Supplementary Information for *Chem. Commun.*

Globally Folded Structure Based on Localized Rigidification: Helical Oligo(*m*-phenylene ethynylenes)

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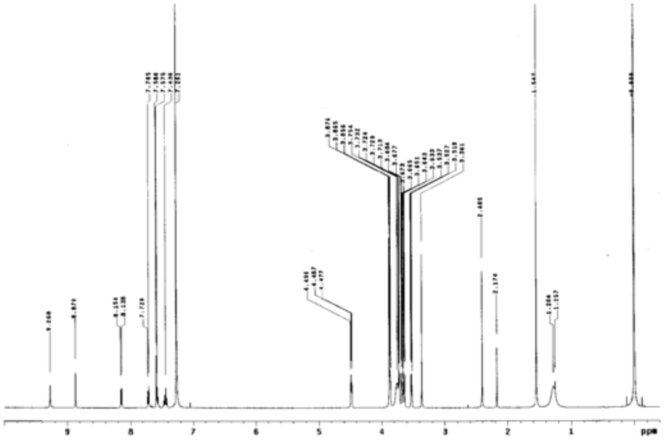
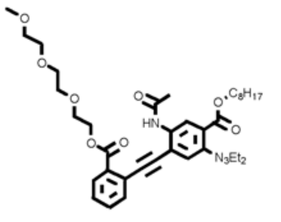
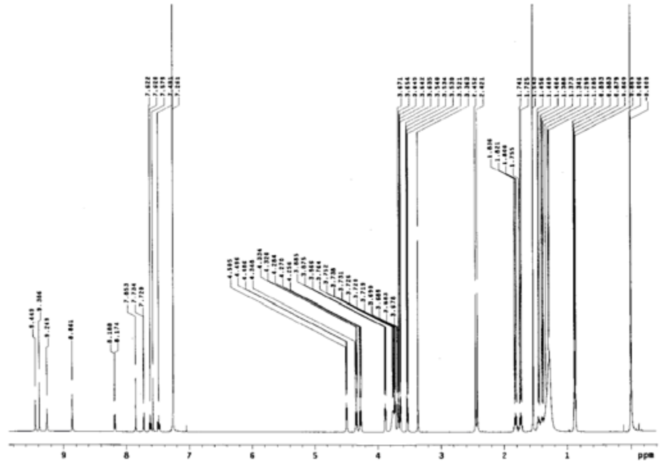
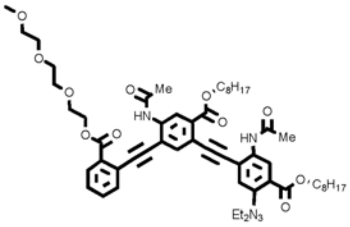
I. 1D ^{1}H NMR Spectra





2d





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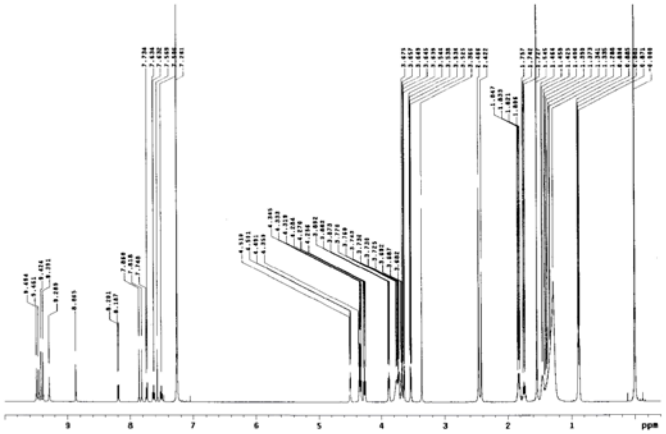
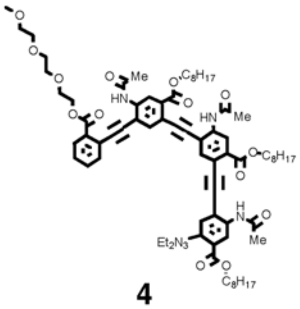
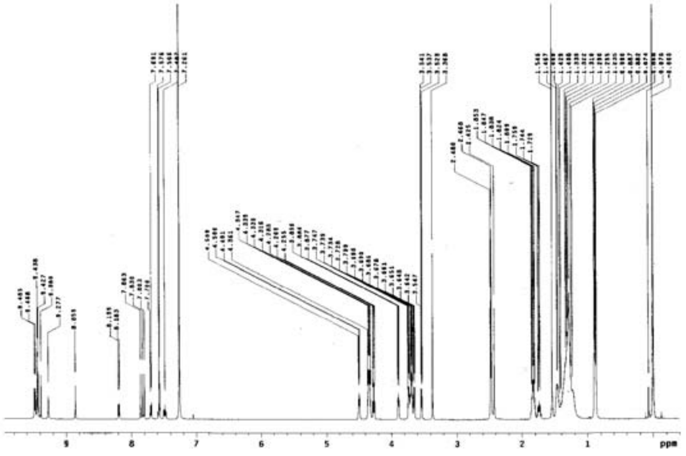
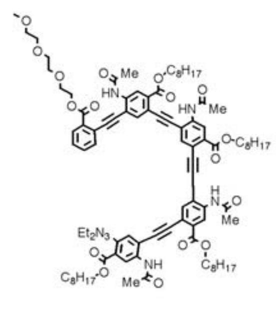


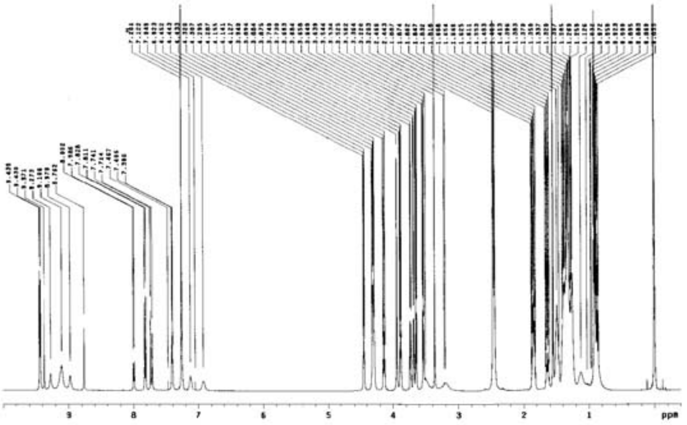


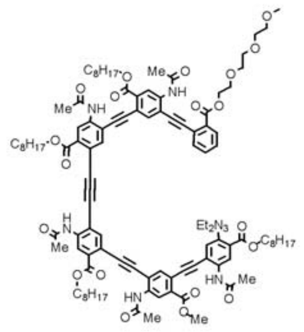
4


9
8
7
6
5
4
3
2
1
ppm


HN
Me
C8H17
HN
Me
O
C8H17
H
N
Me
Et2N3
C8H17
NH
Me
C8H17

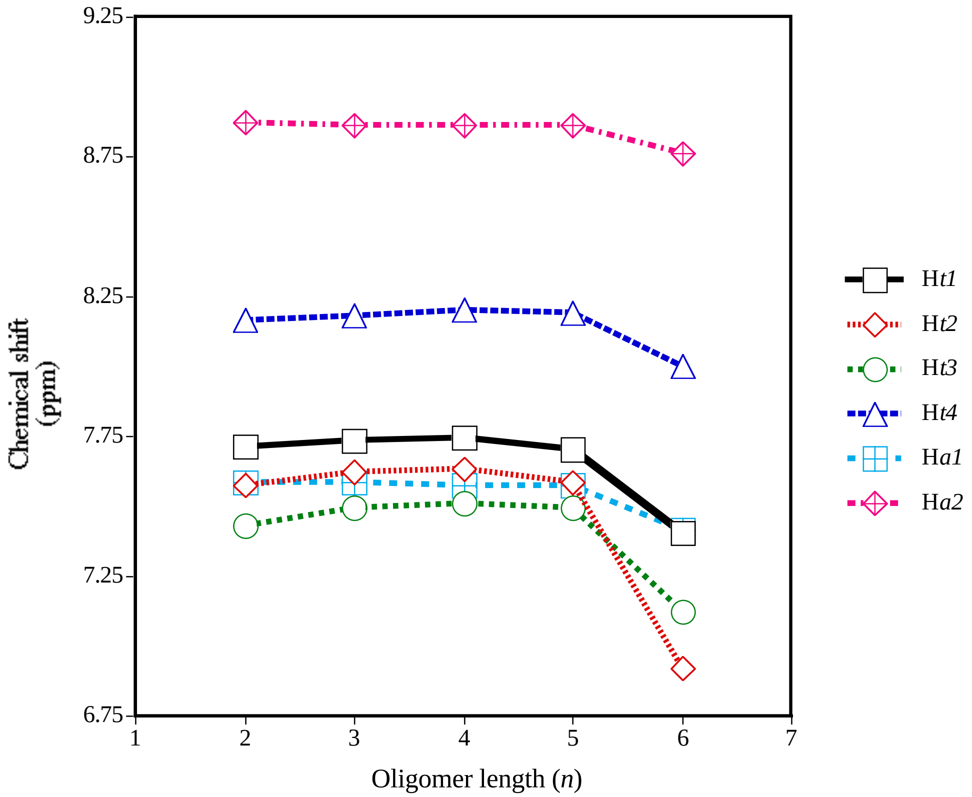
5


9
8
7
6
5
4
3
2
1
ppm

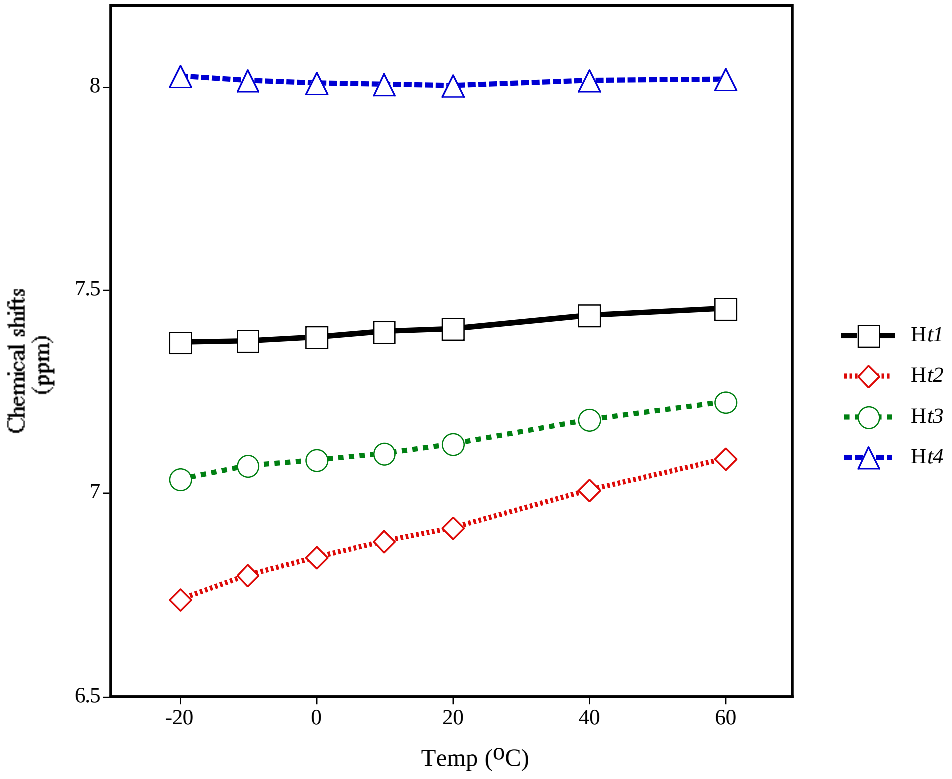

C8H17
Me
NH
Me
NH
C8H17
H
N
Me
Et2N3
C8H17
HN
Me
C8H17
HN
Me
Me

6

II. Chemical shifts of protons *t1-t4* and *a1-a2* vs the chain length of oligomers 2d-6. (b)

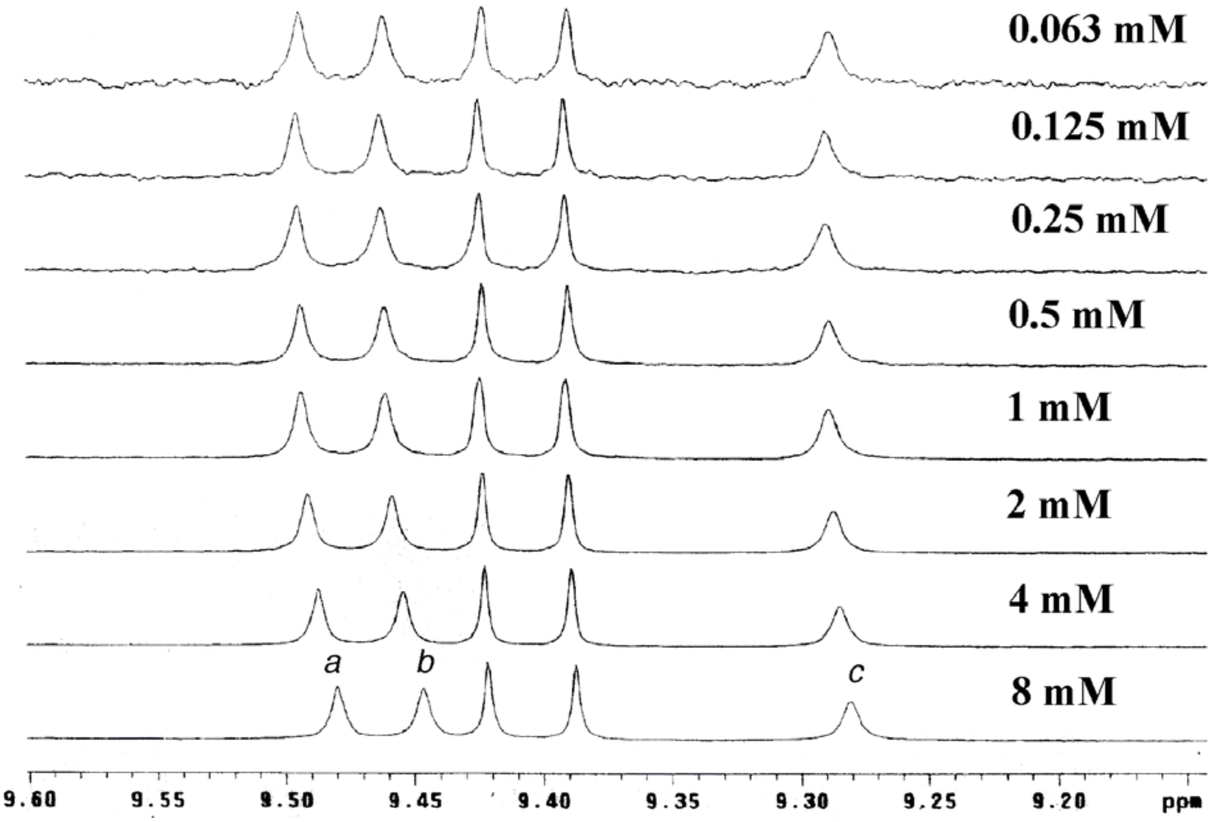


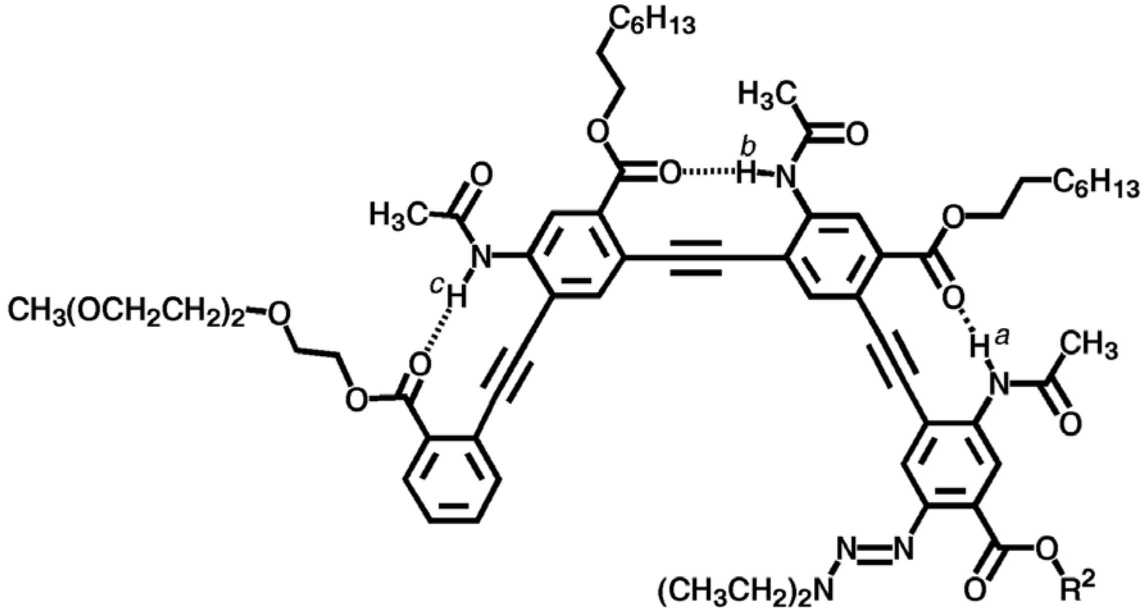
III.The chemical shifts of protons *t1-t4* of hexamer 6 vs temperature.



IV. Concentration-dependent changes of amide ^{1}H chemical shifts of tetramer 4

(500 MHz, $CDCl_3$, 295 K)





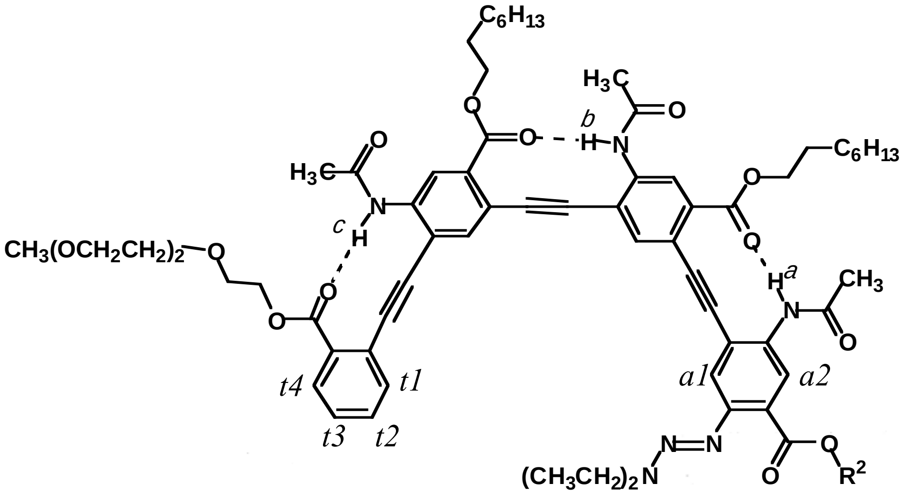
V. Chemical shifts (ppm) of the aromatic and ethyl protons on the end residues of oligomers 2d-6

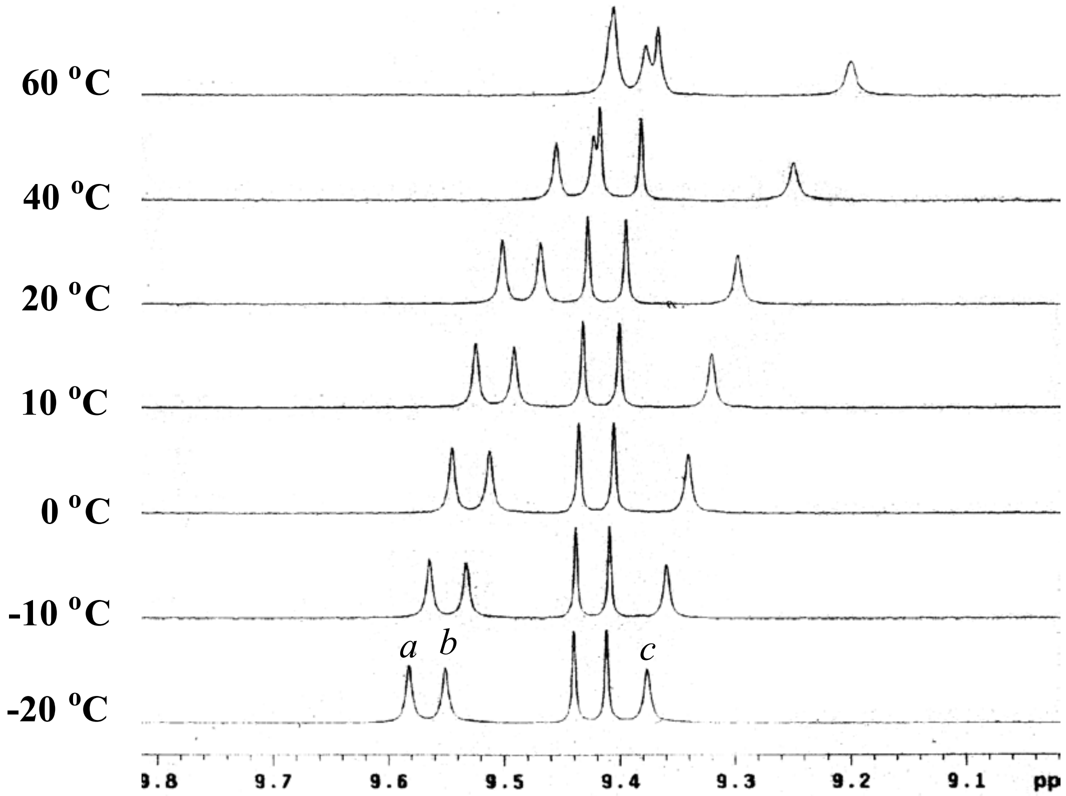
Compd	Aromatic protons						Ethyl protons	
	H*t1*	H*t2*	H*t3*	H*t4*	H*a1*	H*a2*	H(CH_3)	H(CH_2)
2d	7.71	7.57	7.43	8.16	7.58	8.87	1.25/1.35	3.73/3.81
3	7.73	7.62	7.49	8.18	7.58	8.86	1.2-1.38	3.75/3.76
4	7.74	7.63	7.51	8.20	7.57	8.86	1.2-1.39	3.71/3.76
5	7.70	7.58	7.49	8.19	7.57	8.86	1.12/1.22	3.57/3.67
6	7.40	6.92	7.12	8.00	7.41	8.76	0.79/1.10	3.05/3.54

VI. Temperature-dependent changes of amide and aromatic ^{1}H chemical shifts

(500 MHz, 2 mM in $CDCl_3$)

1. Tetramer 4

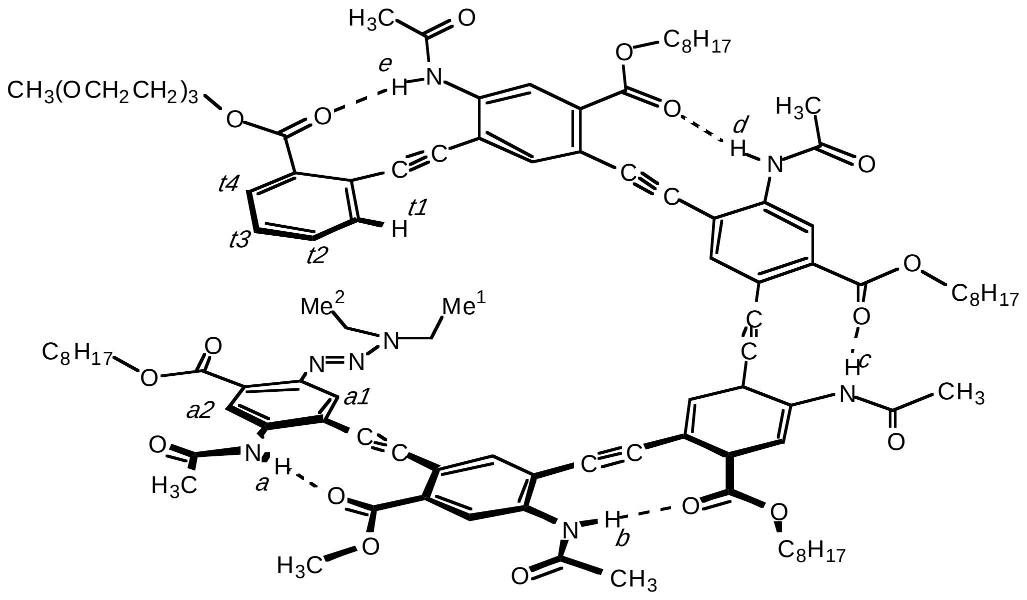


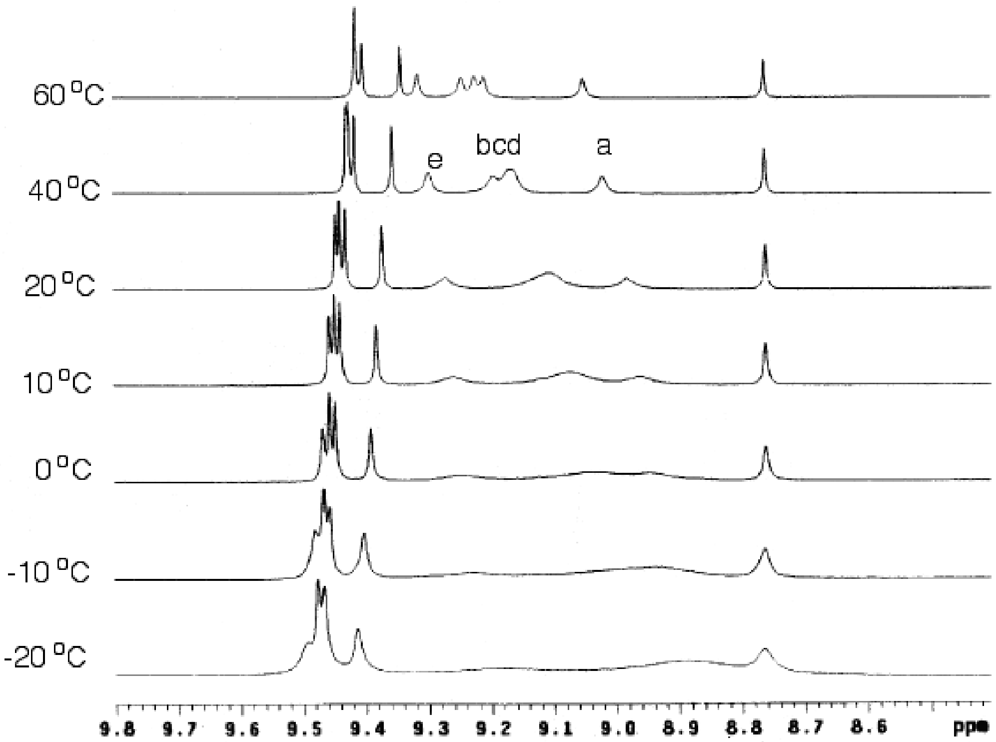


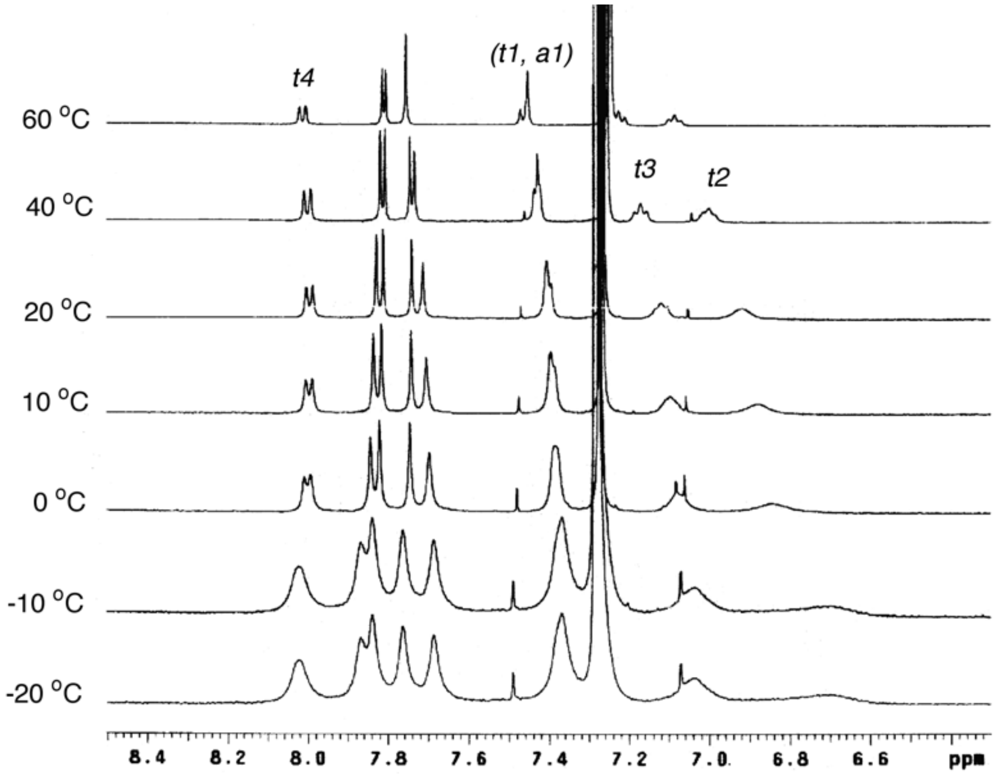
Temperature-dependent ^{1}H chemical shift values of tetramer **4**.

Temp. (°C)	H*t1*	H*t2*	H*t3*	H*t4*	H*a*	H*b*	H*c*
60	7.737	7.482	7.606	8.176	9.402	9.372	9.194
40	7.743	7.494	7.620	8.190	9.453	9.421	9.247
20	7.748	7.507	7.634	8.204	9.500	9.467	9.295
10	7.751	7.513	7.642	8.211	9.522	9.490	9.319
0	7.754	7.519	7.649	8.218	9.544	9.512	9.339
-10	7.752	7.521	7.652	8.222	9.560	9.527	9.355
-20	7.759	7.531	7.662	8.233	9.582	9.551	9.377

2. Hexamer 6




60 °C
40 °C
20 °C
10 °C
0 °C
-10 °C
-20 °C
e
bcd
a
9.8
9.7
9.6
9.5
9.4
9.3
9.2
9.1
9.0
8.9
8.8
8.7
8.6
ppm


t4
(t1, a1)
t3
t2
60 °C
40 °C
20 °C
10 °C
0 °C
-10 °C
-20 °C
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
ppm

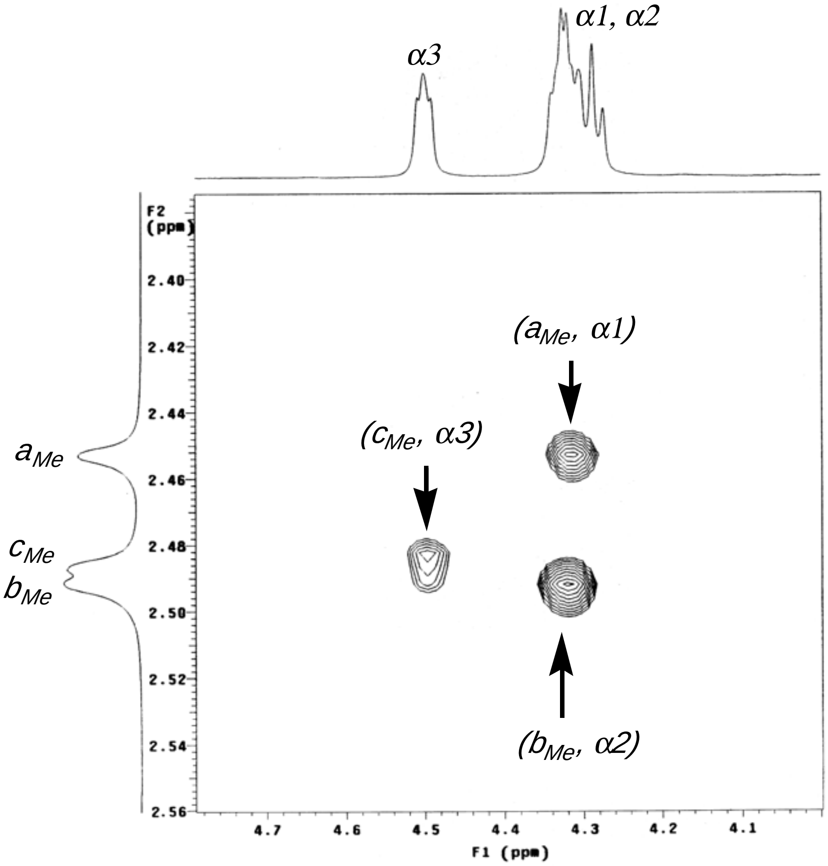
Temperature-dependent ^{1}H chemical shift values of hexamer **6**.

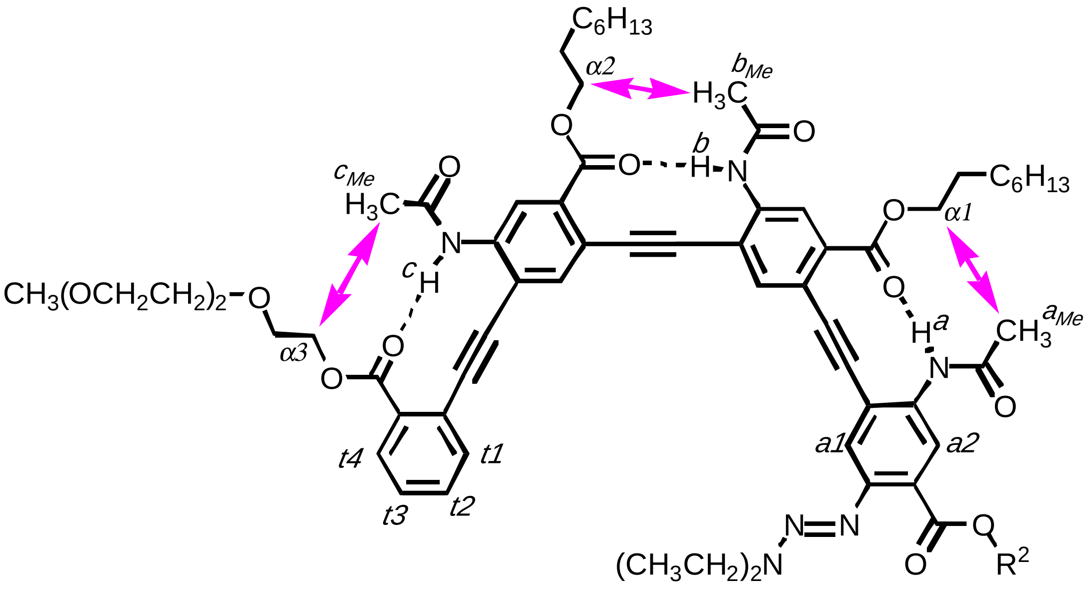
Temp. (°C)	H*t1*	H*t2*	H*t3*	H*t4*	H*a*	H*b*/H*c*/H*d*	H*e*
60	7.452	7.085	7.225	8.019	9.051	9.21/9.225/9.245	9.315
40	7.436	7.008	7.179	8.016	9.027	9.173/9.203	9.306
20	7.405	6.916	7.120	8.003	8.980	9.106	9.274
10	7.396	6.881	7.096	8.004	9.260	9.071	8.964
0	7.385	6.842	7.082	8.008	9.249	9.038	8.950
-10	7.375	6.798	7.066	8.015	9.228	-	-
-20	7.369	6.739	7.035	8.024	9.181	-	-

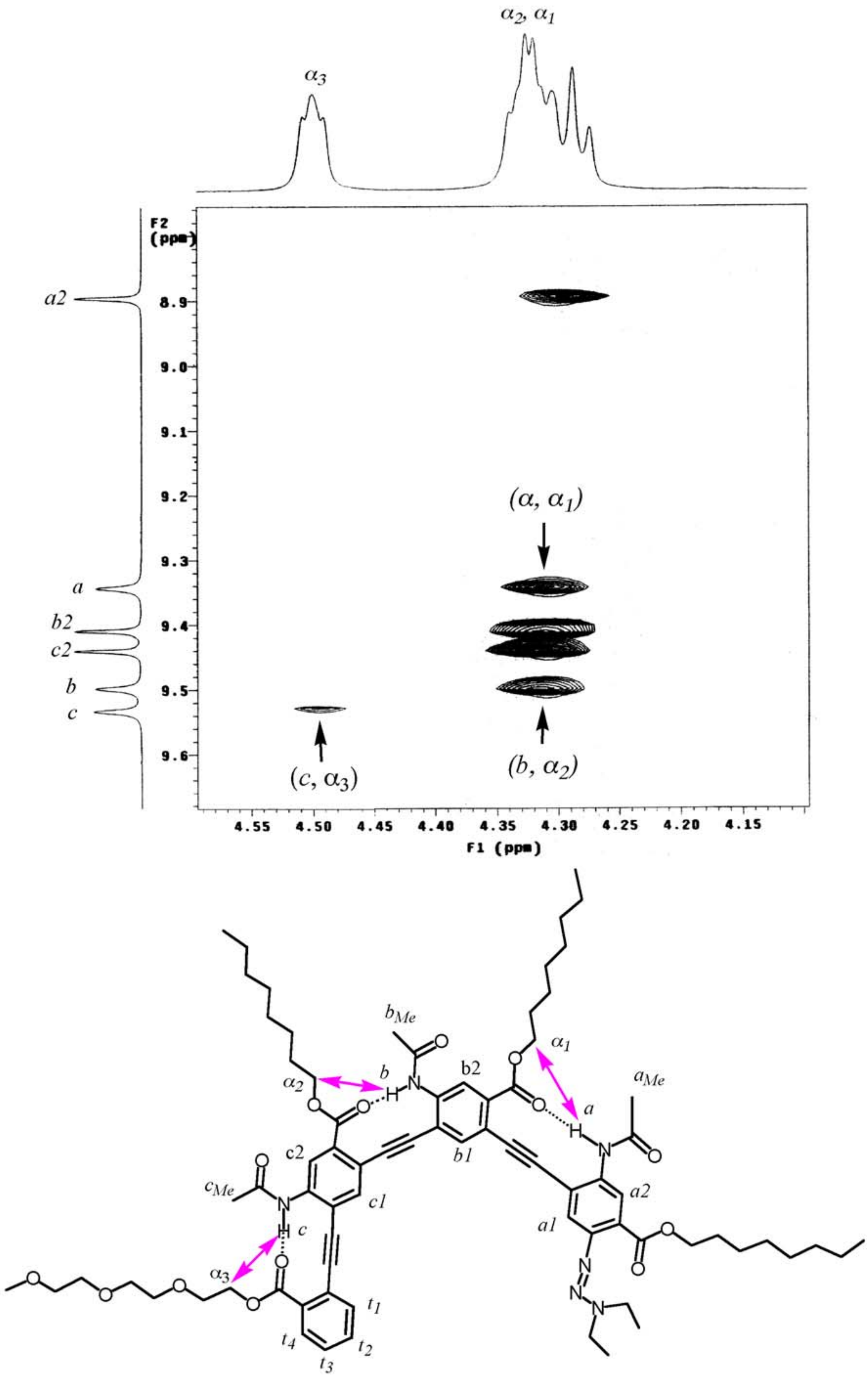
VII. 2D NMR Spectra

1. Partial NOESY Spectrum of Tetramer 4

NOEs between the amide protons and ester side chains α-CH_2 protons
(500 MHz, $CDCl_3$, 263K, con. = 8 mM, mixing time = 0.3 s)



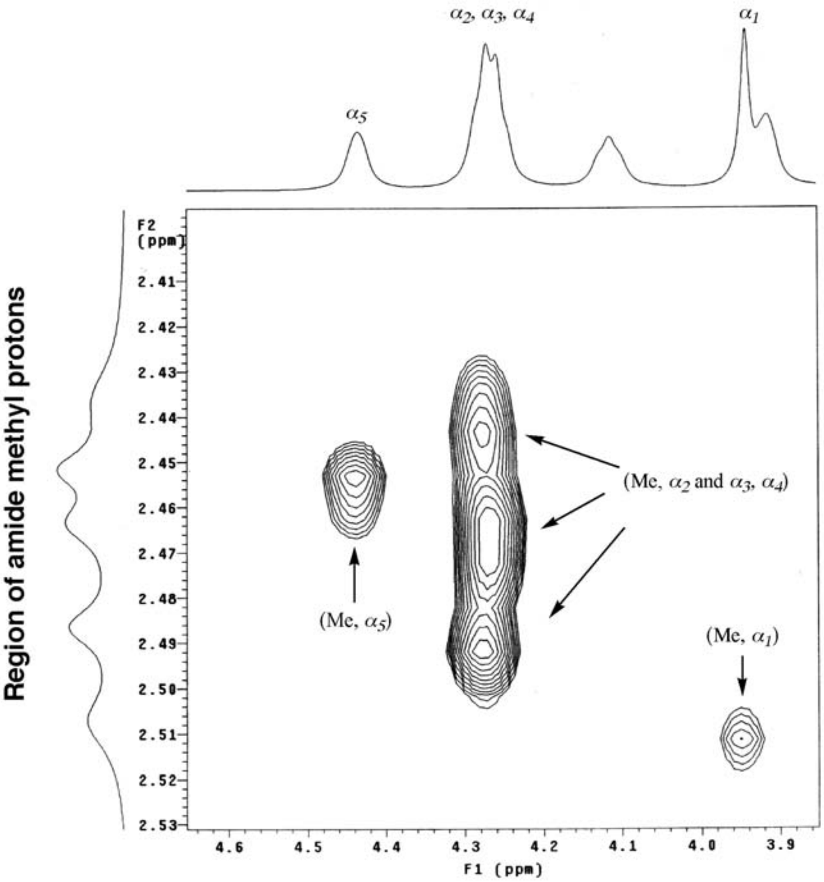


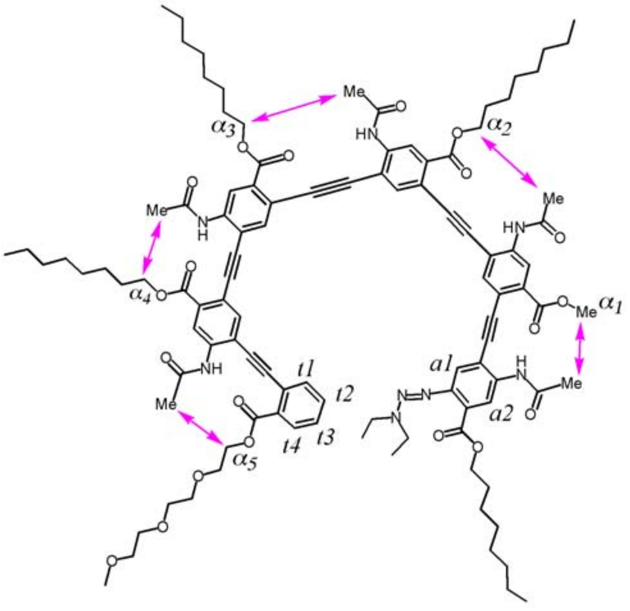

α_2, α_1
α_3
F2 (ppm)
a2
a
b2
c2
b
c
8.9
9.0
9.1
9.2
9.3
9.4
9.5
9.6
(α, α_1)
(b, α_2)
(c, α_3)
4.55
4.50
4.45
4.40
4.35
4.30
4.25
4.20
4.15
F1 (ppm)
b_{Me}
α_1
b
b2
α_2
a_{Me}
a
c2
b1
c_{Me}
c1
a2
a1
c
α_3
t_1
t_4
t_2
t_3

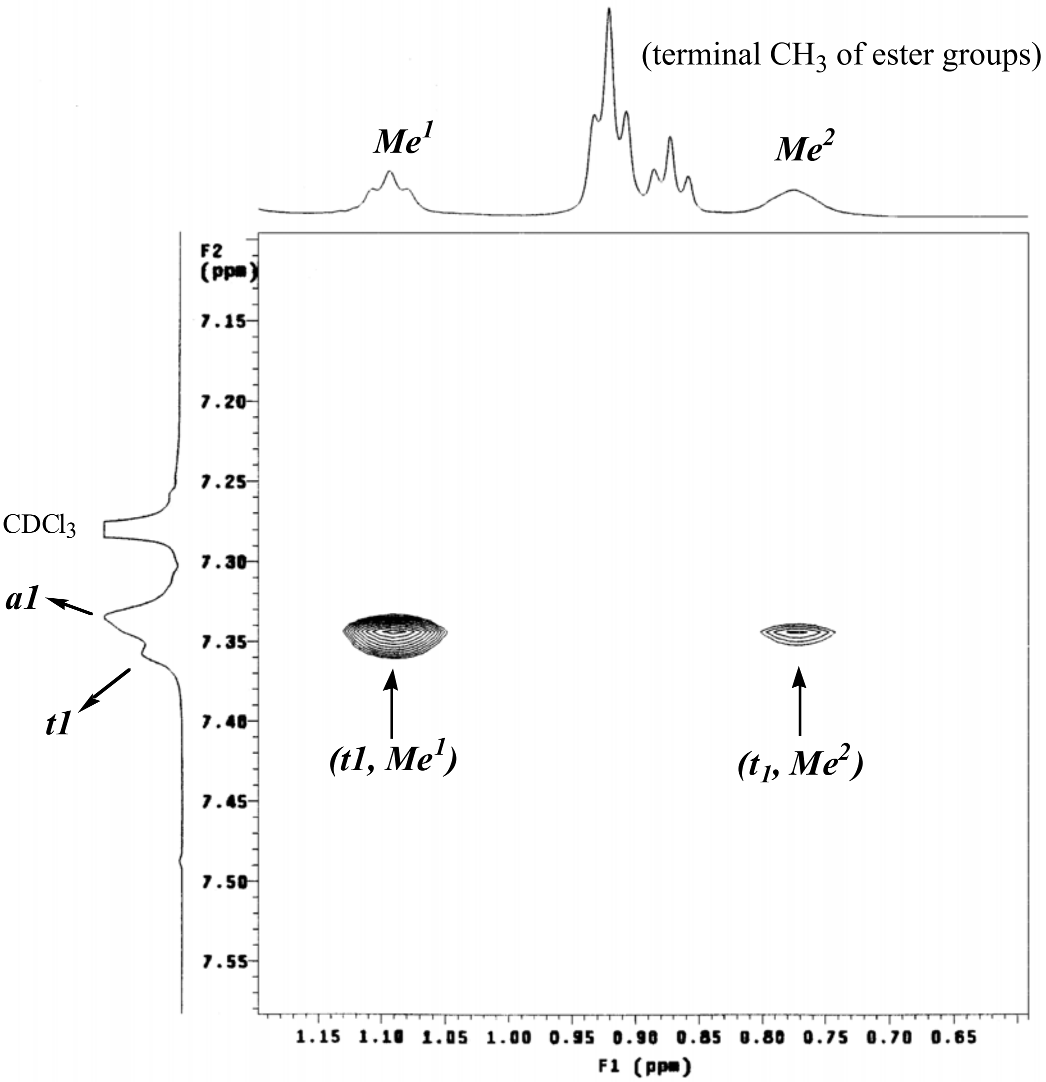
2. Partial NOESY spectrum of hexmer 6

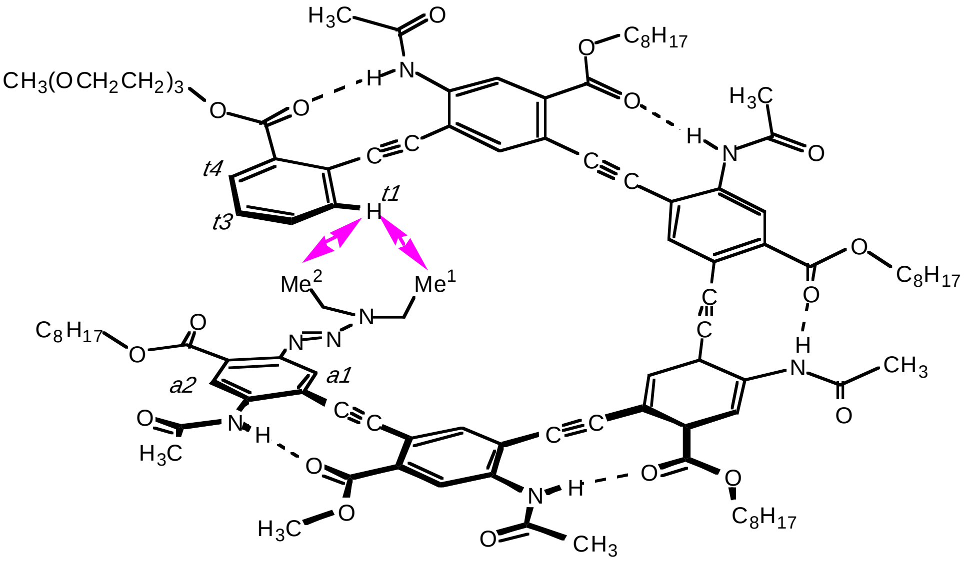
Contacts between the methyl group and side chains methene protons

(500 MHz, $CDCl_3$, 263K, con.= 8 mM, mixing time = 0.3 s)



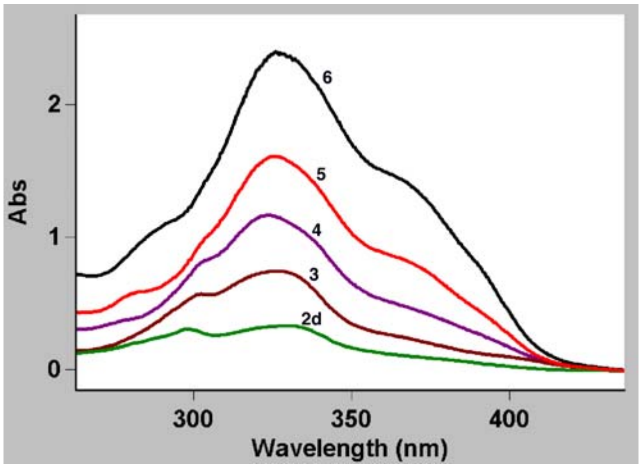



(terminal CH3 of ester groups)
Me1
Me2
CDCl3
a1
t1
F2 (ppm)
7.15
7.20
7.25
7.30
7.35
7.40
7.45
7.50
7.55
(t1, Me1)
(t1, Me2)
1.15
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
F1 (ppm)

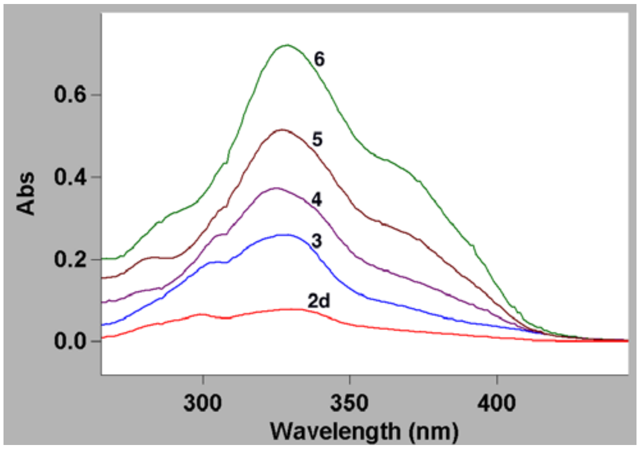

H3C
O
N
H
CH3(OCH2CH2)3
O
O
C≡C
O
C8H17
O
H3C
H
N
O
t4
t3
t1
H
Me2
Me1
N
N=N
C8H17
O
O
a1
a2
O
C8H17
C
C
O
H
N
CH3
O
N
H
O
H3C
O
H3C
O
N
H
O
O
C8H17
O
CH3

VIII. UV Spectra of Oligomers 2d-6 at Room Temperature

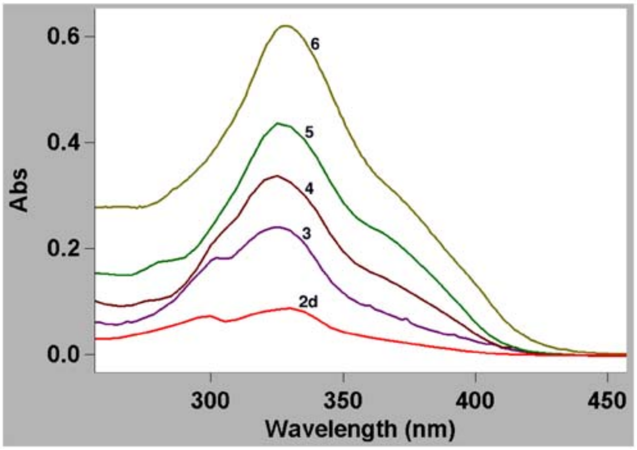
(a) 10 μM in chloroform



(b) 2 μM in chloroform



(c) 2 μM in chloroform/methanol (v/v 1/1)



IX. Fluorescence Experiments and Emission Spectra of Oligomers 2d-6 at Room Temperature

1. Experimental

The solvent for all spectroscopic experiments was acetonitrile.

All absorbance spectra were recorded on a Milton-Roy model 1201 UV-Vis spectrophotometer.

All fluorescence experiments (low micromolar n-mer) were performed with an SLM-AMINCO 48000 multiharmonic Fourier (MHF) spectrofluorometer (Spectronic Instruments). The excitation and emission spectral bandpasses were kept at 4 nm and 2 nm, respectively. All spectra were background corrected. The background contribution was generally small except for the dimer species where the emission was at least an order-of-magnitude weaker in comparison to the other n-mers.

Table 1 list the positions of the longest wavelength absorbance transition and the emission of each n-mer.

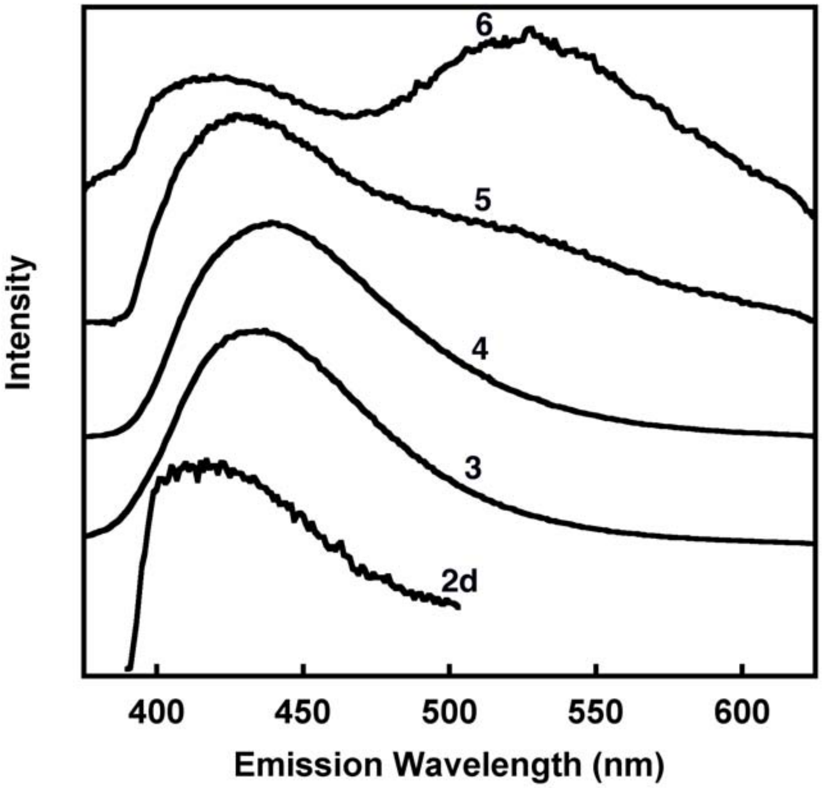
Table 1. Longest wavelength absorbance and emission maxima

Species	Absorbance Maximum (nm)	Emission Maxima (nm)
Dimer	320	420 (w)
Trimer	318	435
Tetramer	324	440
Pentamer	330	430,525
Hexamer	332	420,530

Typical emission spectra for the n-mers is shown in Figure 1 (excitation = 350 nm). The overall spectroscopy shows that the red-edge absorbance maxima shift slightly to the red as the n-mer increases from dimer to hexamer. The molar absorptivity for these transitions do not change significantly, remaining at 3-4,000 $cm^{-1}M^{-1}$. The highest energy emission feature remains between 420 and 440 nm in each n-mer and the emission from the dimer is significantly weaker in comparison to the other n-mers. However, a new emission feature appears for the pentamer and more so for the hexamer to the red side of the emission spectrum. The emission wavelength-dependent excitation scans of the pentamer and hexamer[1] (not shown) are consistent with the red-edge emission arising from ground pre-association of the chromophores.

[1] Zagrobelny, J.; Betts, T.A.; Bright, F.V. *J. Am. Chem. Soc.* **1992,** *114*, 5249-5257.

2. Emission spectra of 2d-6



X. Computational Details

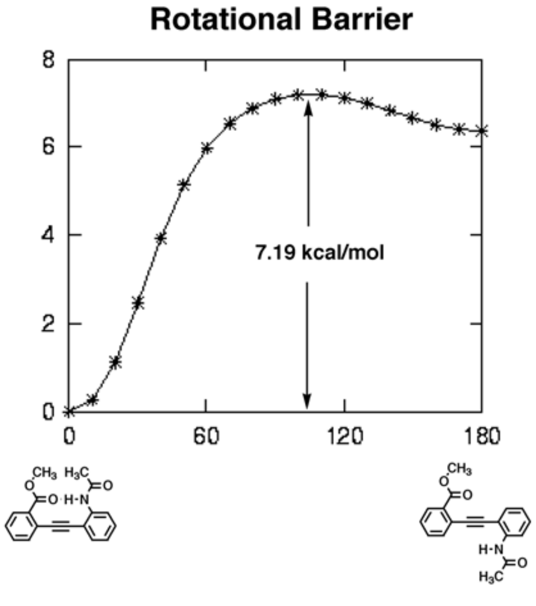
The computations were carried out using the Gaussian 98 revision A.9. The geometry of each conformation was optimized at the B3LYP/6-31G(d,p) level. The two optimized structures were used to compute the single point energy at the MP2/6-31G(d) level. One of the C-Ph bonds of the optimized conformer 1a structure was rotated 180 degrees to get the structure of conformer **2b**. The same was done for conformer **2b** to get a structure of **2a**.

Results and Discussions

Geometry and Energy. Conformer **2a**, which has a hydrogen bond, is the stable conformation. Conformer **2b**, the one with no hydrogen bonding, is 5.78 kcal/mol higher in energy. When we rotate the C-Ph bond of conformer 1a to create conformer **2b**, we see an energy barrier of 7.19 kcal/mol higher than the energy of conformer **2a**. This barrier occurs when the bond is rotated 100 to 110 degrees towards conformer **2b**. When rotating the C-Ph bond from conformer **2b** to **2a**, we see an energy barrier of about 1.21 kcal/mol. Again, this happens at around 100 degrees towards conformer **2b**.

We note that by simply rotating the C-Ph bond 180 degrees from conformer **2a**, does not create the optimized structure of conformer **2b**. This is due to the fact that the hydrogen bonding causes conformer **2a** to be a completely planar conformation whereas conformer **2b** which has the intramolecular H-bond interrupted is not completely planar. To get a better understanding of the energy barriers, the energies were studied by rotating one of the C-Ph bonds of the optimized conformer **2a** model to make conformer **2b**, and then from the optimized structure of conformer **2b** to make conformer **2a**.

As noted above, the energy barrier occurs when the C-Ph bond is rotated 100 to 110 degrees towards conformer **2b** from the optimized structure of conformer **2a**. The major factor in this barrier is due to the fact that the hydrogen bonding is a strong one with an O--H bond distance of 1.92 Å, and an N-H—O angle of 176.65 degrees.

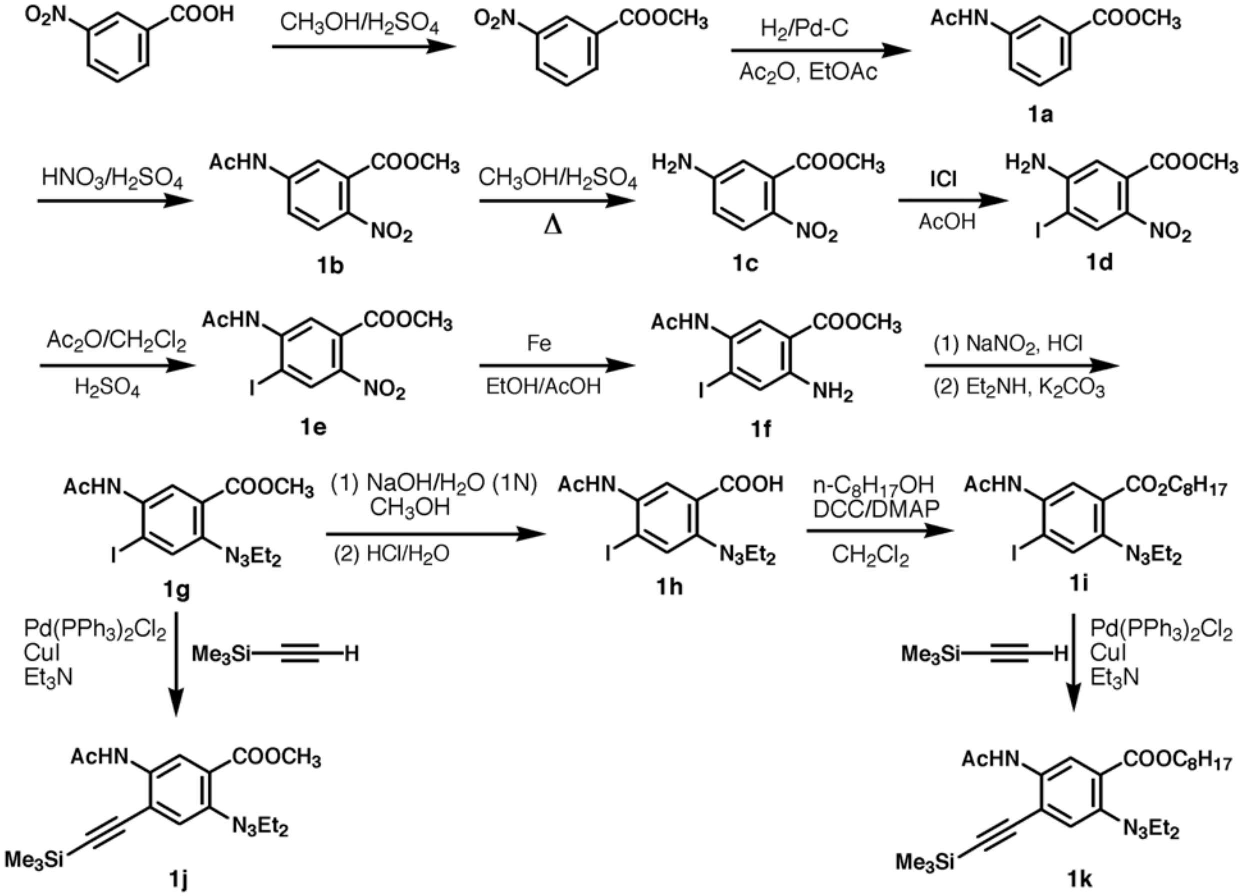


XI. Synthetic Procedures

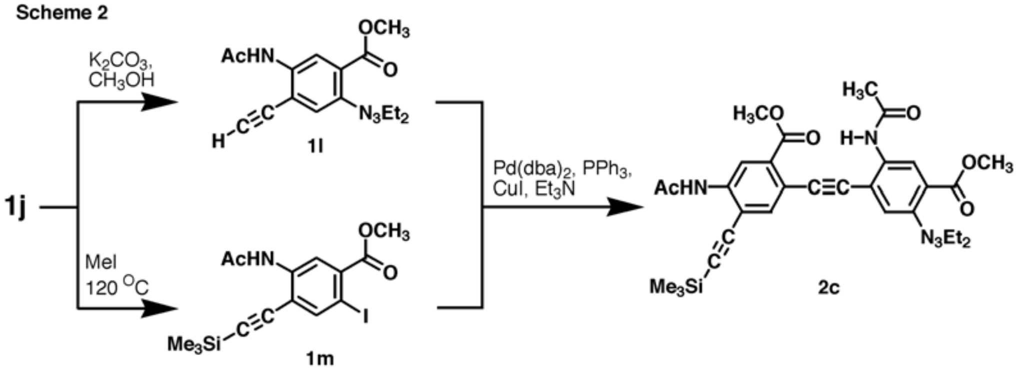
General

All chemicals were purchased from Aldrich or Acros and were used as received unless otherwise noted. Triethylamine was dried from sodium and degassed before use. The coupling reactions were carried out under dry argon. All reactions were followed by thin-layer chromatography (precoated 0.25 mm silica gel plates from Aldrich), and silica gel column chromatography was carried out with silica gel 60 (mesh 230-400). The ^{1}HNMR spectra and ^{13}C NMR were recorded on a spectrometer of 500 MHz. NMR chemical shifts are reported in ppm relative to internal standard TMS, and coupling constant, *J*, is reported in Hertz (Hz). The following splitting patterns are designed as s, singlet; d, double; t, triplet; q, quartet; b, broad; m, multiplet.

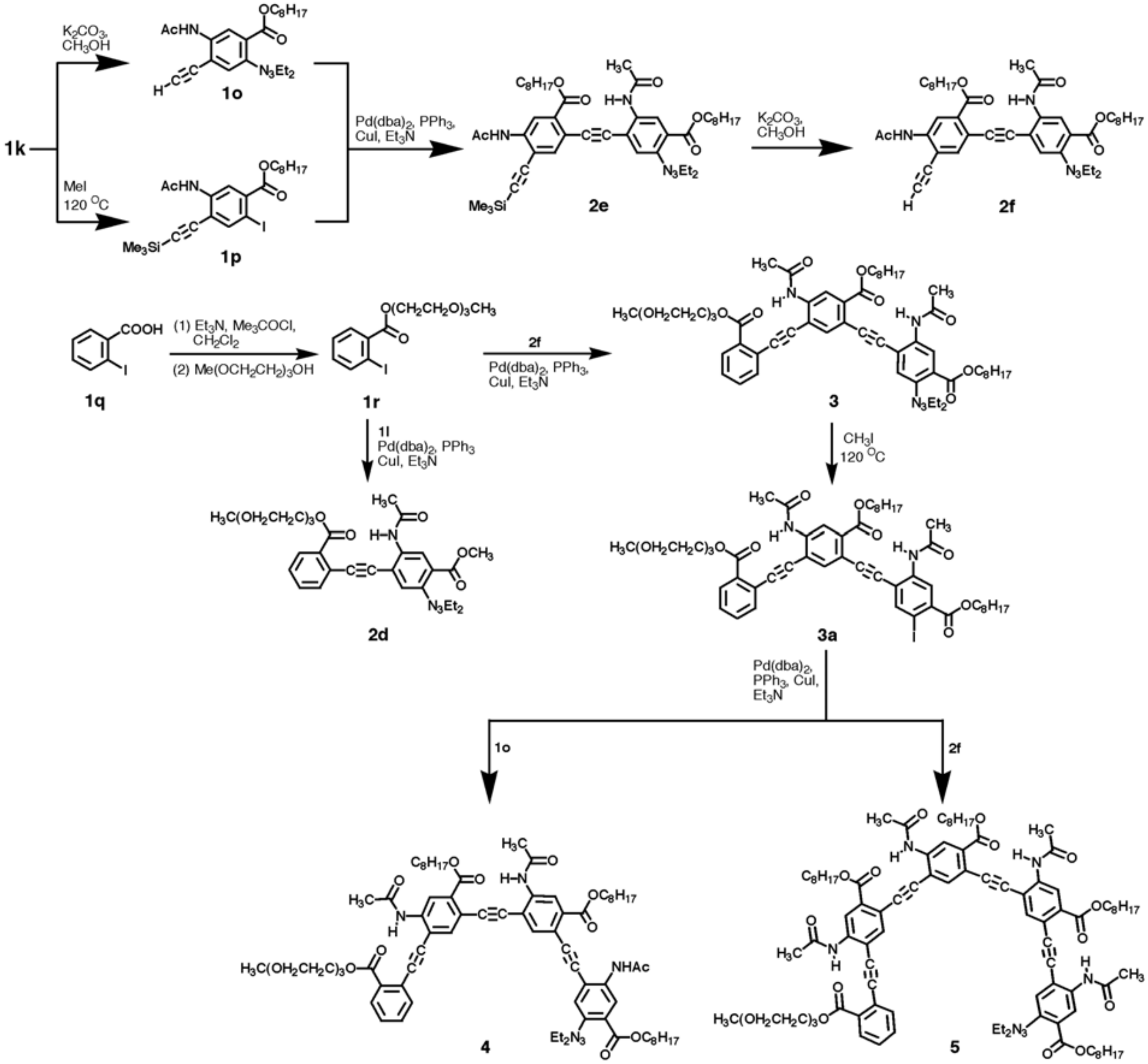
Scheme 1

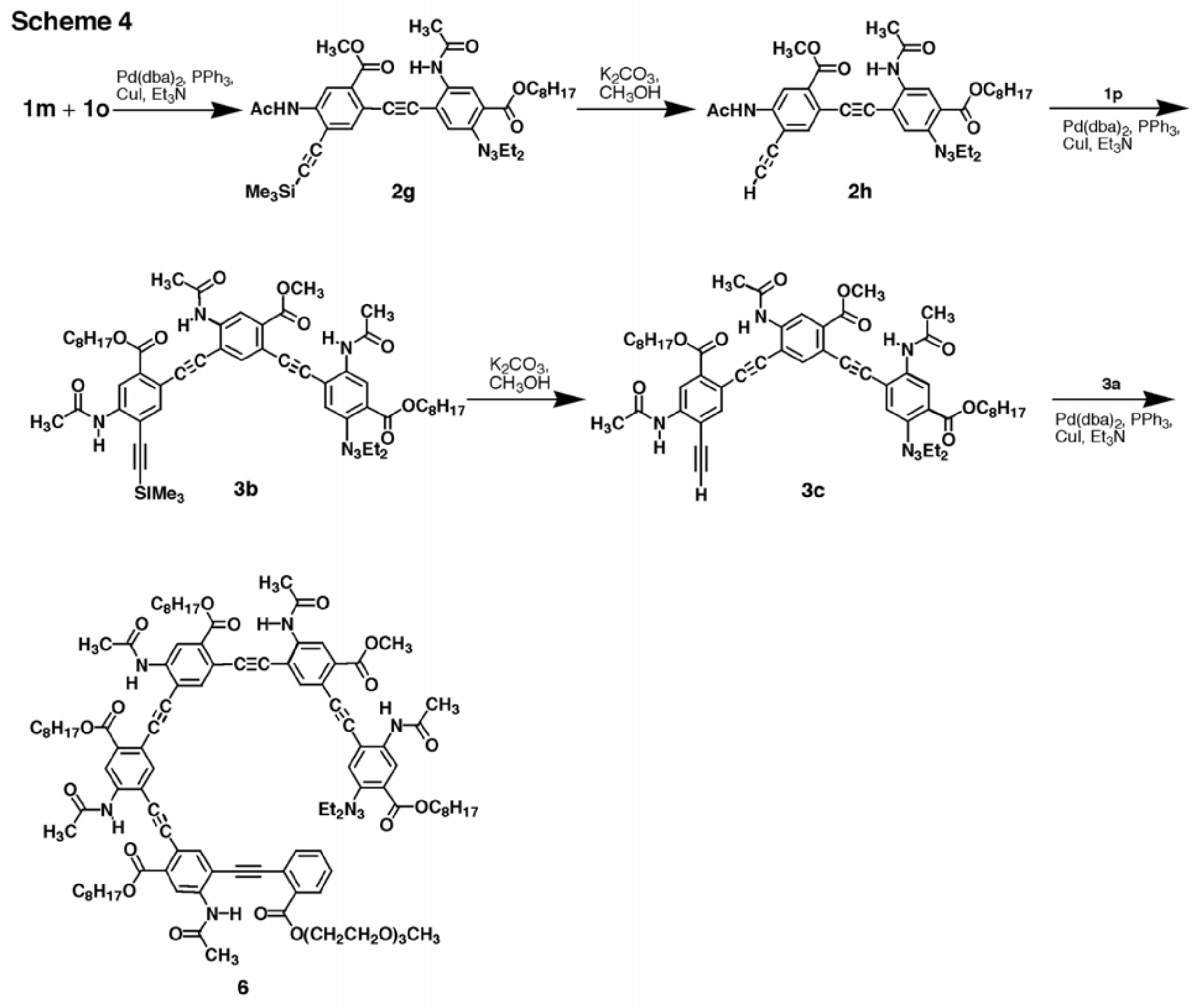


Scheme 2



Scheme 3





Scheme 4

Methyl 5-acetylaminobenzoate (1a). Compound **1a** was synthesized starting from commercially available 3-nitrobenzoic acid which was initially esterified (98.9 %) followed by reduction of the nitro group and protection of the corresponding amino group using acetic anhydride (94.3%) to afford a white solid. TLC, $R_f = 0.40$ (petroleum ether/EtOAc, 1/2), ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.20 (s, 3H, Ac), 3.90 (s, 3H, MeO), 7.39 (t, 1H, Ar-H), 7.65 (s, 1H, NH), 7.78 (d, 1H, Ar-H, *J* = 7.5 Hz), 7.92 (d, 1H, Ar-H, *J* = 7.5 Hz), 8.02 (s, 1H, Ar-H).

Methyl 5-acetamido-2-nitrobenzoate (1b). Compound **1a** (35 g, 181 mmol) was added to concentrated H_2SO_4 (120 mL) cooled in an ice-water bath. To this solution, a cooled mixture of 70 % HNO_3 (12.3 mL) and con. H_2SO_4 (58 mL) was added dropwise over a period of 0.5 h at 0 °C. After being stirred for 20 min., the reaction mixture was poured into cracked ice (1 kg) and the mixture was extracted with dichloromethane (150 mL × 3). The combined extracts were then washed with aqueous $NaHCO_3$ and water respectively, dried over anhydrous Na_2SO_4, filtered and concentrated to provide a brown residue. The resulting solid was recrystallized from dichloromethane to afford 24 g (55.7 %) of **1b** as a pale yellow needle. TLC, $R_f = 0.36$ (petroleum ether/EtOAc, 1/3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.24 (*s*, 3H, Ac), 3.93 (*s*, 3H, MeO), 7.61 (d, 1H, Ar-H), 7.86 (dd, 1H, Ar-H), 7.94 (b, 1H, NH), 7.98 (d, 1H, Ar-H, *J* = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.11, 54.03, 119.49, 121.18, 126.35, 130.37, 142.46, 143.55, 167.28, 167.78

Methyl 5-amino-2-nitrobenzoate (1c). To a solution of **1b** (2.17 g, 9.12 mmol) in MeOH (50 mL) was added con. H_2SO_4 (0.9 mL) with stirring. The solution was refluxed for 0.5 h and the solvent was removed *in vacuo* to provide a pale yellow oil. The oil was dissolved in dichloromethane (30 mL) and washed with $NaHCO_3$, water and brine. After washing, the organic layer was dried over Na_2SO_4 and filtered. The filtrate was then concentrated *in vacuo* to yield a light yellow solid, which was recrystallized from EtOAc to afford 1.65 g (92.3 %) of **1c** as a colorless solid. TLC, R_f= 0.24 (petroleum ether/EtOAc, 3/2). ^1H NMR (500 MHz, $CDCl_3$): δ 3.92 (s, 3H, MeO), 4.56 (s, 2H, NH_2), 6.61 (m, 2H, Ar-H), 7.94 (d, 1H, Ar-H, *J*=9.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ53.19, 112.99, 114.31, 127.23, 132.11, 151.77, 167.54.

Methyl 5-amino-4-iodo-2-nitrobenzoate (1d). To a vigorously stirred solution of **1c** (4.42 g, 22.6 mmol) in glacial acetic acid (20 mL) was added dropwise a solution of ICl (3.67 g, 22.6 mmol) in glacial acetic acid (5 mL). After 10 min., a yellow precipitate appeared and the solution was allowed to stir for another 12 h. Upon completion, the yellow solution was poured into water (50 mL), and filtered to yield a yellow solid, which was recrystallized from MeOH to afford 5.7 g (78.3 %) of the yellow solid **1d**. TLC, R_f = 0.42 (petroleum ether/EtOAc, 3/2). ^1H NMR (500 MHz, $CDCl_3$): δ 3.91 (s, 3H, MeO), 4.88 (b, 2H, NH_2), 6.73 (s, 1H, Ar-H), 8.42 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 53.57, 81.67, 94.81, 111.87, 114.38, 131.46, 136.17, 151.61.

Methyl 5-N-acetylamino-4-iodo-2-nitrobenzoate (1e). To a solution of **1d** (1.6 g, 4.97 mmol) in dichloromethane (15 mL) was added con. H_2SO_4 (0.85 mL) at 0 °C. After 5 min., a solution of acetic anhydrous (1.17 mL, 12.38 mmol) in dichloromethane (5 mL) was added dropwise at 0 °C. Upon addition, the mixture was warmed to room temperature and stirred for 1 h until completion detected by TLC. The resulting solution was washed with water, aqueous $NaHCO_3$, and brine, dried over anhydrous Na_2SO_4 and filtered. The resulting filtrate was evaporated *in vacuo* to yield a pale yellow solid, which was recrystallized from MeOH to afford 1.6 g (93.8 %) of **1e** as a white solid. TLC, R_f= 0.48 (petroleum ether/EtOAc, 1/2). ^1H NMR (500 MHz, $CDCl_3$): δ 2.31 (s, 3H, Ac), 3.93 (s, 3H, MeO), 7.71 (b, 1H, NH), 8.44 (s, 1H, Ar-H), 8.67 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.56, 53.97, 89.43, 119.96, 130.55, 135.17, 142.45, 143.53, 166.02, 168.91.

Methyl 5-N-acetylamino-4-iodo-2-aminobenzoate (1f). To a mixture of **1e** (5.6 g, 15.4 mmol) in absolute ethanol (88 mL) and glacial acetic acid (88 mL)was added iron powder (2.58 g, 46.7 mmol). The mixture was then heated to reflux for 2 h. The red reaction solution was allowed to cool to room temperature, diluted with water (300 mL), and extracted with dichloromethane (100 mL×3). The combined organic extracts were then washed with water, and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* to provide a pale yellow solid, which was recrystallized from MeOH to afford 4.36 g (84.8 %) of **1f** as a white needle. TLC, R_f= 0.36 (petroleum ether/EtOAc, 1/2). ^1H NMR (500 MHz, $CDCl_3$): δ 2.22 (s, 3H, Ac), 3.87 (s, 3H, MeO), 5.69 (b, 2H, NH_2), 7.06 (b, 1H, NH), 7.18 (b, 1H, Ar-H), 8.29 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.19, 51.81, 101.0, 111.24, 126.11, 126.26, 127.31, 148.29, 167.87, 168.43.

Methyl 5-N-acetylamino-4-iodo-2-[3,3-diethyl-1-triazenyl] benzoate (1g). A solution of sodium nitrite (0.49 g, 7.1 mmol) in water (4.5 mL) was cooled to 0 °C and then added dropwise over a 10 min. period to a 0 °C solution of **1f** (2.13 g, 6.38 mmol) and con. hydrochloric acid (1.8 mL) in water (12 mL) and acetonitrile (20 mL). The mixture was stirred for 0.5 h at 0 °C and then added dropwise to a solution of diethylamine (2.33 mL, 22 mmol) and potassium carbonate (2.9 g, 21 mmol) which was pre-cooled to 0 °C. During the addition, more diethylamine (2.3 mL) was added to the reaction solution. After addition, the mixture was warmed to room temperature for 0.5 h. During that period, a yellow solid precipitated. Upon completion, the solution was extracted with dichloromethane (80 mL×2). The combined organic extracts were then washed with brine and water, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to yield a yellow solid, which was recrystallized from MeOH to afford 2.39 g (86.2 %) of **1g** as a colorless needle. TLC, R_f= 0.23 (petroleum ether/EtOAc, 3/2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (*b*, 6H, Me), 2.24 (*s*, 3H, Ac), 3.74 (*b*, 4H, CH_2), 3.85 (*s*, 3H, MeO), 7.35 (b, 1H, NH), 7.86 (s, 1H, Ar-H), 8.41 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.09, 14.52, 24.71, 41.80, 49.20, 52.08, 93.94, 121.97, 127.15, 128.79, 134.63, 146.74, 167.83, 167.98.

5-N-Acetylamino-4-iodo-2-[3,3-diethyl-1-triazenyl] benzoic acid (1h). A solution of **1g** (1.4 g, 3.35 mmol) in MeOH (9 mL) was heated to reflux, to which was added dropwise aqueous NaOH (3.7 mL, 1N). The resulting solution was refluxed for 0.5 h and then cooled down to room temperature. Upon cooling, water (20 mL) was introduced. The solution was then extracted with Et_2O and the water phase was neutralized to pH 3 with 1N HCl. After filtration, the solid was dried *in vacuo* to afford 1.27 g (93.8 %) of **1h** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (t, 3H), 1.44 (t, 3H), 2.24 (s, 3H, Ac), 3.78 (q, 2H), 3.95 (q, 2H), 7.43 (s, 1H, NH), 8.12 (s, 1H, Ar-H), 8.71 (s, 1-H, Ar-H), 13.96 (s, 1H, COOH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.27, 14.36, 24.44, 43.47, 51.03, 98.62, 122.24, 125.98, 126.26, 135.98, 145.30, 166.34.

Octyl 5-N-acetylamino-4-iodo-2-[3,3-diethyl-1-triazenyl] benzoate (1i). A solution of the white acid **1h** (3.0 g, 7.43 mmol), DCC (1.6 g, 7.77 mmol), and DMAP (0.27 g, 2.21 mmol) in dichloromethane (40 mL) was stirred for 1 h at room temperature, to which was added n-octanol (1.11 g, 8.54 mmol) and more DCC (1.6 g, 7.77 mmol) respectively. The reaction mixture was stirred for 48 h at rt., filtered, and concentrated to give a red oil, which was purified by silica gel flash column chromatography (petroleum ether/ EtOAc: 4/1) to provide 3.27 g (85.3 %) of **1i** as a pale yellow oil. TLC, R_f = 0.33 (petroleum ether/EtOAc, 2/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, 3H), 1.22-1.39 (m, 16H), 1.72 (m, 2H), 2.20 (s, 3H, Ac), 3.75 (b, 4H, CH_2), 4.23 (t, 2H, CH_2O), 7.42 (s, 1H, Ar-H), 7.87 (s, 1H, NH), 8.37 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.46, 14.33, 14.78, 22.88, 24.93, 26.12, 28.89, 29.39, 29.50, 32.03, 41.91, 49.40, 65.59, 94.02, 122.07, 127.97, 128.93, 134.83, 146.79, 167.85, 168.23.

Octyl 5-N-acetylamino-2-[3,3-diethyl-1-triazenyl]-4-[2-(1,1,-trimethylsilyl)-1-ethynyl] benzoate (1k). A 50 mL flask under argon was charged with **1i** (0.77 g, 1.49 mmol), dichlorobis(triphenylphosphine) palladium (II) (21 mg, 0.030 mmol), copper(I) iodide (5.7 mg, 0.03 mmol), and triethylamine (23 mL). The solution was then stirred and warmed to 40 °C, to which was added dropwise degassed trimethylsilylacetylene (220 ul, 1.54 mmol) by syringe. The reaction mixture was allowed to stir for 12 h at the same temperature, filtered and then concentrated to yield a dark oil. The oil was purified by flash silica gel column chromatography (petroleum/EtOAc 8/1) to afford 0.68 g (93.8 %) of **1k** as a colorless solid. TLC, R_f= 0.39 (petroleum ether/EtOAc, 5/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.30 (s, 9H, $SiMe_3$), 0.88 (t, 3H), 1.29 (b, 16H), 1.72 (m, 2H), 2.20 (s, 3H, Ac), 3.73 (b, 4H, CH_2), 4.26 (t, 2H, CH_2O), 7.49 (s, 1H, Ar-H), 7.92 (s, 1H, NH), 8.61 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 0.099, 11.89, 14.27, 14.33, 22.84, 24.94, 26.16, 28.89, 29.36, 29.47, 32.00, 41.97, 49.23, 65.54, 100.18, 103.35, 114.36, 119.21, 121.61, 128.69, 136.17, 145.05, 167.85, 168.09. Anal. Calcd for $C_{26}H_{42}N_4O_3Si$.C, 64.16; H, 8.70; N, 11.51. Found C, 64.14; H, 8.60; N, 11.61.

Methyl 5-N-acetylamino-2-[3,3-diethyl-1-triazenyl]-4-[2-(1,1,-trimethylsilyl)-1-ethynyl] benzoate (1j). Compound **1j** was prepared from **1g** (6.12 g, 14.64 mmol) as described for **1k** to afford a brown oil. The oil was purified by silica gel column chromatography (petroleum ether/EtOAc 2/1) to afford 5.58 g (98.2 %) of **1j** as a pale yellow solid. TLC, R_f = 0.38 (petroleum ether/EtOAc, 2/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.30 (s, 9H, $SiMe_3$), 1.26 (b, 6H, CH_3), 2.20 (s, 3H, Ac), 3.73 (b, 4H, CH_2), 3.86 (s, 3H, MeO), 7.49 (s, 1H, Ar-H), 7.92 (b, 1H, NH), 8.63 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 0.39, 11.09, 14.57, 25.26, 42.08, 49.83, 52.57, 100.4, 103.85, 114.92, 119.70, 121.96, 128.29, 136.41, 145.55, 168.19, 168.65. Anal. Calcd for $C_{19}H_{28}N_4O_3Si$: C, 58.73; H, 7.26; N, 14.42. Found C, 58.77; H, 7.26; N, 14.48.

Methyl 5-N-acetylamino-2-[3,3-diethyl-1-triazenyl]-4-ethynyl benzoate (1l). To a solution of **1j** (0.50 g, 1.29 mmol) in methanol (8 mL) was added potassium carbonate (12 mg, 0.087 mmol). The solution was stirred for 5 min. at room temperature, diluted with water (10 mL), and then extracted with dichloromethane (10 mL× 20). The pale yellow extracts were washed with water, dried over Na_2SO_4 and concentrated to yield a oil. The oil was purified by silica gel column chromatography (petroleum ether/EtOAc, 1/1) to afford 0.39 g (96.2 %) of **1l** as a pale yellow solid. TLC, R_f= 0.57 (petroleum ether /EtOAc, 1/3), ^{1}HNMR (500 MHz, $CDCl_3$): δ 1.26 (m, 6H, CH_3), 2.22 (s, 3H, Ac), 3.53 (s, 1H, CCH), 3.72 (m, 4 H, CH_2), 3.86 (s, H, MeO), 7.53 (s, 1H, Ar-H), 7.82 (s, 1H, NH), 8.62 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.02, 52.27, 79.18, 85.21, 113.54, 119.84, 122.50, 128.36, 136.20, 145.29, 168.11, 168.32.

Methyl 5-N-acetylamino-2-iodo-4-[2-(1,1,-trimethylsilyl)-1-ethynyl] benzoate (1m). To a sealed tube was added **1j** (2.39 g, 6.16 mmol) and iodomethane (10 mL) under argon. The mixture was stirred for 12 h at 120 °C. After filtration the filtrate was concentrated to yield a brown oil, which was purified by silica gel column chromatography (petroleum ether/EtOAc 3/1) to afford 2.09 g (81.9 %) **1m** as a white solid. TLC, R_f= 0.53 (petroleum ether/EtOAc, 2/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.31 (s, 9H, $SiMe_3$), 2.22 (s, 3H, Ac), 3.92 (s, 3H, MeO), 7.90 (s, 1H, Ar-H), 7.99 (s, 1H, Ar-H), 8.86 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ -0.041, 25.02, 52.90, 85.46, 97.90, 106.29, 116.10, 120.95, 136.03, 139.42, 143.37, 166.54, 168.25.

Dimer 2c. A dry flask was charged with **1l** (0.77 g, 2.44 mmol), **1m** (0.64 g, 1.54 mmol), bis(dibenzylideneacetone) palladium (28 mg, 0.031 mmol), triphenylphosphine (48 mg, 0.18 mmol), copper (I) ioide (5.9 mg, 0.031 mmol), dry acetonitrile (60 mL), and triethylamine (15 mL) under argon. The mixture was degassed three times and stirred for 12 h at 70 °C. The resulting solution was then filtered and concentrated to yield a dark oil, which was purified by silica gel column chromatography (petroleum ether/EtOAc 1/1) to afford 0.89 g (95.8 %) of dimer **2c** as a yellow solid. TLC, $R_f = 0.50$ (petroleum ether/EtOAc, 1/3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.33 (s, 9H, $SiMe_3$), 1.28 (m, 6H, CH_3), 2.26 (s, 3H, Ac), 2.42 (s, 3H, Ac), 3.75 (m, 4H, CH_2), 3.87 (s, 3H, MeO), 3.94 (s, 3H, MeO), 7.54 (s, 1H, Ar-H), 7.76 (s, 1H, Ar-H), 8.03 (s, 1H, NH), 8.86 (s, 1H, Ar-H), 9.14 (s, 1H, Ar-H), 9.22 (s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ -0.03, 24.71, 24.76, 52.21, 52.88, 90.41, 94.75, 98.38, 106.61, 114.39, 118.70, 119.85, 120.90, 121.73, 128.14, 130.86, 136.82, 136.88, 137.74, 139.04, 144.84, 165.94, 168.37, 168.53, 169.84. Anal. Calcd for $C_{31}H_{37}N_5O_6Si$: C, 61.67; H, 6.18; N, 11.60. Found C, 61.76; H, 6.22; N, 11.64.

Octyl 5-N-acetylamino-2-[3,3-diethyl-1-triazenyl]-4-ethynyl benzoate (1o). To a solution of the compound **1k** (0.95 g, 1.95 mmol) in MeOH (15 mL) was added potassium carbonate (15 mg, 0.11 mmol) as described for **1l** to yield a brown oil. The oil was then purified by silica gel column chromatography (petroleum ether/EtOAc: 2/1) to afford 0.73 g (90.2 %) of **1o** as a light yellow oil. TLC, $R_f = 0.48$ (petroleum ether/EtOAc, 1/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, 3H), 1.26-1.38 (m, 16H), 1.72 (m, 2H), 2.20 (s, 3H, Ac), 3.55 (s, 1H), 3.72 (b, 4H), 7.54 (s, 1H, Ar-H), 7.91 (s, 1H, NH), 8.58 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.41, 14.28, 14.67, 22.83, 24.94, 25.98, 26.14, 28.85, 29.48, 31.98, 32.97, 41.80, 49.26, 63.06, 65.57, 79.08, 85.35, 113.56, 119.75, 122.40, 128.843, 136.17, 145.08, 168.18, 168.33.

Octyl 5-N-acetylamino-2-iodo-4-[2-(1,1,-trimethylsilyl)-1-ethynyl] benzoate (1p). The compound was synthesized from **1k** (0.97 g, 1.99 mmol) by a similar procedure for **1m** to yield a light yellow oil. The oil was then purified by silica gel column chromatography (petroleum ether/EtOAc, 15/1, 10/1) to afford a colorless oil, which was stood overnight to afford 0.81 g (79.4 %) of **1p** as a white wax. TLC, $R_f = 0.58$ (petroleum ether/EtOAc, 5/1). ^{1}HNMR (500 MHz, $CDCl_3$): ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.31 (s, 9H, $SiMe_3$), 0.88 (t, 3H), 1.29 (m, 10H), 1.78 (m, 2H), 2.22 (s, 3H, Ac), 4.32 (t, 2H, CH_2O), 7.91 (s, 1H, NH), 7.97 (s, 1H, Ar-H), 8.83 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ -0.032, 14.29, 22.83, 25.00, 26.11, 28.72, 28.85, 29.38, 31.97, 66.30, 85.25, 97.94, 106.08, 115.91, 120.83, 136.66, 139.43, 143.20, 166.32, 168.20.

Dimer 2e. Following the procedure as described for **2c**, the acetylene **1o** (0.74 g, 1.79 mmol), **1p** (0.76 g, 1.48 mmol), bis(dibenzylideneacetone) palladium (22 mg, 0.024 mmol), copper (I) iodine (4.7 mg, 0.024 mmol), and triphenylphosphine (33 mg, 0.12 mmol) in dry triethylamine (20 mL) was stirred at 70 °C for 24 h under argon. The reaction solution was then concentrated to yield a dark oil, which was purified by silica gel column chromatography (petroleum ether/EtOAc: 5/1) to afford 1.05 g (88.9 %) of dimer **2e** as a yellow solid. TLC, $R_f = 0.63$ (petroleum ether/EtOAc, 2/1). ^{1}HNMR (500 MHz, $CDCl_3$): δ 0.33 (s, 9H, $SiMe_3$), 0.88 (m, 6H), 1.27-1.44 (m, 26H), 1.74 (m, 2H), 1.80 (m, 2H), 2.26 (s, 3H, Ac), 2.41 (s, 3H, Ac), 3.76 (m, 4H, CH_2), 4.27(t, 2H), 4.33 (t, 2H), 7.55 (s, 1H), 7.75 (s

1H), 8.03 (s, 1H), 8.84 (s, 1H), 9.16 (s, 1H), 9.22 (s, 1H). ^{13}CNMR (125 MHz, $CDCl_3$): δ -0.009, 14.33, 22.87, 24.74, 25.08, 26.13, 26.19, 28.74, 28.91, 29.38, 29.40, 29.43, 29.52, 31.99, 32.04, 65.53, 66.23, 90.41, 94.73, 98.43, 106.47, 114.17, 118.66, 119.62, 120.79, 121.69, 128.77, 131.33, 136.83, 137.80, 139.06, 144.63, 165.52, 168.32, 169.88.

Dimer 2f. To a solution of dimer **2e** (0.58 g, 0.72 mmol) in MeOH (8 mL) and dichloromethane (1 mL) was added potassium carbonate (5 mg, 0.026 mmol). The mixture was allowed to stir for 10 min. at room temperature and then water (8 mL) was added. Upon addition, the solution was extracted with dichloromethane (10 mL × 3) and the resulting organic extracts were then washed with water (10 mL), dried over Na_2SO_4, filtered and concentrated to afford 0.51 g (96.5%) of dimer **2f** as a pure pale yellow oil. TLC, R_f = 0.39 (petroleum ether/EtOAc, 1/3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (m, 6H), 1.28-1.45 (m, 26H), 1.78 (m, 4H), 2.26 (s, 3H, Ac), 2.40 (s, 3H, Ac), 3.66 (s, 1H, CCH), 3.74 (b, 4H), 4.27 (m, 4H, CH_2O), 7.52, (s, 1H, Ar-H) 7.74 (s, 1H, Ar-H), 7.96 (s, 1H, NH), 8.84 (s, 1H, Ar-H), 9.12 (s, 1H, NH), 9.18 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.27, 22.84, 24.69, 25.04, 26.11, 28.73. 28.91, 29.35, 29.37, 29.41, 29.49, 31.97, 32.01, 65.51, 66.22, 77.72, 87.54, 90.42, 94.60, 114.10, 114.90, 118.68, 119.60, 121.36, 121.74, 128.81, 131.61, 137.44, 137.79, 139.32, 144.59, 165.42, 168.37, 168.60, 169.82.

2-[2-(2-Methoxyethoxy) ethoxy]ethyl 2-iodobenzoate (1r). To a solution of 2-iodobenzoic acid **1q** (1.26 g, 5.08 mmol) and triethylamine (2.5 mL) in dichloromethane (20 mL) was added dropwise trimethylacetyl chloride (1.8 mL) at 0 °C. The reaction solution was allowed to warm to room temperature and stirred for 1h. Then the solution was then cooled in an ice-water bath, to which a solution of triethyleneglycol monomethyl ether (1.05 g, 6.40 mmol) in dichloromethane (10 mL) was added dropwise. The reaction mixture was allowed to stir for 12 h at rt., washed with water, dried over Na_2SO_4, filtered, and concentrated to afford a red oil. The oil was purified by silica gel column chromatography (petroleum ether /EtOAc, 3/1) to afford 1.92 g (96.0 %) of **1r** as a pale yellow oil. TLC, R_f = 0.48 ($CHCl_3$/acetone, 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.35 (s, 3H, MeO), 3.52 (m, 2H), 3.63-3.85 (m, 6H), 3.85 (t, 2H), 4.89 (t, 2H), 7.15 (m, 1H), 7.40 (m, 1H), 7.83 (d, 1H), 7.96 (d, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.34, 59.16, 63.67, 64.80, 69.10, 70.78, 72.08, 94.29, 128.06, 131.26, 132.84, 15.19, 141.40, 166.51.

Dimer 2d. A mixture of the acetylene **1l** (78 mg, 0.25 mmol), **1r** (112 mg, 0.28 mmol), bis(dibenzylideneacetone) palladium (4.6 mg, 0.0053 mmol), copper (I) iodine (1 mg, 0.0052 mmol), and triphenylphosphine (6.9 mg, 0.025 mmol) in triethylamine (15 mL) was heated at 70 °C under argon for 12 h. The solution was concentrated to yield a brown oil, which was purified by PTLC (CH_2Cl_2/acetone, 10/1) to afford 130 mg (89.1%) of **2d** as a yellow solid. TLC, R_f = 0.34 ($CHCl_3$/acetone, 8/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (m, 6H), 2.40 (s, 3H, Ac), 3.36 (s, MeO, 3H), 3.52 (t, CH_2O, 2H), 3.63-3.76 (m, 10 H), 3.87 (m, 5H), 4.48 (t, CH_2O, 2H), 7.43 (t, 1H), 7.58 (m, 2H), 7.71 (d, 1H, J = 7.5 Hz), 8.15 (d, 1H, J = 8.0 Hz), 8.87 (s, 1H), 9.27 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.76, 52.22, 59.22, 64.85, 69.18, 70.82, 70.86, 70.99, 72.13, 90.79, 95.60, 114.50, 119.89, 122.02, 124.17, 128.14, 128.55, 130.21, 131.13, 132.73, 134.21, 137.77, 144.90, 165.85, 168.54, 169.77.

Trimer 3. Following the coupling procedure as described for **2e,** the mixture of the acetylene **2f** (139 mg, 0.19 mmol), **1r** (102 mg, 0.26 mmol), bis(dibenzylideneacetone) palladium (3.5 mg, 0.0038 mmol), copper (I) iodine (1 mg, 0.0052 mmol), and triphenylphosphine (5.2 mg, 0.019 mmol) in triethylamine (10 mL) was heated at 70 °C under argon for 5 h. The solution was then filtered and concentrated to yield a dark oil, which was purified by silica gel column chromatography (dichloromethane/MeOH: 30/1, 20/1) to afford 131 mg (69.4%) of **3** as a yellow solid. TLC, R_f= 0.45 ($CHCl_3$/acetone, 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (s, 6H), 1.39 (m, 26H), 1.74 (m, 2H), 1.82 (m, 2H), 2.42 (s, 3H, Ac), 2.45 (s, 3H, Ac), 3.36 (s, 3H, MeO), 3.53 (m, 2H), 3.67-3.76 (m, 10 H), 3.87 (t, 2H), 4.27(t, 2H), 4.32 (t, 2H), 4.49 (t, 2H), 7.49 (t, 1H), 7.58 (s, 1H),), 7.85 (s, 1H, Ar-H), 7.62 (t, 1H), 7.72(d, 1H, *J* = 7.5 Hz), 8.17 (d, 1H, *J* = 8.0 Hz), 8.86 (s, 1H), 9.27 (s, 1H), 9.38 (s, 1H), 9.45 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.09, 22.65, 24.49, 24.54, 24.63, 24.68, 25.92, 25.97, 28.56, 28.70, 29.17, 29.22, 29.30, 31.79, 31.82, 59.06, 64.79, 65.28, 65.94, 68.94, 70.65, 70.68, 70.82, 71.94, 89.01, 89.85, 94.79, 97.40, 114.15, 115.57, 117.90, 121.25, 121.46, 121.52, 123.39, 128.44, 130.20, 131.09, 131.20, 132.73, 134.12, 136.84, 136.88, 137.62, 140.57, 144.45, 165.56, 165.69, 168.08, 169.68, 170.11. Anal. Calcd for $C_{56}H_{75}N_5O_{11}$. C, 67.65; H, 7.60; N, 7.04. Found C, 67.80; H, 7.63; N, 7.09.

Trimer 3a. To a sealed tube was added with trimer **3** (0.23 g, 0.23 mmol) and iodomethane (1.5 mL). The mixture was stirred for 24 h at 120 °C to yield a brown residue. The residue was then purified by silica gel column chromatography (dichloromethane/MeOH: 15/1, 10/1) to afford 173 mg (73.7 %) of **3a** as a yellow solid. TLC, R_f = 0.52 ($CHCl_3$/acetone, 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): 0.88 (m, 6H), 1.29-1.46 (m, 20H), 1.81 (m, 4H), 2.41 (s, 3H, Ac), 2.44 (s, 3H, Ac), 3.36 (s, 3H, MeO), 3.52 (t, 2H), 3.64-3.73 (m, 6H), 3.88 (t, 2H), 4.31 (m, 4H), 4.46 (m, 2H), 7.47 (t, 1H, Ar-H), 7.59 (t, 1H, Ar-H), 7.67 (d, 1H, *J* = 7.5 Hz), 7.75 (s, 1H, Ar-H), 8.01 (s, 1H, Ar-H), 8.15 (d, 1H, *J* = 8 Hz), 9.08 (s, 1H, Ar-H), 9.27 (s, 1H, NH), 9.38 (s, 1H, Ar-H), 9.40 (s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.33, 22.87, 24.78, 24.81, 24.89, 26.13, 26.12, 28.72, 29.39, 29.43, 32.00, 32.02, 59.24, 59.27, 65.01, 66.18, 66.22, 69.11, 70.85, 71.00, 72.12, 84.79, 87.83, 88.95, 97.20, 97.94, 115.87, 116.17, 117.31, 121.40, 123.43, 129.17, 130.13, 131.11, 131.31, 132.98, 134.39, 135.87, 137.20, 140.96, 141.19, 143.27, 165.57, 165.73, 166.39, 170.30, 170.36.

Tetramer 4. Following the coupling procedure as described for trimer **3**, the compound **1o** (31 mg, 0.075 mmol), the trimer **3a** (51 mg, 0.050 mmol), bis(dibenzylideneacetone) palladium (1 mg, 0.0011 mmol), copper (I) iodine (0.5 mg, 0.0026 mmol), and triphenylphosphine (1.5 mg, 0.0056 mmol), in triethylamine (15 mL) was heated at 70 °C under argon for 28 h. The solution was filtered and concentrated to give a dark oil, which was purified by silica gel column chromatography (dichloromethane/acetone: 10/1) to give 48.5 mg (74.3 %) of **4** as a yellow solid. TLC, R_f = 0.53 ($CHCl_3$/acetone, 5/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (m, 9H), 1.29-1.46 (m, 36H), 1.76 (m, 2H), 1.83 (m, 4H), 2.42 (s, 3H, Ac), 2.47 (s, 6H, Ac), 3.37 (s, 3H, MeO), 3.53 (m, 2H), 3.65-3.89 (m, 12H), 4.27 (m, 2H, CH_2O), 4.33 (m, 4H, CH_2O), 4.51 (t, 2H), 7.51 (t, 1H, Ar-H, *J* = 8 Hz), 7.57 (s, 1H), 7.63 (t, 1H), 7.75 (d, 1H, *J* = 7 Hz), 7.82 (s, 1H), 7.86 (s, 1H), 8.20 (d, 1H, *J* = 7 Hz), 8.86 (s, 1H), 9.29 (s, 1H), 9.39 (s, 1H), 9.42 (s, 1H), 9.46 (s, 1H), 9.49 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$):

δ 14.12, 22.66, 24.54, 24.62, 24.71, 25.92, 25.98, 28.54, 28.55, 28.70, 29.18, 29.24, 29.31, 31.80, 31.83, 59.07, 64.84, 65.29, 65.92, 66.09, 68.93, 70.65, 70.67, 70.82, 71.92, 88.17, 88.78, 89.69, 94.92, 97.14, 97.71, 114.22, 115.74, 115.77, 117.12, 117.82, 119.47, 121.22, 121.35, 121.53, 123.25, 128.33, 129.01, 130.14, 130.90, 131.14, 131.25, 132.74, 134.15, 136.60, 136.89, 137.00, 137.65, 140.54, 141.11, 144.41, 165.56, 165.66, 168.11, 169.76, 170.25, 170.27. Anal. Calcd for $C_{75}H_{98}N_6O_{14}$. C, 68.89; H, 7.55; N, 6.43; O, 17.43. Found C, 68.66; H, 7.56; N, 6.40.

Pentamer 5. A mixture of dimer **2f** (47 mg, 0.065 mmol), trimer **3a** (50.9 mg, 0.05 mmol), bis(dibenzylideneacetone) palladium (2 mg, 0.0022 mmol), copper (I) iodine (0.5 mg, 0.0026 mmol), and triphenylphosphine (3.1 mg, 0.012 mmol) in triethylamine (10 mL) was stirred at 70 °C under argon for 28 h. After removal of solvent, the resulting residue was purified by silica gel PTLC (dichloromethane/acetone: 10/1) to afford 64 mg (60.8 %) of yellow solid **5**. TLC, R_f= 0.47 ($CHCl_3$/acetone, 5/1). ^{1}HNMR (500 MHz, $CDCl_3$): δ 0.88 (s, 12H), 1.32 (m, 46H), 1.73 (m, 2H), 1.83 (m, 6H), 2.42 (s, 3H, Ac), 2.48 (s, 9H), 3.37 (s, 3H), 3.55 (t, 2H), 3.73 (m, 10 H), 3.89 (m, 2H), 4.32(m, 8H), 4.49 (t, 2H), 7.41 (t, 1H), 7.46 (t, 1H), 7.51 (s, 1H), 7.63 (d, 1H, J=8.0 Hz), 7.75 (s, 1H), 7.78, 7.80 (d, 2H), 8.15 (d, 1H, *J* = 7.5 Hz), 8.82 (s, 1H), 9.20 (s, 1H), 9.33, 9.36, 9.38, 9.39 (q, 4H), 9.42 (s, 1H). 9.43 (s, 1H). ^{13}CNMR (125 MHz, $CDCl_3$): δ 14.12, 22.68, 24.68, 24.75, 25.96, 28.58, 28.74, 29.21, 29.29, 29.33, 31.83, 59.05, 64.88, 65.25, 65.92, 66.08, 66.14, 68.96, 70.67, 70.70, 70.84, 71.96, 87.95, 88.03, 88.71, 89.59, 94.82, 95.01, 97.29, 97.48, 97.75, 114.25, 115.74, 115.80, 115.92, 117.02, 117.08, 117.78, 119.40, 121.08, 121.19, 121.28, 121.37, 121.44, 123.19, 128.32, 130.01, 130.69, 130.81, 131.08, 131.15, 132.60, 136.60, 136.89, 137.10, 140.59, 141.07, 141.22, 144.28, 165.45, 165.58, 168.03, 169.75, 170.25, 170.27, 170.35. Anal. Calcd for $C_{94}H_{121}N_7O_{17}$. C, 69.65; H, 7.52; N, 6.05. Found C, 69.43; H, 7.55; N, 5.90.

Dimer 2g. A mixture of **1 m** (0.52 mg, 1.25 mmol), **1o** (0.58 g, 1.40 mmol), bis(dibenzylideneacetone) palladium (21 mg, 0.023 mmol), copper (I) iodine (4.4 mg, 0.023 mmol), and triphenylphosphine (31 mg, 0.12 mmol) in triethylamine (30 mL) was stirred at 70°C under argon for 12 h. The solution was then filtered and concentrated to yield a brown residue, which was purified by silica gel column (petroleum/EtOAc: 3/2) to afford 0.81g (92.4 %) of the dimer **2g** as a yellow solid. TLC, R_f= 0.43 (petroleum ether/EtOAc, 1/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.33 (s, 9H, $SiMe_3$), 0.88 (t, 3H), 1.29 (m, 16 H), 1.74 (t, 2H, CH_2), 2.25 (s, 3H, Ac), 2.42 (s, 3H, Ac), 3.75 (b, 4H, CH_2), 3.94 (s, 3H, MeO), 4.27 (t, 2H, CH_2O), 7.54 (s, 1H, Ar-H), 7.75 (s, 1H, Ar-H), 8.03 (s, 1H, NH), 8.88 (s, 1H, Ar-H), 9.12 (s, 1H, Ar-H), 9.21 (s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ -0.032, 14.29, 22.85, 24.72, 25.03, 26.18, 28.91, 29.38, 29.50, 32.02, 52.89, 65.50, 90.50, 94.61, 98.40, 106.57, 114.10, 118.76, 119.64, 120.90, 120.90, 121.71, 128.86, 130.84, 136.84, 137.79, 139.03, 144.62, 165.94, 168.29, 168.35, 169.81. Anal. Calcd for $C_{38}H_{51}N_5O_6Si$. C, 65.02; H, 7.32; N, 9.98. Found C, 64.87; H, 7.22; N, 10.13.

Dimer 2h. To a solution of the dimer **2g** (0.57 g, 0.81 mmol) in MeOH (10 mL) was added potassium carbonate (6 mg, 0.043 mmol) and the reaction was carried out as described for **2f** to afford 0.46 g (90.2 %) of the desired **2h** as a yellow oil. TLC, R_f = 0.55 (petroleum ether/EtOAc, 1/3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, 3H), 1.29 (m, 16 H), 1.74 (m, 2H), 2.26 (s, 3H, Ac), 2.42 (s, 3H, Ac), 3.65 (s, 1H, CCH), 3.74 (b, 4H, CH_2), 3.93 (s, 3H, MeO), 4.27 (b, 2H, CH_2O), 7.52 (s, 1H, Ar-H), 7.73 (s, 1H, Ar-H), 7.95 (s, 1H, NH), 8.83 (s, 1H, Ar-H), 9.09 (s, 1H, Ar-H), 9.16 (s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.27, 22.84, 24.71, 25.04, 26.18, 28.91, 29.37, 29.49, 32.01, 52.90, 65.54, 77.67, 87.61, 90.48, 94.54, 114.05, 115.11, 119.78, 119.58, 121.45, 121.75, 128.85, 131.06, 137.47, 139.26, 144.56, 165.83, 168.42, 168.64, 169.85.

Trimer 3b. A mixture of **2 h** (263 mg, 0.42 mmol), **1 p** (300 mg, 0.58 mmol), bis(dibenzylideneacetone) palladium (7.6 mg, 0.0083 mmol), copper (I) iodine (2 mg, 0.01 mmol), and triphenylphosphine (15 mg, 0.056 mmol) in dry triethylamine (28 mL) was stirred at 70 °C under argon for 24 h. The solution was then filtered and concentrated to yield a brown oil, which was purified by silica gel column (petroleum ether/dichloromethane/MeOH: 3/1/0.5) to afford 280 mg (66.0 %) of **3b** as a yellow oil. TLC, R_f= 0.51 (petroleum ether/$CHCl_3$/acetone, 1/1/0.5). ^{1}H NMR (500 MHz, $CDCl_3$): 0.88 (m, 6H), 1.29-1.46 (m, 26 H), 1.75 (t, 2H), 1.81 (t, 2H), 2.26 (s, 3H, Ac), 2.42 (s, 6H, Ac), 3.75 (b, 4H), 3.92 (s, 3H, MeO), 4.29 (m, 4H, CH_2O), 7.54 (s, 1H, Ar-H), 7.73 (b, 2H, Ar-H), 8.01 (s, 1H, NH), 8.87 (s, 1H, Ar-H), 9.17 (s, 1H), 9.22 (s, 1H, NH), 9.32 (s, 1H, NH), 9.34 (s, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ -0.05, 14.28, 22.85, 24.74, 24.79, 25.00, 26.12, 26.18, 28.71, 28.92, 29.35, 29.38, 29.42, 29.50, 31.97, 32.02, 52.82, 65.47, 66.35, 88.58, 89.97, 94.96, 97.15, 98.18, 106.76, 114.27, 115.95, 116.03, 117.84, 118.11, 119.59, 120.96, 121.39, 121.74, 128.66, 130.57, 136.91, 137.82, 139.64, 140.66, 144.58, 165.41, 166.11, 168.30, 168.39, 169.89, 170.38.

Hexamer 6. To a solution of **3b** (30 mg, 0.029 mmol) in MeOH (3 mL) was added potassium carbonate (0.5 mg, 0.0036 mmol). The reaction solution was stirred for 10 min. at r.t., and then water (5 mL) was introduced. Upon addition, the mixture was extracted with chloroform (5 mL×3), and the combined organic extracts were washed with water, dried over Na_2SO_4 and concentrated to yield 26 mg of a yellow oil. The oil was a single spot on TLC plate and was used for the next step without purification. To the above oil (26 mg, 0.028 mmol) was added trimer **3a** (21.5 mg, 0.021 mmol), bis(dibenzylideneacetone) palladium (0.8 mg, 0.87 umol), copper (I) iodine (0.5 mg, 2.6 umol), triphenylphosphine (2.1 mg, 0.008 mmol) and triethylamine (20 mL). The reaction mixture was then stirred at 70 °C under argon for 24 h. After removal of solvent, the resulting residue was purified by PTLC (chloromethane/acetone: 10/1) to afford 28 mg (72.7 %) of hexamer **6** as a yellow solid. TLC, R_f= 0.45 ($CHCl_3$/acetone, 3/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88-0.96 (m, 18 H), 1.13 (b, 3H), 1.26-1.40 (m, 40 H), 1.49 (m, 3H), 1.65 (m, 2H), 1.86 (m, 6H), 2.44-47 (m, 15H, Ac), 3.22 (b, 2H), 3.37 (s, 3H, MeO), 3.53 (m, 4H), 3.65 (m, 2H), 3.69 (m, 2H), 3.73 (m, 2H), 3.88 (t, 2H), 3.93 (s, 3H, MeO), 3.94 (s, 3H), 4.14 (t, 2H, J=5 Hz), 4.31 (m, 6H), 4.45 (t, 2H, *J* = 4 Hz),6.87 (b, 1H, Ar-H), 7.08 (b, 1H, Ar-H), 7.38 (b, 2H), 7.69 (s, 1H, Ar-H), 7.73 (s, 1H, Ar-H), 7.80 (s, 1H, Ar-H), 7.82 (s, 1H, Ar-H), 7.98 (d, 1H, Ar-H, *J* = 7.5 Hz), 8.75 (s, 1H, Ar-H), 8.95 (b, 1H), 9.05 (m, 3H), 9.23 (b, 1H), 9.37 (s, 1H), 9.42 (ts, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.11, 14.14, 22.66, 22.71, 24.65, 24.72, 25.75, 26.01, 28.54, 28.56, 28.68, 29.22, 29.32, 29.38, 29.39, 31.83, 31.86, 52.64, 59.01, 64.86, 64.98, 66.08, 66.13, 66.22, 68.96, 70.64, 70.66, 70.76, 71.93, 78.03, 87.69,87.74,87.79, 88.09, 89.51, 94.43, 97.34, 97.68, 97.73, 97.98, 113.58, 115.77, 115.79, 115.85, 115.89, 117.02, 117.12, 117.85, 118.65, 120.62, 120.79, 122.69, 128.52, 129.09, 129.45, 130.05, 130.11, 130.24, 130.65, 132.20, 134.29, 136.80, 137.19, 137.47, 140.39, 140.97, 141.11, 143.48, 164.76, 164.81, 164.89, 164.99, 165.50, 167.94, 169.87, 170.27, 170.32, 170.40, 170.45. Anal. Calcd for $C_{106}H_{130}N_8O_{20}$. C, 69.33; H, 7.14; N, 6.10. Found C, 69.26; H, 7.21; N, 5.87.