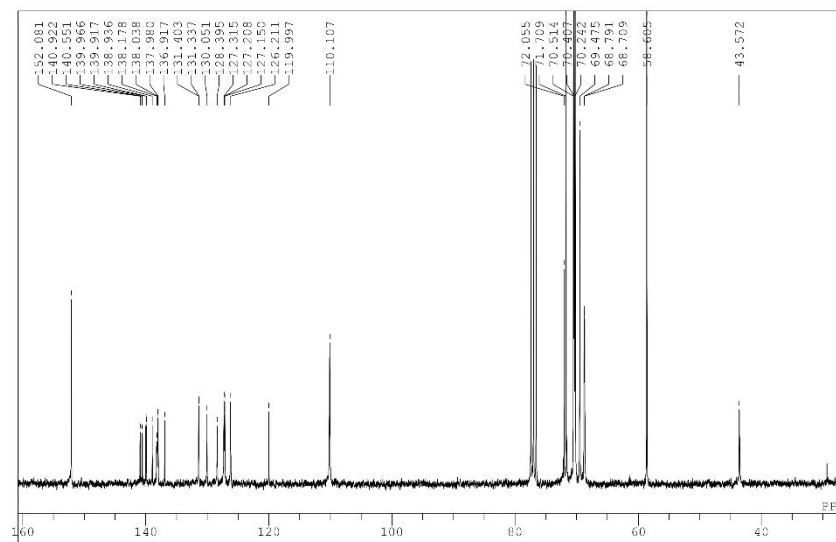


Figure S8. ^{13}C NMR spectrum of **4**.

2-Bromo-6,13-bis(3,4,5-tris[1-n-dodecyloxy]benzyl)-5,6,7,12,13,14-hexaazapentacene (5).

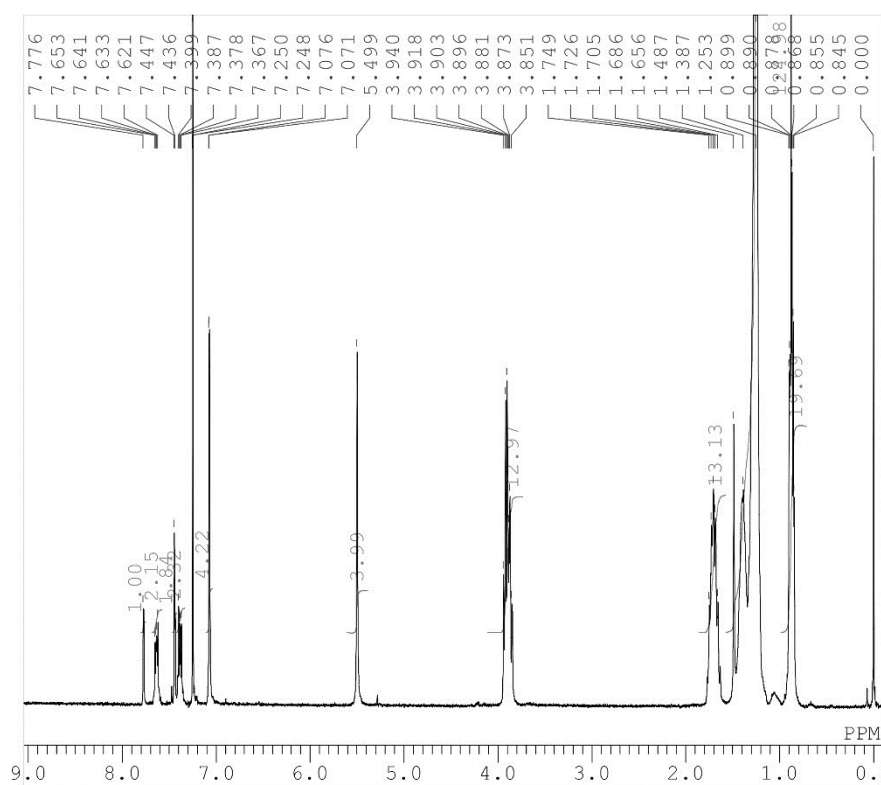


Figure S9. Proton NMR spectrum of **5**.

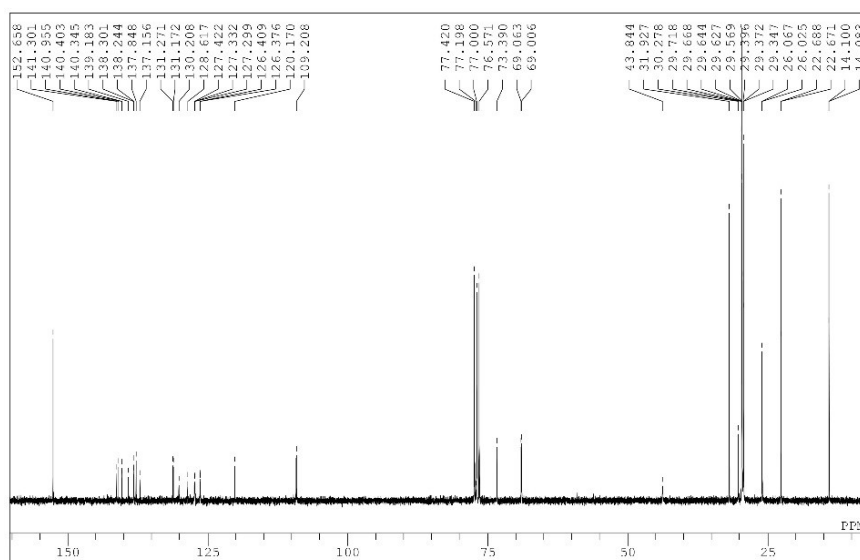


Figure S10. ^{13}C NMR spectrum of **5**.

2(3)-Bromo-6-(3,4,5-*tris*[1-*n*-dodecyloxy]benzyl)-13-(3,4,5-*tris*[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl-5,6,7,12,13,14-hexaazapentacene (6).

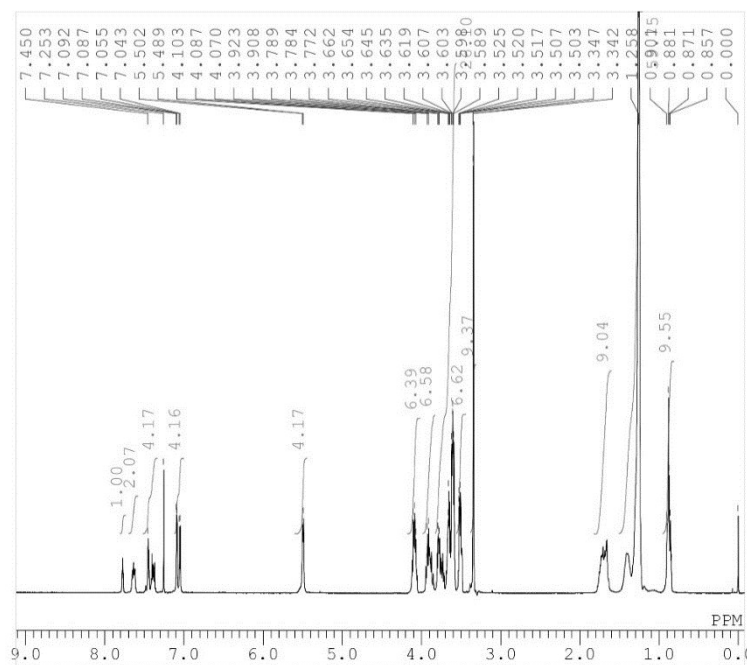


Figure S11. Proton NMR spectrum of **6**.

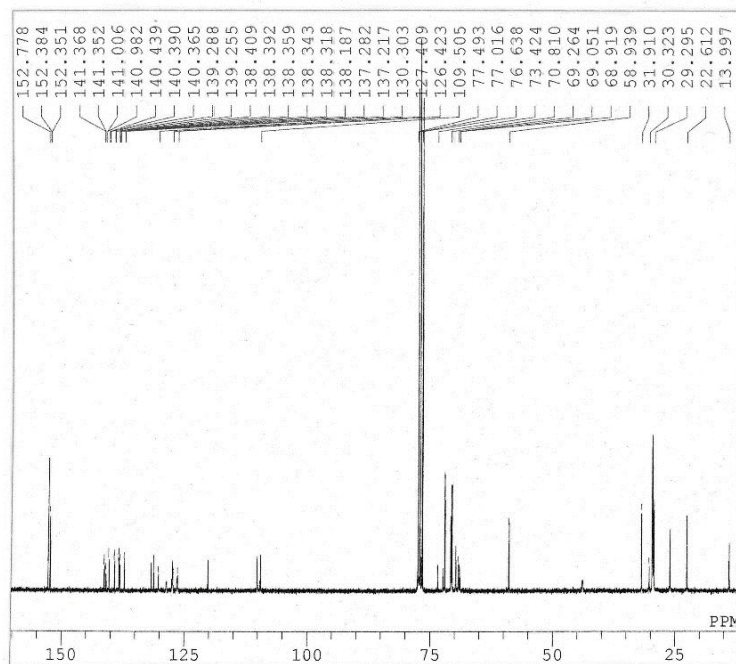


Figure S12. ^{13}C NMR spectrum of **6**.

6,13-Bis(3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl)-[a,c,l,n]-tetrabenzo-5,6,7,12,13,14-hexaazapentacene (7).

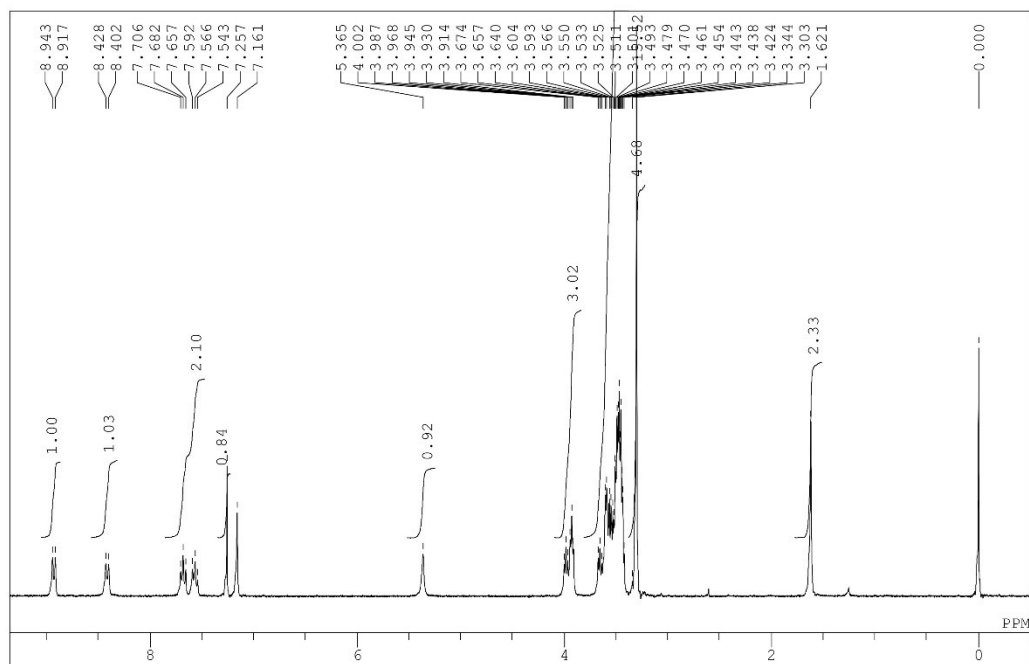


Figure S13. Proton NMR spectrum of **7**.

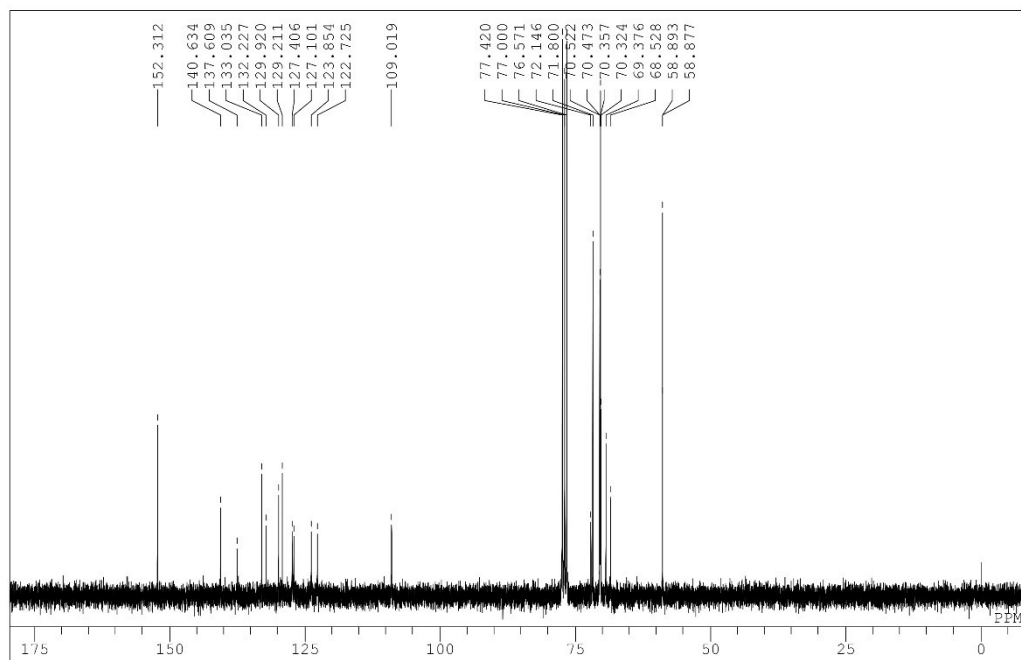


Figure S14. ^{13}C NMR spectrum of **7**.

6,13-Bis(3,4,5-tris[1-n-dodecyloxy]benzyl)-[a,c,l,n]-tetrabenzo-5,6,7,12,13,14-hexaazapentacene (8).

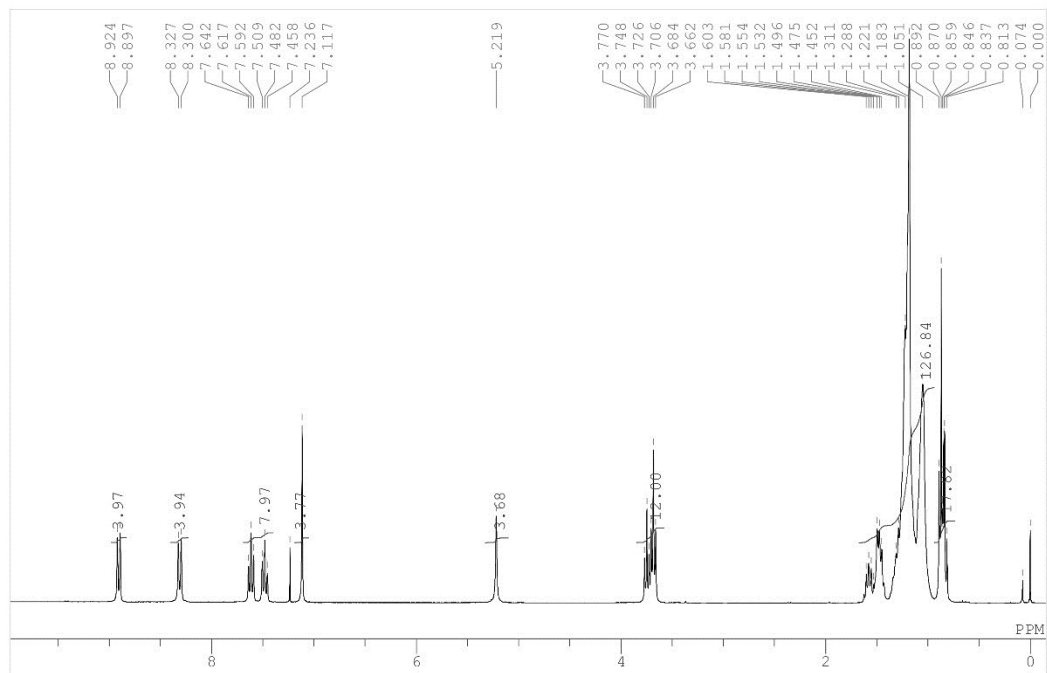


Figure S15. Proton NMR spectrum of 8.

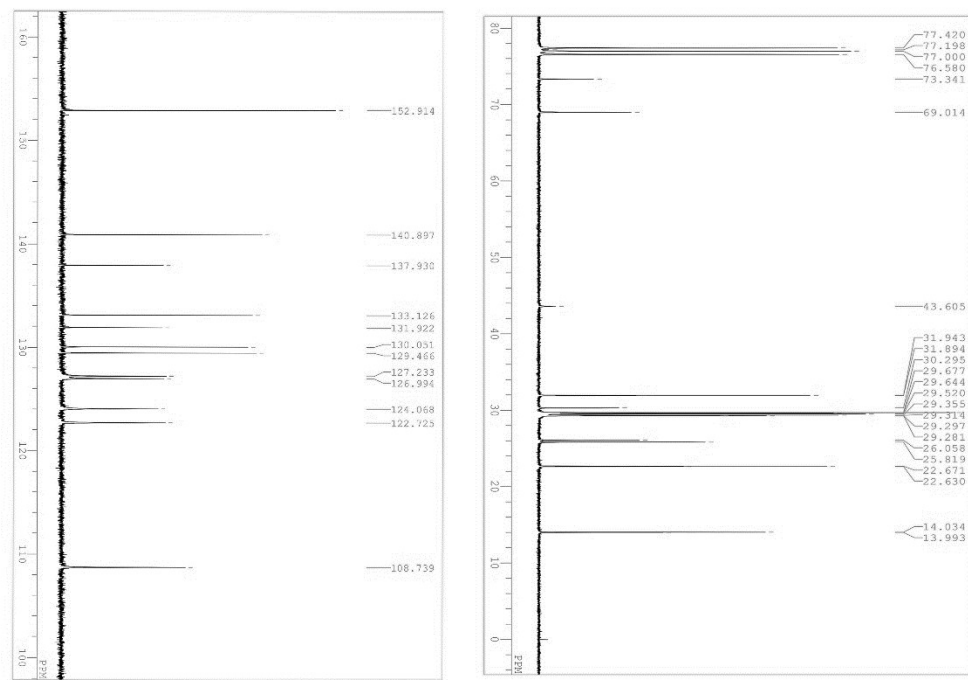


Figure S16. ^{13}C NMR spectrum of 8.

6-(3,4,5-Tris[1-n-dodecyloxy]benzyl)-13-(3,4,5-tris[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]benzyl)-[a,c,l,n]-tetrabenzo-5,6,7,12,13,14-hexaazapentacene (9).

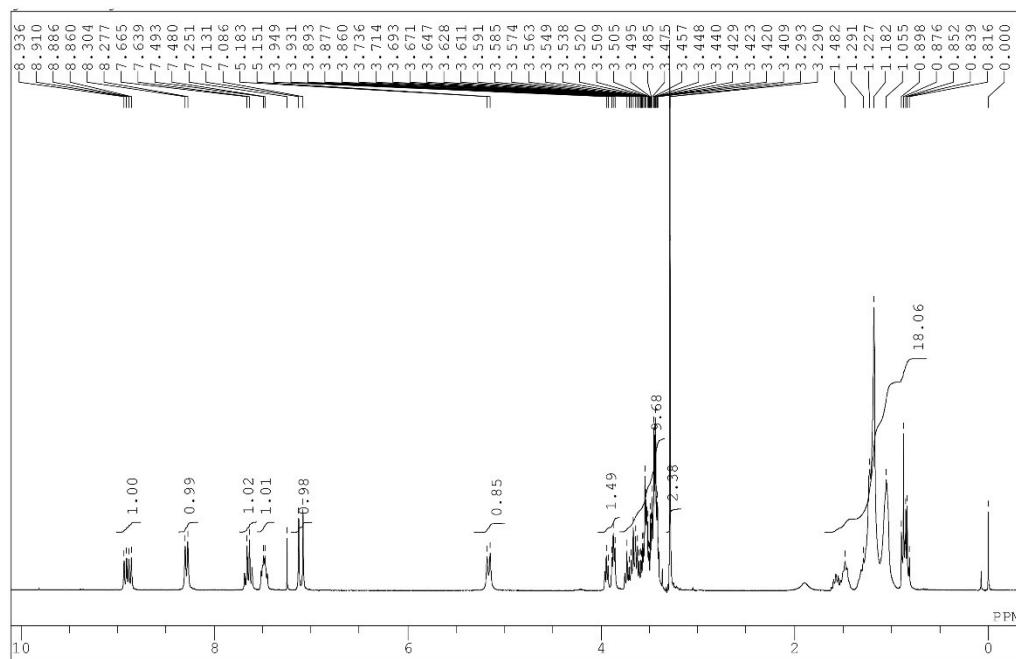


Figure S17. Proton NMR spectrum of 9.

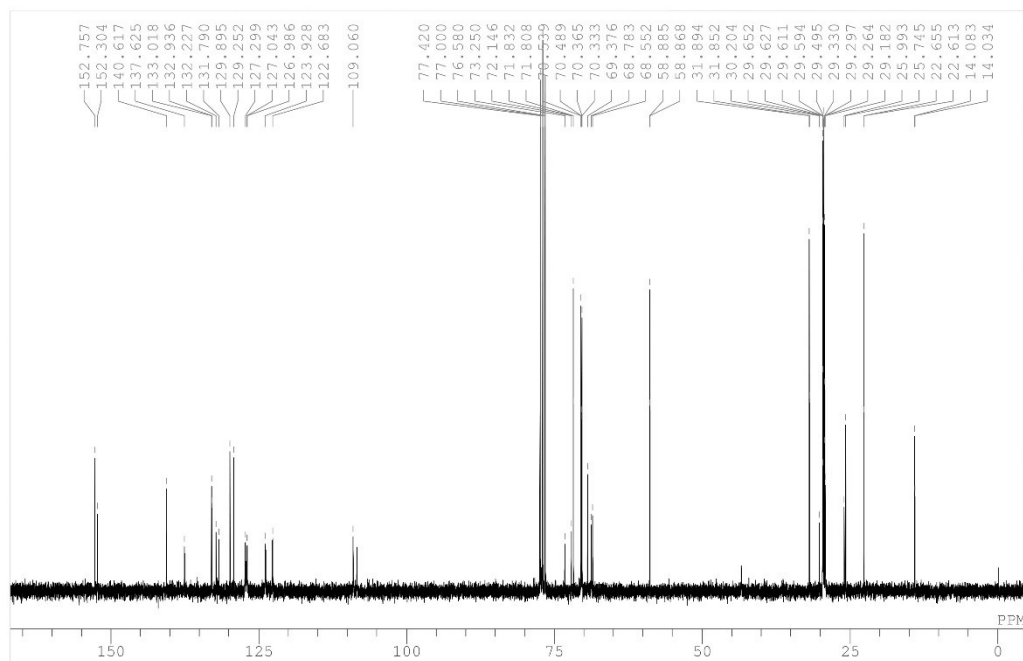


Figure S18. ¹³C NMR spectrum of 9.

3.0 Differential Scanning Calorimetry

Phases ^a	
1	I
2	Cr (100.5 ^b /-) I
3	M (70.9/62.21) I
4	Sm _x (40.4/15.61) I
5	Cr (101 ^b /-) I
6	Col _r (?) (73.9/48.87) I
7	Smectic soft crystal (202.5/41.28) I
8	Cr ₁ (36.2/21.44) Cr ₂ (150.4/28.04) Col _{cr} (221.6/31.30) I
9	Cr (109.4/1.33) Cr ₁ (123.1/0.67) Cr ₂ /Col _r (190.5,197.4/41.33 ^c) I

1 is an isotropic liquid in the temperature range studied. **2** is crystalline with a clearing point at 100.5 °C. **5** is also a crystalline solid with clearing point at 101 °C.

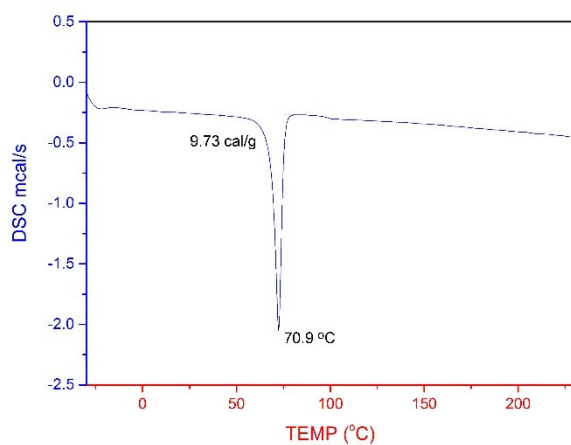


Figure S19. DSC of **3** (2nd heating).

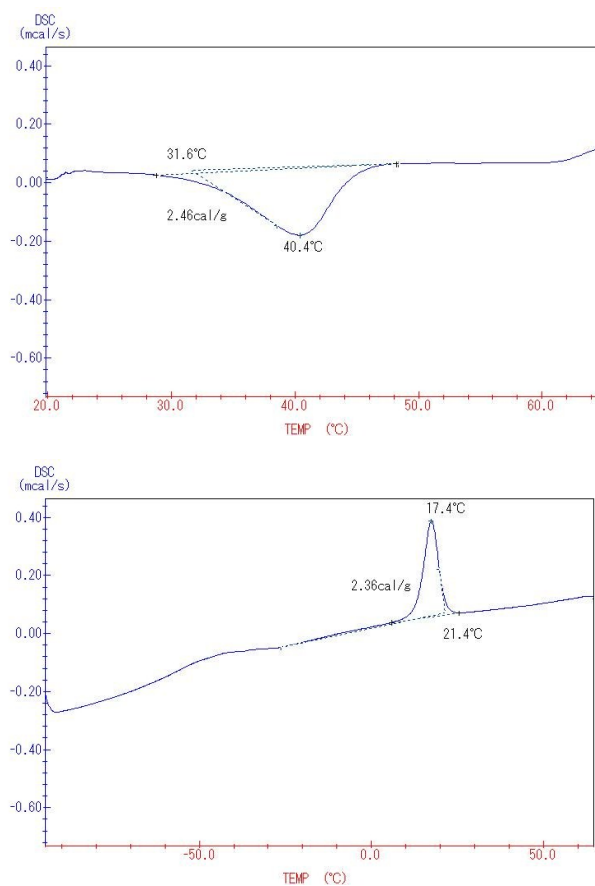


Figure S20. DSC of **4**. Upper panel: 1st heating; lower panel: 1st cooling.

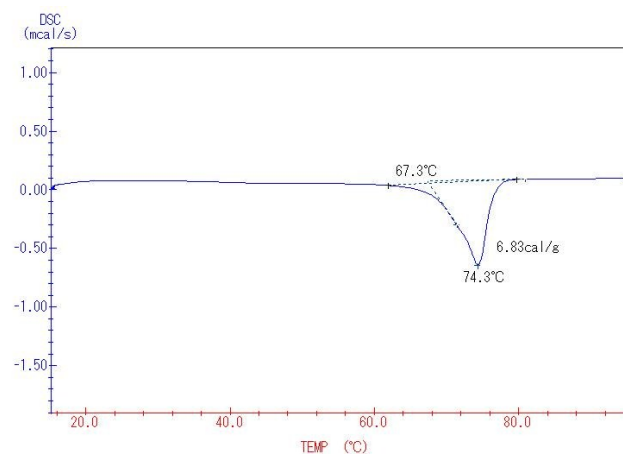


Figure S21. DSC of **6** (2nd heating).

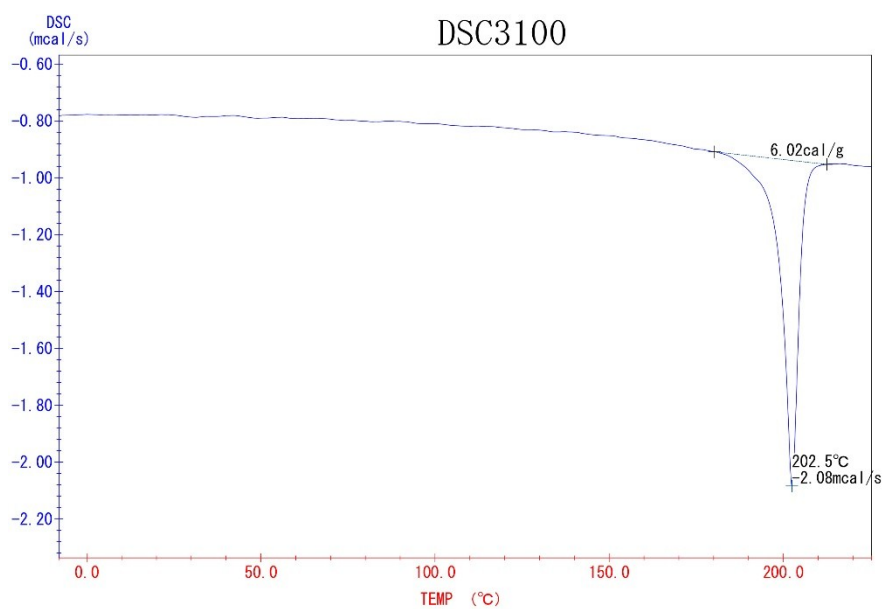


Figure S22. DSC of **7** (2nd heating).

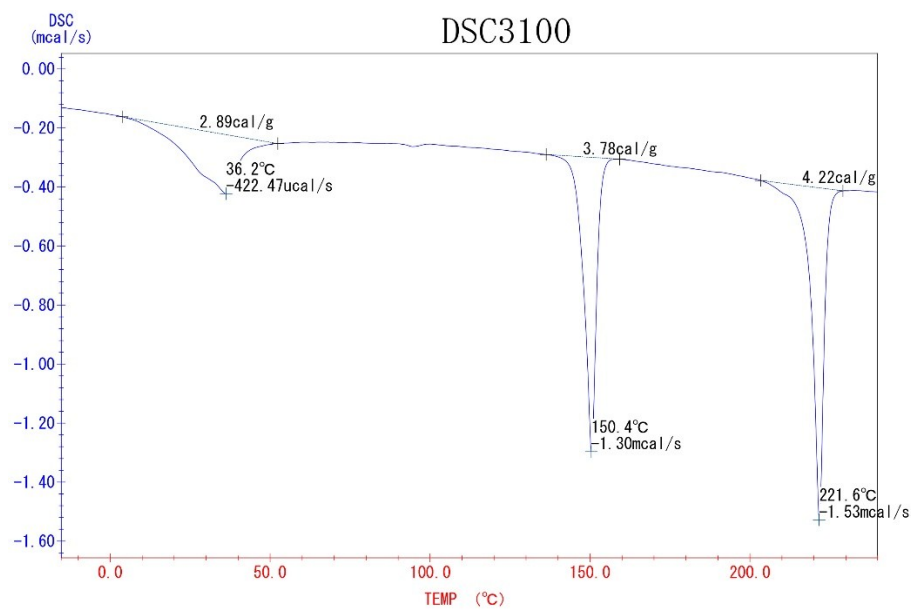


Figure S23. DSC of **8** (2nd heating).

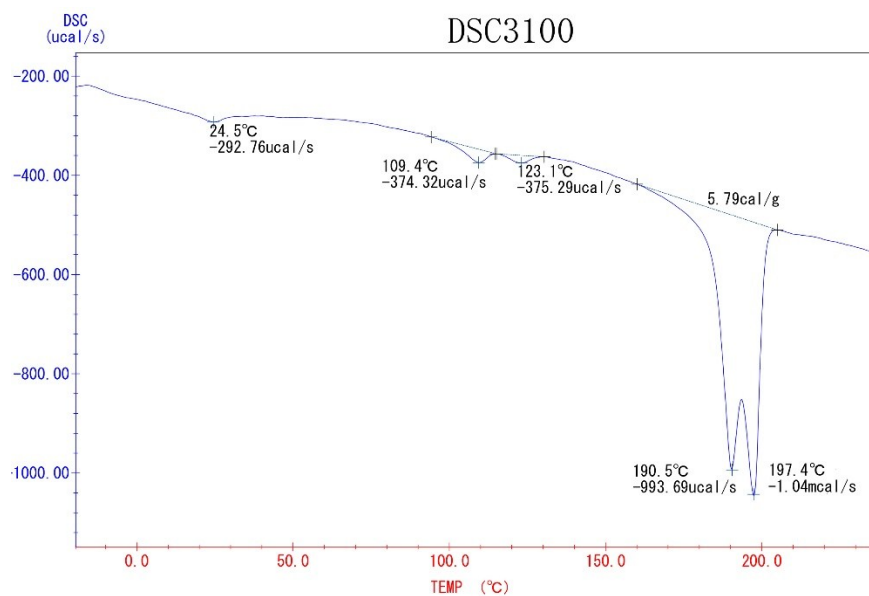


Figure S24. DSC of **9** (2nd heating).

4.0 Thermogravimetric analyses

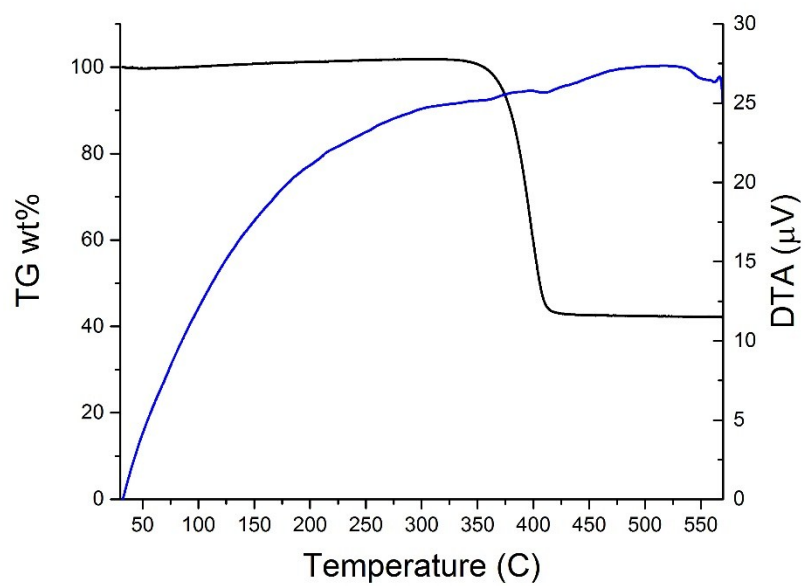


Figure S25. TGA and DTA for compound 1.

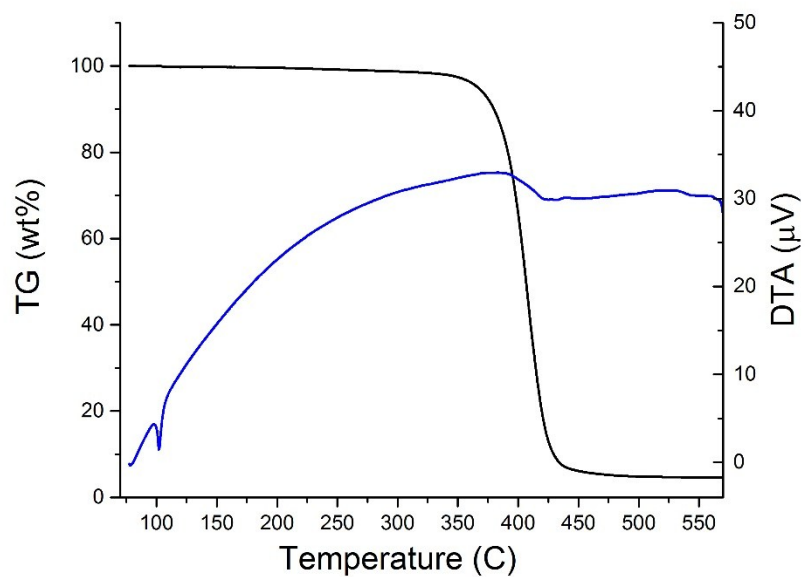


Figure S26. TGA and DTA for compound 2.

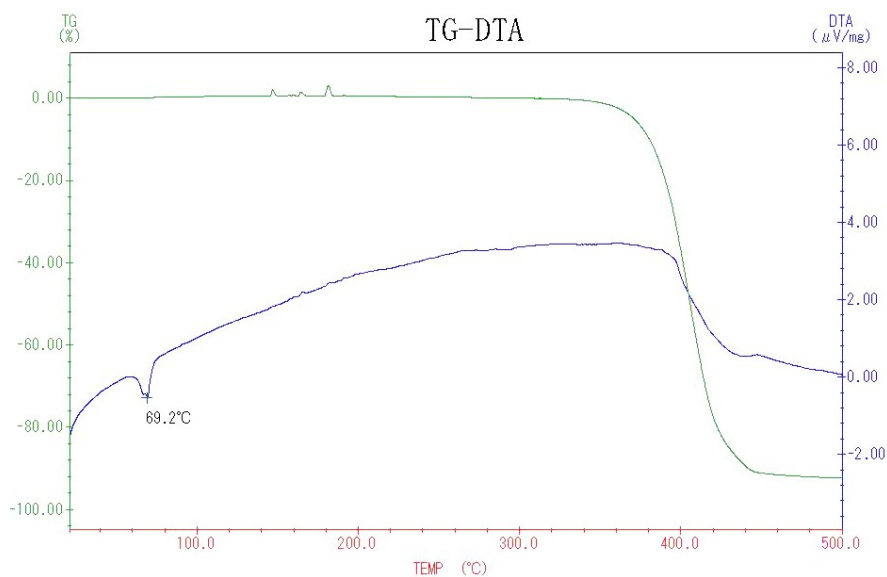


Figure S27. TGA and DTA for compound 3.

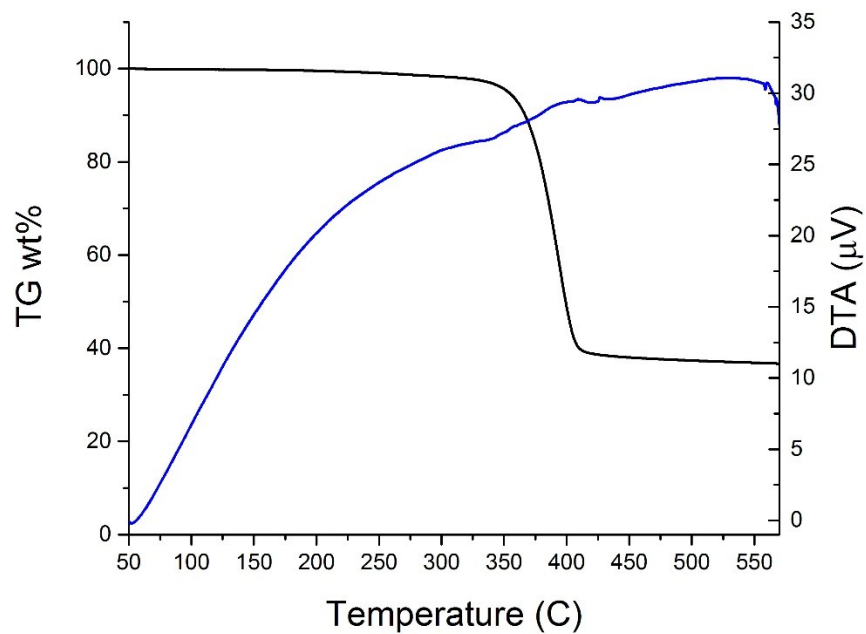


Figure S28. TGA and DTA for compound 4.

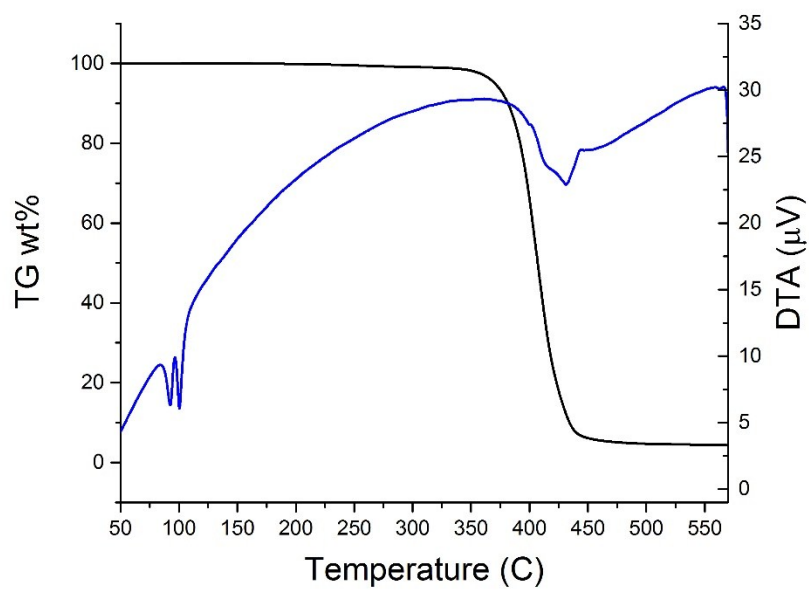


Figure S29. TGA and DTA for compound **5**.

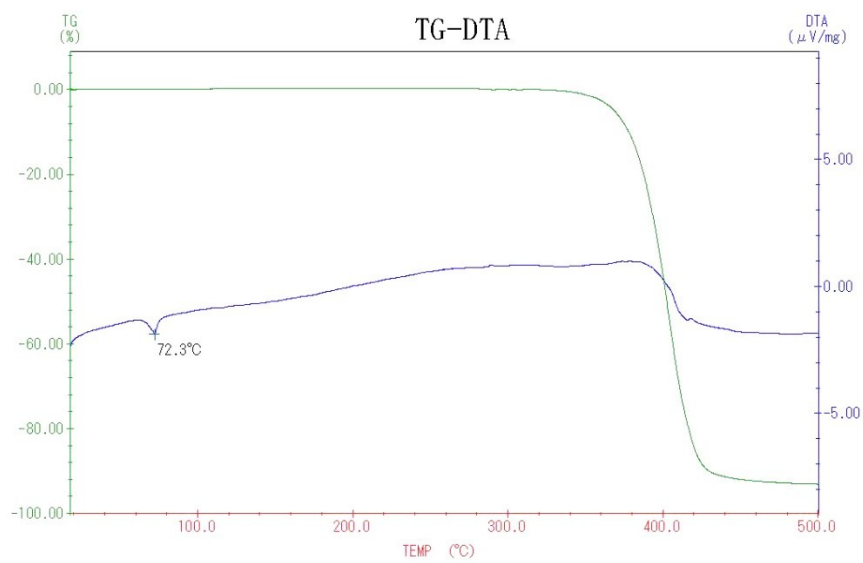


Figure S30. TGA and DTA for compound **6**.

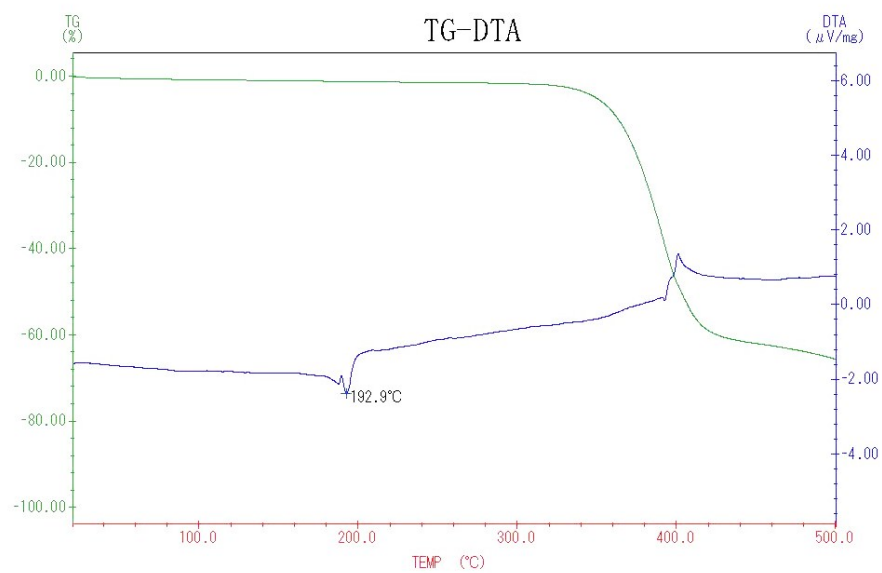


Figure S31. TGA and DTA for compound **7**.

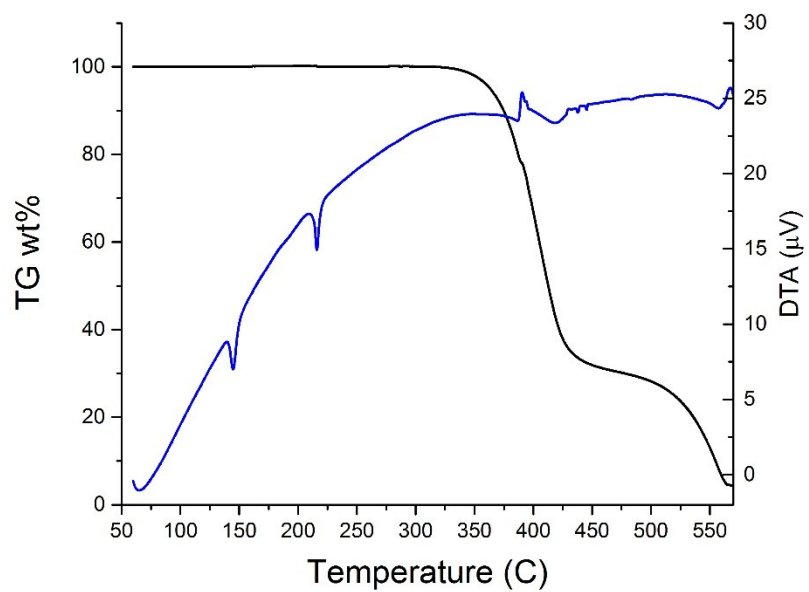


Figure S32. TGA and DTA for compound **8**.

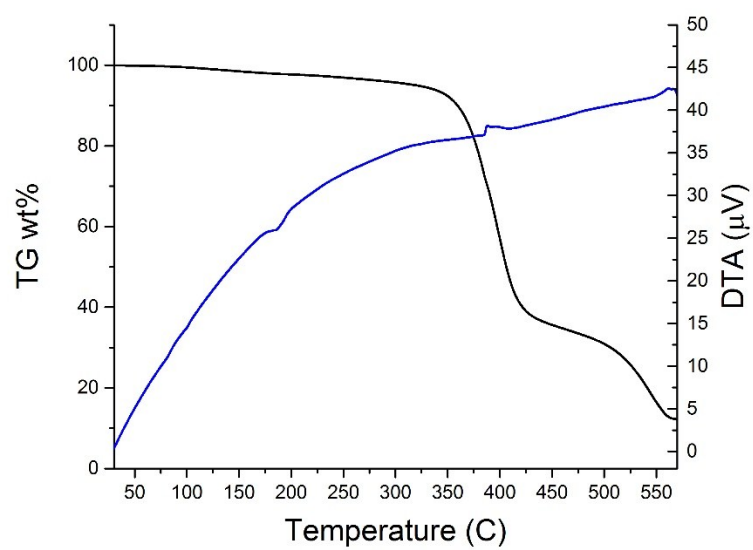


Figure S33. TGA and DTA for compound **9**.