Convenient syntheses of cyclic carbazole oligomers by 1-pot Knoevenagel reaction

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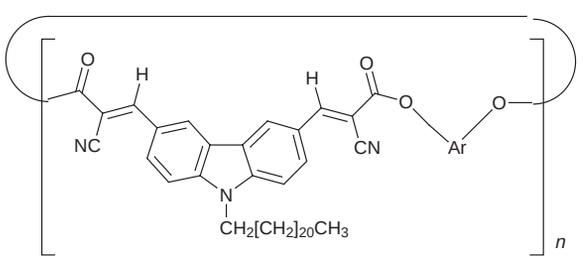
Syntheses of cyclic carbazole oligomers by a 1-pot Knoevenagel reaction without using high dilution methods are described. Cyclic carbazole oligomers of several ring sizes could be obtained in high yields when 3,6-diformyl-9-docosylcarbazole and appropriate aromatic compounds having a bis(cyanoacetate) group were reacted in THF using DMAP as a base at 40 °C.

Introduction

Syntheses and developments of cyclic oligomers are important in several fields of research including supramolecular chemistry and materials science. In supramolecular chemistry, cyclic oligomers such as crown ethers,[1] calixarenes,[2] and cyclodextrins[3] are useful for molecular recognition, and in materials science, cyclic oligomers are also useful for organic light-emitting diodes.[4] In our laboratory, we focus on carbazole molecules as a multifunctional material, and several types of main-chain and hyperbranched polymers with carbazole moieties have been synthesized by Knoevenagel reaction and show reasonable second-order nonlinear optical (NLO) and electroluminescence properties.[5,6] In a series of experiments, we found that cyclic carbazole oligomers (tetramer **1** and dimer **3**; alkyl = heptyl)



1-5

could be easily synthesized by 1-pot Knoevenagel reaction in high yields when 3,6-diformyl-9-heptylcarbazole and 3,6-bis(cyanoacetoxymethyl)-9-heptylcarbazole or 1,4-bis(cyanoacetoxymethyl)benzene were reacted in THF using DMAP as a base.[7] Usually, cyclic compounds are synthesized by using the high dilution method and purified by column chromatography, so their yields are low.[8] However, we found that cyclic oligomers could be synthesized under the normal conditions without using purification by column chromatography, so that yields are high. Our results show that several kinds of cyclic carbazole oligomers can be easily synthesized by a 1-pot reaction like calixarene derivatives[9] if we select appropriate aromatic compounds which have a bis(cyanoacetate) group. In this paper we report on the syntheses of cyclic carbazole oligomers by 1-pot Knoevenagel reaction. These cyclic oligomers would be useful for new material, host–guest chemistry, and aggregation behavior. These cyclic oligomers are also expected to act as useful multifunctional chromophores for NLO and organic light-emitting diodes. The optical properties of these cyclic oligomers are now underway.

Results and discussion

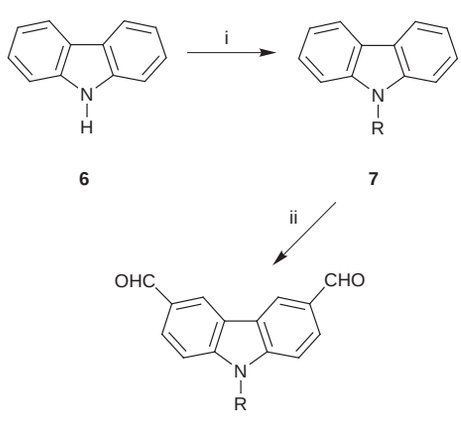
Molecular design for cyclic oligomers

According to the Corey–Pauling–Koltun (CPK) model, cyclic oligomers **1**–**5** might be synthesized by using the appropriate aromatic moiety. Based on these molecular designs, we tried to synthesize cyclic oligomers **1**–**5**.

Syntheses of cyclic oligomers

The key materials in these reactions are 9-alkyl-3,6-diformylcarbazole and bis(cyanoacetoxymethyl) aromatics. We chose the docosyl group as the alkyl chain to increase solubility.

Synthesis of 3,6-diformyl-9-docosylcarbazole. The diformylcarbazole unit was synthesized as shown in Scheme 1. A



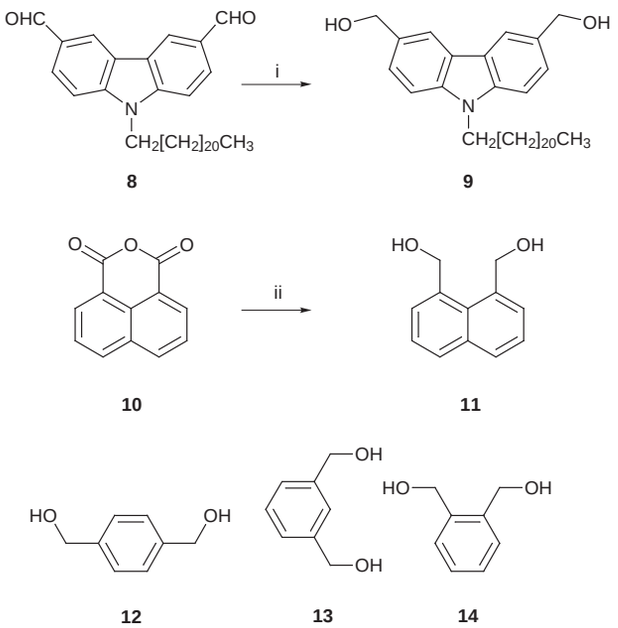
6 **7** **8**

R = $CH_2[CH_2]_{20}CH_3$

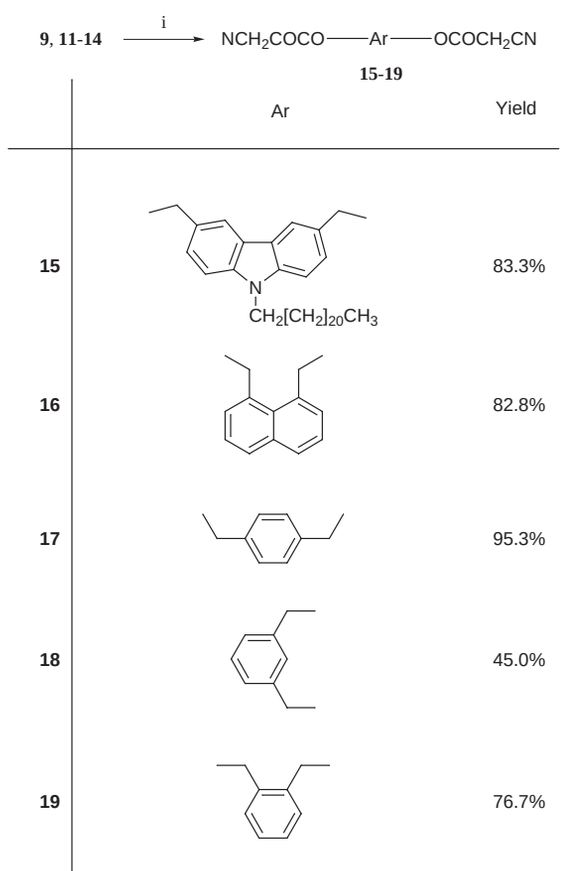
Scheme 1 *Reagents and conditions:* i) $CH_3[CH_2]_{20}CH_2Br$, NaH, THF–DMF (3:1 v/v), room temp., quant.; ii) DMF–$POCl_3$, 1,2-dichloroethane, 90 °C, 38.6%.

carbazole **6** reacted with 1-bromodocosane in the presence of NaH to give 9-docosylcarbazole **7** in quantitative yield. 3,6-Diformyl-9-docosylcarbazole **8** was synthesized by Vilsmeier formylation from **7** in 38.6% yield.

Syntheses of bis(cyanoacetoxymethyl) aromatics. Several bis-(cyanoacetoxymethyl) aromatics were synthesized as shown in Schemes 2 and 3. 3,6-Bis(hydroxymethyl)-9-docosylcarbazole



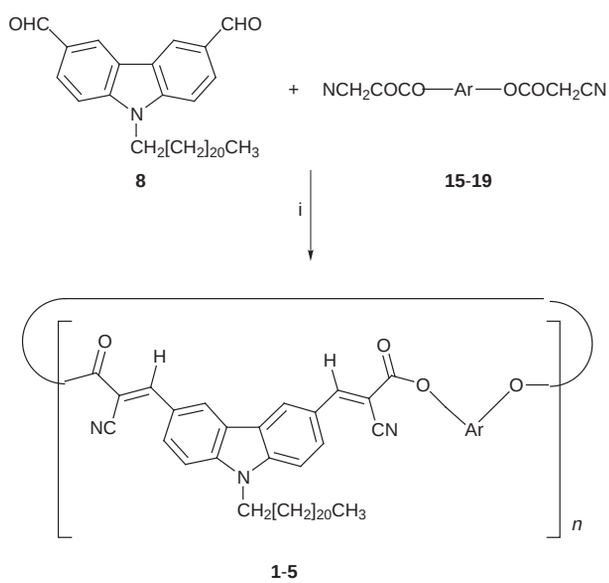
Scheme 2 *Reagents and conditions:* i) $NaBH_4$, THF–EtOH, room temp., 96.6%; ii) $LiAlH_4$, THF, reflux, 48.7%; **12**–**14** were commercially available.

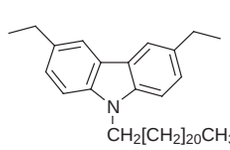
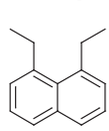
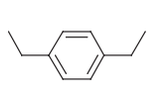
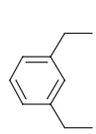
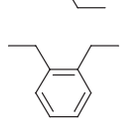


Scheme 3 *Reagents and conditions:* i) $NCCH_2COOH$, DCC or EDC·HCl, NEt_3, CH_2Cl_2, 0 °C to reflux.

9 was prepared by reduction of **8** with $NaBH_4$ in 96.6% yield. 1,8-Bis(hydroxymethyl)naphthalene **11** was synthesized by reduction of 1,8-naphthalic anhydride (naphthalene-1,8-dicarboxylic anhydride) **10** with $LiAlH_4$ in 48.7% yield. Bis-(cyanoacetoxymethyl) aromatics **15**–**19** were synthesized by esterification of **9**, **11**–**14** with cyanoacetic acid in the presence of DCC or 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) as a water acceptor. We initially used DCC as a water acceptor, but it was difficult to remove by-products such as ureas and *N*-acylureas so yields were low. In order to increase yields and simplify work up, we used EDC as a water acceptor because the remaining EDC and its by-products can be easily removed by washing with dilute acid or water without using purification by column chromatography and/or recrystallization.[10]

Syntheses and characterization of cyclic oligomers 1–5. The cyclic oligomers **1**–**5** were synthesized according to Scheme 4. 3,6-Diformyl-9-docosylcarbazole **8** and aryl cyanoacetate **15**–**19** were stirred in THF in the presence of DMAP at 40 °C,



	Ar	*n*	Yield
1		4	33.0%
2		4	58.8%
3		2	89.2%
4		2	56.7%
5		2	6.0%

Scheme 4 *Reagents and conditions:* i) DMAP, THF, 40 °C.

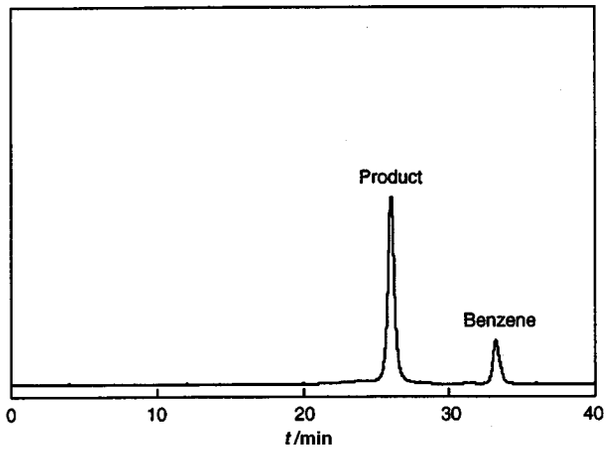


Fig. 1 The GPC spectrum of **2** using $CHCl_3$ as eluent.

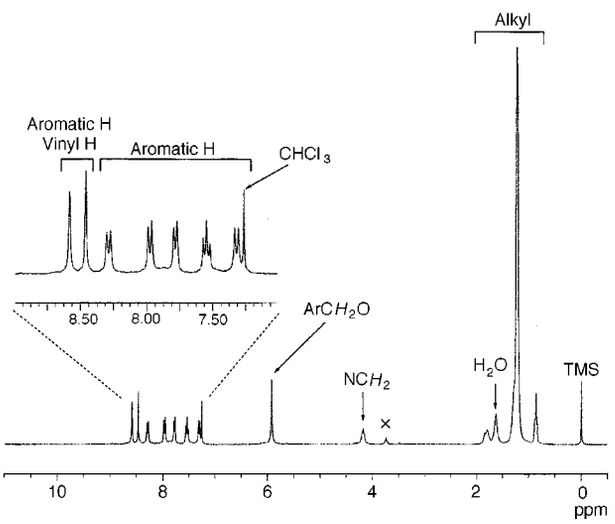


Fig. 2 ^1H NMR spectrum of **2** in $CDCl_3$ at room temp.

to give the cyclic oligomer **1**–**5**. For example, the synthesis of cyclic oligomer **2** is as follows: 3,6-diformyl-9-docosylcarbazole **8** (1.001 g; 1.882 mmol) and 1,8-bis(cyanoacetoxymethyl)-naphthalene **16** (0.606 g; 1.880 mmol) were stirred in THF (5 ml) using DMAP (0.524 g; 4.289 mmol) as a base at 40 °C, to give the cyclic oligomer **2** as a precipitate. The precipitate was collected and washed with THF. Finally, by reprecipitation from chloroform–methanol, we obtained the cyclic oligomer **2** as a yellow powder. The yield was 58.8%. As gel permeation chromatography (GPC) analysis of product **2** (Fig. 1) showed monodispersity of molecular weight, it indicated that only one species was present. The structure of cyclic oligomer **2** was assigned by ^1H NMR, Fourier transform infrared (FT-IR), and fast atom bombardment mass (FAB-MS) spectra. The proton resonance signals of the terminal groups, such as the proton of the formyl group and the proton of the cyanoacetate, were not observed in the ^1H NMR spectrum, and a symmetrical spectrum was obtained (Fig. 2). FAB-MS of this oligomer exhibited the molecular ion M^+ (requires *m*/*z* 3272; found *m*/*z* 3272) which corresponds to a cyclic tetramer. The FT-IR spectrum showed the signals of CN, C=O, and a flexible long chain. From these spectral data, we assigned product **2** as a cyclic oligomer. The cyclic oligomers **1**, **3**–**5** could also be synthesized and assigned by the same methods. For the MS spectrum, the measurement of **1** was performed by Matrix Assisted Laser Desorption/Ionization Time-of-Flight Mass (MALDI-TOF-MS) spectroscopy, because the signal of **1** could not be found in the FAB-MS spectrum.

In our system, all the cyclic oligomers except **5** precipitated spontaneously because of their low solubility in THF, and this allowed the cyclic oligomers to be separated by filtration. In this reaction, the other products were polymeric materials. We found the purification of cyclic oligomer **5** more difficult due to its solubility in THF; however, the solubility of **5** in THF was lower than that of the corresponding polymer, so that we could separate a small amount of **5**. The reason why highly selective formation of the dimers and tetramers is observed would be due to the relatively rigid nature of the precursors used.

Conclusion

We have demonstrated that cyclic carbazole oligomers can be easily synthesized by 1-pot Knoevenagel reaction in high yields.

Experimental

Materials

All chemical reagents and anhydrous solvents were commercially available and used without further purification. 1,8-Bis(hydroxymethyl)naphthalene **11** was synthesized as described in ref. 11. Analytical thin layer chromatography was performed on commercial Merck plates coated with silica gel $60F_{254}$. The silica gel used for chromatography was Merck silica gel 60.

Instrumentation

^1H NMR spectra were recorded in $CDCl_3$ solution on JEOL EX-270 (270 MHz) and JEOL JNM-AL300 (300 MHz) spectrometers. Chemical shifts are reported in ppm downfield from TMS, and coupling constants are in hertz. FAB-MS spectra were recorded on a JEOL JMS-HX110 mass spectrometer using 3-nitrobenzyl alcohol as a matrix. MALDI-TOF-MS spectra were recorded on a Bruker REFLEX mass spectrometer using 2,5-dihydroxybenzoic acid as a matrix. FT-IR spectra were recorded on a JASCO FT/IR-4100 infrared spectrometer as KBr pellets. Elemental analyses were performed at the Division of Chemical Analysis of RIKEN. The analytical GPC experiments were performed under the following conditions: columns, Waters Ultrastyragel HR2, HR3, and HR4; detector, Shimadzu SPD-10A; eluent, chloroform (1.0 ml min^{-1}).

Synthesis of the diformylcarbazole unit

9-Docosylcarbazole 7. A mixture of carbazole **6** (20.001 g, 0.120 mol) and 1-bromodocosane (46.589 g, 0.120 mol) was stirred in THF–DMF (90 ml: 30 ml) at rt. A suspension of sodium hydride (60% in oil, 5.812 g, 0.145 mol) was gradually added to the solution and stirred for 1 day. Methanol was added to the solution to quench the remaining sodium hydride, and the solvent was evaporated *in vacuo*. The residue was taken up in dichloromethane (200 ml)–3 M HCl aq. (200 ml) twice. The organic layer was washed with water (200 ml), dried over Na_2SO_4, and filtered. The solvent was evaporated *in vacuo* and the residue was reprecipitated from methanol to give **7**. We used this material in the following steps without further purifications; δ_H (270 MHz; $CDCl_3$; TMS) 0.88 (3H, t, *J* 6.6 Hz, CH_3), 1.19–1.31 (38H, m, CH_2), 1.81–1.89 (2H, m, NCH_2CH_2), 4.29 (2H, t, *J* 7.2 Hz, NCH_2), 7.22 (2H, t, *J* 7.4 Hz, arom. H), 7.38–7.49 (4H, m, arom. H), 8.10 (2H, d, *J* 7.9 Hz, arom. H).

3,6-Diformyl-9-docosylcarbazole 8. To DMF (32.113 g, 0.439 mol) at 0 °C, phosphorus oxychloride (65.800 g, 0.429 mol) was added dropwise under a nitrogen atmosphere. The solution was allowed to warm to rt, and 9-docosylcarbazole **7** (10.281 g, 21.608 mmol) and 1,2-dichloroethane (40 ml) was added. The resulting solution was heated to 90 °C and kept at this temperature for 4 days. The solvent was evaporated by heating, then the residue was poured into crushed ice. The resulting precipitate was collected, dried and purified by

column chromatography using chloroform–ethyl acetate (99:1 v/v) as an eluent to give **8** (4.436 g, 38.6%); δ_H(270 MHz; $CDCl_3$; TMS) 0.88 (3H, t, *J* 6.6 Hz, CH_3), 1.185–1.35 (38H, m, CH_2), 1.89–1.94 (2H, m, CH_2), 4.39 (2H, t, *J* 7.3 Hz, NCH_2), 7.555 (2H, d, *J* 8.6 Hz, arom. H), 8.09 (2H, dd, *J* 8.6 and 1.7 Hz, arom. H), 8.68 (2H, d, *J* 1.3 Hz, arom. H), 10.14 (2H, s, C*H*O).

Syntheses of bis(cyanoacetoxymethyl) aromatics

3,6-Bis(hydroxymethyl)-9-docosylcarbazole 9. A mixture of **8** (1.510 g, 2.839 mmol) and $NaBH_4$ (0.665 g, 17.577 mmol) was stirred in THF–ethanol (20 ml:20 ml) at rt for 7 h. The solution was poured into water (300 ml) and the resulting precipitate was collected and dried (1.470 g, 96.6%); δ_H (270 MHz; $CDCl_3$; TMS) 0.88 (3H, t, *J* 6.4 Hz, CH_3), 1.23–1.25 (38H, m, CH_2), 1.825–1.85 (2H, m, CH_2), 4.29 (2H, t, *J* 7.1 Hz, NCH_2), 4.855 (4H, s, ArCH_2OH), 7.39 (2H, d, *J* 8.2 Hz, arom. H), 7.49 (2H, dd, *J* 8.2 and 1.3 Hz, arom. H), 8.09 (2H, s, arom. H).

3,6-Bis(cyanoacetoxymethyl)-9-docosylcarbazole 15. A mixture of **9** (1.499 g, 2.797 mmol), DCC (1.940 g, 9.402 mmol) and cyanoacetic acid (1.022 g, 12.015 mmol) was stirred in dichloromethane (60 ml) under 5 °C for 8 h. The solution was washed with water (200 ml) twice. The organic layer was dried over Na_2SO_4 (anhydrous), filtered, and the solvent was evaporated *in vacuo*. The residue was dissolved in dichloromethane and the resulting solution was filtered and passed through silica gel. The solvent was evaporated *in vacuo* and the residue was recrystallized from acetone–water to give **15**. We used this material in the following steps without further purifications; δ_H (270 MHz; $CDCl_3$; TMS) 0.88 (3H, t, *J* 6.6 Hz, CH_3), 1.25–1.37 (38H, m, CH_2), 1.85–1.96 (2H, m, CH_2), 3.49 (4H, s, NCCH_2CO), 4.30 (2H, t, *J* 7.2 Hz, NCH_2), 5.42 (4H, s, ArCH_2O), 7.41 (2H, d, *J* 8.3 Hz, arom. H), 7.51 (2H, dd, *J* 8.2 and 1.6 Hz, arom. H), 8.13 (2H, d, *J* 1.3 Hz, arom. H).

1,8-Bis(cyanoacetoxymethyl)naphthalene 16. A mixture of **11** (1.507 g, 8.006 mmol) and EDC·HCl (3.231 g, 20.467 mmol) was stirred in dichloromethane (50 ml) in the presence of triethylamine (2.5 ml, 17.973 mmol) under nitrogen. Cyanoacetic acid (1.741 g, 20.467 mmol) was added, and the resulting solution was refluxed for 10 h. The solution was cooled to room temp. and washed with 5% HCl aq. (200 ml) twice, saturated aq. $NaHCO_3$ (200 ml), water (200 ml), dried with $MgSO_4$ (anhydrous), and filtered. The solvent was removed *in vacuo*, and the residue was dried to give **16** (2.136 g, 82.8%); δ_H (300 MHz; $CDCl_3$; TMS) 3.49 (4H, s, NCCH_2), 5.795 (4H, s, ArCH_2O), 7.51 (2H, t, *J* 7.5 Hz, arom. H), 7.73 (2H, d, *J* 6.9 Hz, arom. H), 7.96 (2H, *J* 8.1 Hz, arom. H).

1,4-Bis(cyanoacetoxymethyl)benzene 17. A mixture of **12** (1.002 g, 7.252 mmol) and EDC·HCl (4.125 g, 21.518 mmol) was stirred in dichloromethane (50 ml) in the presence of triethylamine (3.0 ml, 21.568 mmol) under nitrogen. Cyanoacetic acid (1.905 g, 22.395 mmol) was added, and the resulting solution was refluxed for 12 h. The solution was cooled to room temp. and washed with 5% HCl aq. (200 ml) twice, saturated aq. $NaHCO_3$ (200 ml), water (200 ml), dried with $MgSO_4$, and filtered. The solvent was removed *in vacuo*, and the residue was dried to give **17** (1.881 g, 95.3%); δ_H (300 MHz; $CDCl_3$; TMS) 3.50 (4H, s, NCCH_2), 5.23 (4H, s, ArCH_2O), 7.40 (4H, s, arom. H).

1,3-Bis(cyanoacetoxymethyl)benzene 18. A mixture of **13** (3.002 g, 21.727 mmol), cyanoacetic acid (4.621 g, 54.325 mmol), and DCC (9.844 g, 47.710 mmol) was dissolved in dichloromethane (100 ml) and stirred under 5 °C for 5 h. The solution was filtered to remove the resulting dicyclohexylurea and washed with water (200 ml) twice. The organic layer was dried over Na_2SO_4 (anhydrous). The solvent was removed and the resulting residue was purified by column chromatography using chloroform–ethyl acetate (19:1 v/v) as eluent to give **18** (2.622 g, 45.0%); δ_H (270 MHz; $CDCl_3$; TMS) 3.52 (4H, s, NCCH_2CO), 5.24 (4H, s, CH_2O), 7.36–7.39 (4H, m, arom. H).

1,2-Bis(cyanoacetoxymethyl)benzene 19. A mixture of **14** (2.000 g, 14.475 mmol), cyanoacetic acid (3.066 g, 36.044 mmol), and DCC (6.278 g, 30.427 mmol) was stirred in dichloromethane (40 ml) at 0 °C for 7 h under nitrogen. The solution was filtered to remove insoluble materials and washed with water (200 ml) twice, dried with $MgSO_4$, and filtered. The solvent was removed *in vacuo* and the residue was passed through silica gel to give **19** (3.022 g, 76.7%); δ_H (300 MHz; $CDCl_3$; TMS) 3.52 (4H, s, NCCH_2), 5.35 (4H, s, ArCH_2O), 7.39–7.48 (4H, m, arom. H).

Syntheses of cyclic oligomers

Cyclic tetramer 1. A mixture of **8** (0.476 g, 0.8955 mmol) and **15** (0.601 g, 0.897 mmol) was stirred in THF (5 ml) in the presence of DMAP (0.245 g, 2.005 mmol) at 40 °C for 2 days. The resulting precipitate was filtered and collected. The precipitate was reprecipitated from chloroform–methanol twice following recrystallization from chloroform–THF to give **1** (0.345 g, 33.0%) as a yellow powder (Found: C, 79.16; H, 9.41; N, 4.64. Calc. for $C_{312}H_{432}N_{16}O_{16}\cdot 4H_2O$: C, 79.14; H, 9.37; N, 4.73%); δ_H(300 MHz, $CDCl_3$; TMS) 0.85–0.89 (24H, m, CH_3), 1.24 (304H, m, CH_2), 1.83–1.89 (16H, m, CH_2), 4.25–4.34 (16H, m, NCH_2), 5.56 (16H, s, CH_2O), 7.385 (8H, d, *J* 9.3 Hz, arom. H), 7.42 (8H, d, *J* 8.7 Hz, arom. H), 7.59 (8H, d, *J* 8.1 Hz, arom. H), 8.23 (8H, d, *J* 8.1 Hz, arom. H), 8.29 (8H, s, arom. H or vinyl H), 8.30 (8H, s, arom. H or vinyl H), 8.45 (8H, s, arom. H or vinyl H); ν(KBr)/cm^{-1} 2918.73, 2850.27, 2215.81, 1725.98, 1581.34, 1486.85, 1466.60, 1262.18, 1232.29, 1199.51, 1135.87, 797.42; *m*/*z* 4688 ([M + 2H + Na]$^+$).

Cyclic tetramer 2. A mixture of **8** (1.001 g, 1.882 mmol) and **16** (0.606 g, 1.880 mmol) was stirred in THF (5 ml) in the presence of DMAP (0.524 g, 4.289 mmol) at 40 °C for 14 h under nitrogen. The resulting precipitate was collected, washed with THF, and reprecipitated from chloroform–methanol to give **2** (0.905 g, 58.8%) as a yellow powder (Found: C, 78.01; H, 7.76; N, 4.94. Calc. for $C_{216}H_{252}N_{12}O_{16}\cdot 3H_2O$: C, 77.99; H, 7.82; N, 5.05%); δ_H (300 MHz; $CDCl_3$; TMS) 0.87 (12H, t, *J* 6.6 Hz, CH_3), 1.23–1.29 (152H, m, CH_2), 1.80–1.85 (8H, m, CH_2), 4.16–4.205 (8H, m, NCH_2), 5.93 (16H, s, ArCH_2O), 7.32 (8H, d, *J* 8.7 Hz, arom. H), 7.55 (8H, t, *J* 7.5 Hz, arom. H), 7.78 (8H, d, *J* 6.9 Hz, arom. H), 7.98 (8H, d, *J* 8.1 Hz, arom. H), 8.29 (8H, d, *J* 8.7 Hz, arom. H), 8.47 (8H, s, arom. H or vinyl H), 8.59 (8H, s, arom. H or vinyl H); ν(KBr)/cm^{-1} 2923.56, 2852.20, 2219.67, 1718.26, 1579.41, 1480.10, 1229.40, 1203.36, 1161.90, 1087.66, 808.99; *m*/*z* 3272 (M$^+$).

Cyclic dimer 3. A mixture of **8** (0.800 g, 1.504 mmol) and **17** (0.411 g, 1.510 mmol) was stirred in THF (8 ml) in the presence of DMAP (0.402 g, 3.290 mol) at 40 °C for 12 h under nitrogen. The resulting precipitate was collected, washed with THF following recrystallization from chloroform–methanol to give **3** (1.031 g, 89.2%) as a yellow powder (Found: C, 75.54; H, 7.86; N, 5.32. Calc. for $C_{100}H_{122}N_6O_8\cdot 3H_2O$: C, 75.53, H, 8.11; N, 5.285%); δ_H (270 MHz; $CDCl_3$; TMS) 0.87 (6H, t, *J* 6.6 Hz, CH_3), 1.24–1.33 (76H, m, CH_2), 1.85–1.87 (m, 4H, CH_2), 4.31 (4H, t, *J* 7.3 Hz, NCH_2), 5.395 (8H, s, ArCH_2O), 7.46 (4H, d, *J* 8.6 Hz, arom. H), 7.53 (8H, d, *J* 6.2 Hz, arom. H), 8.21 (4H, d, *J* 7.9 Hz, arom. H), 8.37 (4H, s, arom. H or vinyl H), 8.68 (4H, s, arom. H or vinyl H); ν(KBr)/cm^{-1} 2923.56, 2851.24, 2220.63, 1720.19, 1580.38, 1488.78, 1466.60, 1391.39, 1371.14, 1294.00, 1258.32, 1232.29, 1201.43, 1163.83, 1139.72, 1073.19, 816.71; *m*/*z* 1536 (M$^+$).

Cyclic dimer 4. A mixture of **8** (0.800 g, 1.504 mmol), **18** (0.410 g, 1.504 mmol) and DMAP (0.404 g, 3.309 mmol) was stirred in THF (8 ml) at 40 °C for 5 h. The resulting precipitate was collected and reprecipitated from chloroform–methanol to give **4** (0.655 g, 56.7%) as a yellow powder (Found: C, 78.11; H, 8.10; N, 5.41. Calc. for $C_{100}H_{122}N_6O_8$: C, 78.19; H, 8.01; N, 5.47%); δ_H (270 MHz; $CDCl_3$; TMS) 0.87 (6H, t, *J* 6.6 Hz, C*H*$_3$), 1.24 (76H, br, C*H*$_2$), 1.84 (4H, br, C*H*$_2$), 4.27 (4H, m, NC*H*$_2$), 5.42 (8H, s, C*H*$_2$O), 7.39 (4H, d, *J* 8.9 Hz, arom. H), 7.47–7.57 (8H, m, arom. H), 8.23 (4H, d, *J* 7.9 Hz, arom. H), 8.35 (4H, s, vinyl H), 8.50 (4H, s, arom. H); ν(KBr)/cm^{-1} 2922.59, 2852.20, 2219.67, 1719.23, 1586.16, 1484.92, 1390.42, 1236.15, 1199.51, 1164.79, 1088.62, 800.31; *m*/*z* 1536 (M^+).

Cyclic dimer 5. A mixture of **8** (0.800 g, 1.504 mmol) and **19** (0.410 g, 3.372 mmol) was stirred in THF (5 ml) in the presence of DMAP (0.412 g, 3.372 mmol) at 40 °C for 2 days under nitrogen. In this reaction, the precipitate was not produced. The solution was poured into methanol (300 ml) and the resulting precipitate was collected and reprecipitated from chloroform–methanol. The precipitate was dissolved in a small amount of THF and the resulting solution was left in air to give a small amount of precipitate. It was collected and dried to give **5** (0.069 g, 6.0%) as a yellow powder (Found: C, 74.96; H, 7.72; N, 5.17. Calc. for $C_{100}H_{122}N_6O_8{\cdot}4H_2O$: C, 74.69; H, 8.15; N, 5.225%); δ_H (300 MHz; $CDCl_3$; TMS) 0.87 (6H, t, *J* 6.6 Hz, C*H*$_3$), 1.21–1.24 (76H, m, C*H*$_2$), 1.67 (4H, br, C*H*$_2$), 3.96 (4H, t, *J* 7.5 Hz, NC*H*$_2$), 5.46 (8H, s, ArC*H*$_2$O), 6.98 (4H, d, *J* 9.0 Hz, arom. H), 7.49–7.58 (8H, m, arom. H), 7.98 (4H, d, *J* 8.7 Hz, arom. H), 8.14 (4H, s, arom. H or vinyl H), 8.15 (4H, s, arom. H or vinyl H); ν(KBr)/cm^{-1} 2923.56, 2852.20, 2219.67, 1717.30, 1577.49, 1487.81, 1263.15, 1235.18, 1196.61, 1144.55, 1096.33, 930.49, 760.78; *m*/*z* 1536 (M^+).

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