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m-Diethynylbenzene Macrocycles: Syntheses and Self-Association Behavior in Solution

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Abstract: *m*-Diethynylbenzene macrocycles (DBMs), buta-1,3-diyne-bridged [4_n]metacyclophanes, have been synthesized and their self-association behaviors in solution were investigated. Cyclic tetramers, hexamers, and octamers of DBMs having *exo*-annular octyl, hexadecyl, and 3,6,9-trioxadecyl ester groups were prepared by intermolecular oxidative coupling of dimer units or intramolecular cyclization of the corresponding open-chain oligomers. The aggregation properties were investigated by two methods, the ^{1}H NMR spectra and the vapor pressure osmometry (VPO). Although some discrepancies were observed between the association constants obtained from the two methods, the qualitative view was consistent with each other. The analysis of self-aggregation by VPO revealed unique aggregation behavior of DBMs in acetone and toluene, which was not elucidated by the NMR method. Namely, the association constants for infinite association are several times larger than the dimerization constant, suggesting that the aggregation is enhanced by the formation of dimers (a nucleation mechanism). In polar solvents, DBMs aggregate more strongly than in chloroform due to the solvophobic interactions between the macrocyclic framework and the solvents. Moreover, DBMs self-associate in aromatic solvents such as toluene and *o*-xylene more readily than in chloroform. In particular, the hexameric DBM having a large macrocyclic cavity exhibits extremely large association constants in aromatic solvents. By comparing the aggregation properties of DBMs with the corresponding acyclic oligomers, the effect of the macrocyclic structure on the aggregation propensity was clarified. Finally, it turned out that DBMs tend to aggregate more readily than the corresponding phenylacetylene macrocycles, acetylene-bridged [2_n]metacyclophanes, owing to the withdrawal of the electron density from the aromatic rings by the butadiyne linkages which facilitates $\pi-\pi$ stacking interactions.

Introduction

During the last two decades, conformationally rigid and shape-persistent molecules of nanometer scale, such as large macrocycles,[1] molecular wires,[2] and dendrimers,[1a,3] have attracted a great deal of interest because of their potential as functional materials. Rational design of building blocks plays a crucial role in construction of such molecular architectures. The carbon−carbon triple bond is a useful connecting unit in this respect, because of the structural linearity that does not suffer from fluctuation arising from cis−trans isomerization, small steric demand, and the facility in connecting an sp carbon to an sp^2 or sp carbon center owing to the numerous methods developed over many years.[4] Moreover, because of the isotropic distribution of the π electrons along the C−C axis, acetylene linkages are capable of transmitting electronic perturbation efficiently from one end of conjugated π-systems to the other. These characteristics have been successfully exploited in molecular wires[2] and conjugated dendrimers.[1a,3]

Moore and co-workers reported the synthesis of the acetylene-bridged [2_n]metacyclophanes, called phenylacetylene macrocycles (PAMs),[5,6] and their interesting properties based on their association by weak noncovalent interactions. These include self-association in solution[7] and organization to porous molecular crystals,[8] liquid crystals,[9] and monolayer surfaces.[10] Moreover,

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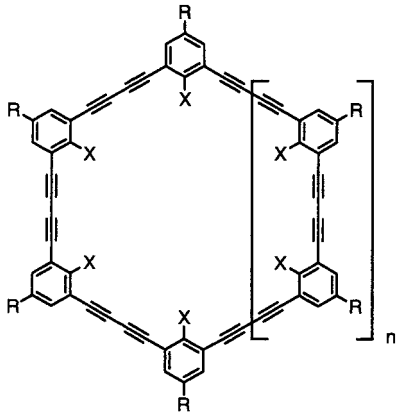
Höger et al. reported the synthesis of macrocyclic metapara-cyclophanes having a large cavity constructed by acetylene and buta-1,3-diyne bridges[11] and their organization in solution,[12] in condensed phase,[13] and on a solid surface,[12] as well as the guest binding ability toward an amine derivative.[14] Recently, Yamaguchi et al. reported the synthesis of PAM analogues incorporating chiral benzo[*c*]phenanthrene units and the diastereoselectivity in their self-aggregation in solution.[15] Cation binding properties of PAMs bearing *endo*-annular methoxy groups were reported by the group of Kawase and Oda.[16] Thus these properties based on noncovalent interactions can, in principle, be fine-tuned by modifying the size and shape of the macrocycles and the nature of the functional groups attached to the periphery and interior of the macrocyclic framework.

We embarked on a research program aimed at the development of the chemistry of new macrocyclic structures **1** based on the butadiyne-bridged metacyclophanes, diethynylbenzene macrocycles (DBMs) or "big brothers" of PAMs,[17,18,19] because we anticipated that the buta-1,3-diyne units would make a substantial difference in the properties of DBMs from those of PAMs in the following respects. (i) Since the ring sizes of the diyne-bridged macrocycles are larger than those of the corresponding PAMs having the same number of aromatic rings, it is possible to introduce binding functionalities along the interior of the macrocycles for a large gust molecule.[20] (ii) The electron density of the aromatic rings of DBMs would suffer from stronger perturbation owing to a stronger electron-withdrawing effect of the buta-1,3-diyne unit than that of the ethyne unit as described later. This will alter the association properties of DBMs due to the $\pi-\pi$ stacking interaction, because it has been well documented, both theoretically[21] and experimentally,[22] that such interaction is susceptible to the electronic effect of the substituents. (iii) There is ample experimental evidence which indicates that buta-1,3-diyne units stack in the crystalline state to parallel alignment with intermolecular distances of 3.5 to 5.0 Å because of their rodlike shape.[23] Moreover, buta-1,3-diyne derivatives are known to undergo topochemically controlled polymerization in the solid state[23,24] or in the liquid crystalline state[25] to give polydiacetylenes, which have interesting electronic and optical properties. It is therefore expected that DBMs would yield upon polymerization highly ordered three-dimensional polydiacetylene structures provided that proper intermoleculer arrangement were attained.[26]



1 n = 0, 1, 2

In this connection, we planned to prepare DBMs, i.e., tetramers **2a**−**c**, hexamers **3a**−**c**, and octamers **4a**,**c**, having *exo*-annular ester groups with straight alkyl chains (**a** and **b**) or methyl ether of triethylene glycol (**c**) and to study their properties due to self-aggragation both in solution and in the condensed phase.[27] The *exo*-annular ester groups would promote self-association owing to the electron-withdrawing effect.[7] The long

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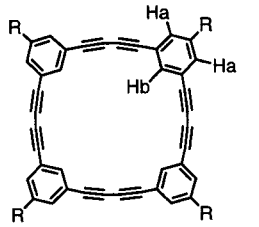
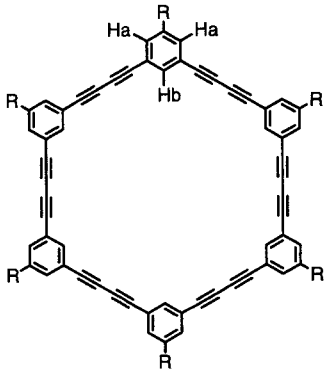
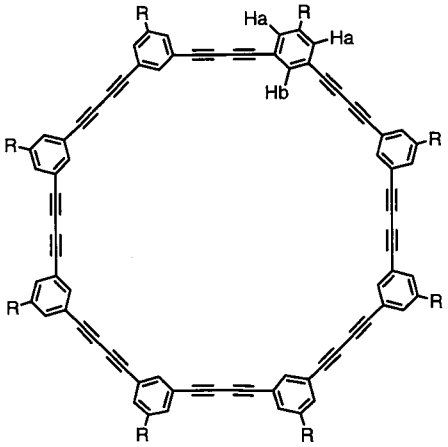
alkyl groups are necessary to ensure enough solubility to examine the aggregation behavior in apolar organic solvents such as chloroform and toluene and the polyether chains would make **2c** and **3c** slightly soluble in polar solvents such as acetone, acetonitrile, and methanol. This paper reports the general, efficient synthetic method for constructing the macrocyclic frameworks of DBMs and their self-aggregation behavior in apolar and polar solvents. The aggregation properties were investigated by two methods, one based on the ^{1}H NMR chemical shifts and the other based on the molal osmotic coefficient determined by the vapor pressure osmometry, and the results obtained by both methods were compared.



2a R = $CO_2C_8H_{17}$
2b R = $CO_2C_{16}H_{33}$
2c R = $CO_2(CH_2CH_2O)_3CH_3$
2e R = $CO_2C_4H_9$



3a R = $CO_2C_8H_{17}$
3b R = $CO_2C_{16}H_{33}$
3c R = $CO_2(CH_2CH_2O)_3CH_3$
3d R = H



4a R = $CO_2C_8H_{17}$
4c R = $CO_2(CH_2CH_2O)_3CH_3$
4d R = H

Results

Synthesis. To minimize the possible number of products, we first prepared even numbered tetrameric, hexameric, or octameric DBMs **2b**, **3b**, and **4b** by intermolecular oxidative coupling of the dimer unit **7b**.[28] However, since this method was not satisfactory in view of the low yields of **2b** and **4b** and the absence of cyclic hexamer **3b**, the stepwise method was employed to prepare tetrameric and hexameric DBMs **2a**,**c** and **3a**−**c** by intramolecular coupling of the corresponding open-chain oligomers **11a**,**c** and **13a**−**c**.

Synthesis of even-numbered linear precursors, dimers (2mers), linear tetramers (4mers), and linear hexamers (6mers) was carried out as outlined in Scheme 1.[29] Oxidative coupling with the Eglinton method[30] of **5a**−**c** gave doubly protected 2mers **6a**−**c**. Exhaustive deprotection of **6a**,**b** yielded fully deprotected 2mers **7a**,**b**, in 91% and 96% yields, respectively, while partial deprotection of **6a**−**c** under carefully controlled conditions gave the corresponding singly protected 2mers **8a**−**c** as the major products, together with **7a-c** and the starting materials **6a**−**c**. 2mers **8a** and **8c** were coupled under the usual Hay coupling conditions[31] to afford the corresponding linear 4mers **10a** and **10c**, which were deprotected to give linear 4mers **11a** and **11c**, respectively. Bromoacetylenes **9a**−**c** were prepared by the bromination of singly protected 2mers **8a**−**c**. Hetero coupling of **7a**−**c** with 2 equiv of the corresponding bromide **9a**−**c** under the modified literature conditions[32] gave linear 6mers **12a**−**c**, respectively. Removal of the triisopropylsilyl (TIPS) groups gave linear 6mers **13a**−**c**.

Cyclization reactions were carried out under Eglinton's conditions. Thus, reaction of **7b** under pseudo-high-dilution conditions (1.3×10^{-3} M) afforded cyclic 4mer **2b** (dimer of **7b**) and cyclic 8mer **4b** (tetramer of **7b**) in 10% and 2% yields, respectively, after purification by preparative HPLC. However, we were not able to isolate the corresponding 6mer **3b** (trimer of **7b**) under these conditions. Although we have no explanation for the absence (or very low yield, if any) of the hexameric DBM, such anomalous behavior has been frequently observed in the copper-mediated oxidative coupling reactions.[17a,18,30b] The cyclization of open-chain 4mers **11a** and **11c** under high dilution conditions (1.3×10^{-3} M) yielded the respective cyclic 4mers **2a** and **2c** and 8mers **4a** and **4c** (dimers of **11a** and **11c**), respectively. Eglinton coupling of linear 6mers **13a**−**c** under high dilution conditions yielded cyclic 6mers **3a**−**c** in 27%, 15%, and 65% yields, respectively. We also prepared 4mer **2e** having peripheral butyl ester groups by transesterification of **2a** with 1-butanol.[33] However, since this compound was sparingly soluble in organic solvents, we did not investigate its association behavior.

Self-Aggregation Behavior. The self-aggregation behavior of DBMs and the linear oligomers was investigated quantitatively on the basis of the concentration dependence of the ^{1}H NMR chemical shifts and the molal osmotic coefficient (ϕ) determined by vapor pressure osmometry (VPO). The aggregation behavior of linear tetramers **11a**,**c** and hexamers **13a**,**c** was also investigated. In addition, concentration dependence of the UV spectra of DBMs and the linear oligomers was studied.

^{1}H NMR spectroscopy is the most frequently used technique for investigation of aggregation due to stacking interaction of nucleic acids and aromatic compounds because of its ease, precision, and the fact that the chemical shift data provide

(28) Although it has been reported that oxidative coupling of 1,3-diethynylbenzene gave the unsubstituted hexamer, we were unable to reproduce the reaction: Ghose, B. N. *J. Prakt. Chem.* **1982**, *324*, 1052−1054.

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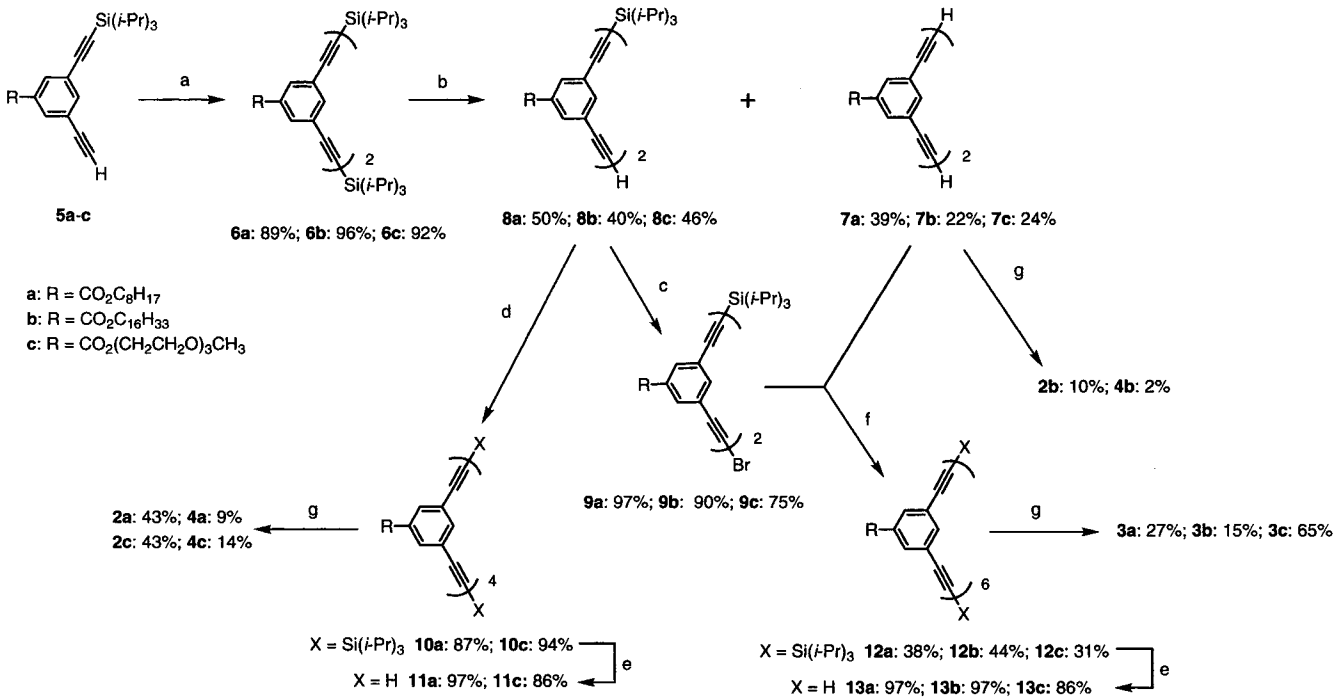
(33) Synthesis of **2e** is described in the Supporting Information.

Scheme 1 [a]

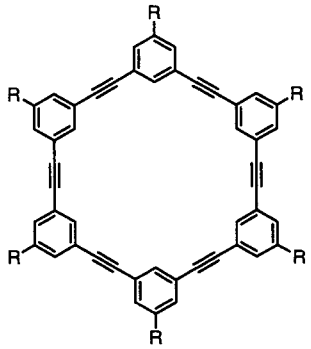


[a] Key: **a**, R = $CO_2C_8H_{17}$; **b**, R = $CO_2C_{16}H_{33}$; **c**, R = $CO_2(CH_2CH_2O)_3CH_3$. (a) $Cu(OAc)_2$, pyridine, room temperature; (b) TBAF, THF, H_2O, room temperature; (c) NBS, $AgNO_3$, acetone, room temperature; (d) CuCl, TMEDA, acetone, O_2, room temperature; (e) TBAF, THF, room temperature; (f) $Pd_2(dba)_3{\cdot}CHCl_3$, CuI, *i*-Pr_2NH, benzene, room temperature; (g) $Cu(OAc)_2$, pyridine, benzene, room temperature.

structural information for the aggregates.[34] Indeed, the ^{1}H NMR chemical shifts of the aromatic protons of DBMs **2a**−**c**, **3a**−**c**, and **4a** in $CDCl_3$ showed remarkable concentration dependence.[35] For example, the chemical shifts of the two anisochronous aromatic protons (H_a and H_b) of cyclic 6mer **3a** moved upfield from δ 8.12 to 7.50 (*exo*-annular proton, H_a) and from δ 7.84 to 7.30 (*endo*-annular proton, H_b) as the concentration increased from 1.53×10^{-4} to 5.36×10^{-3} M at 30 °C. The upfield shift indicates that the aggregates adopt a structure in which the macrocyclic frameworks stack in a face-to-face geometry, as observed frequently in self-association due to $\pi-\pi$ stacking interactions.[7,12,15,34] The association constants (K_2) were determined by assuming that monomer−dimer equilibrium is the predominant process of the self-association, since, in most cases, the analysis based on the osmometric method agreed with this assumption as described later. The least-squares curve fitting to eq 1[36] was carried out to determine K_2, where δ_m and δ_d are

$$\delta = \delta_m + (\delta_d - \delta_m)\left(1 + \frac{1 - \sqrt{8K_2C_t + 1}}{4K_2C_t}\right) \qquad (1)$$

chemical shifts of the monomer and the dimer, respectively, and K_2 and C_t are dimerization constant and total concentration of the substrate, respectively. The dilution curves for **3a** and **3b** are shown in Figure 1. In most cases, the association constants calculated from *exo*-annular proton H_a gave slightly larger K_2 than those calculated from the data for *endo*-annular proton H_b.[37] The thermodynamic parameters for the dimerization of the DBMs were elucidated on the basis of the van't Hoff plots (Figure 2), using K_2 determined at 4−5 different temperatures. The dimerization constants calculated for *exo*-annular proton H_a and the corresponding thermodynamic parameters for the dimerization of DBMs **2a**−**c**, **3a**,**b**,and **4a** in $CDCl_3$ are listed in Table 1, together with those of PAM **14a** reported by Moore[7b] for comparison.



14a R = $CO_2C_4H_9$
14b R = $CO_2(CH_2CH_2O)_3CH_3$
14c R = H

It has been demonstrated that solvophobic interactions of organic solvents exert a crucial effect on the dimerization of rigid cyclophanes[38] and inclusion of an aromatic guest in diphenylmethane-based cyclophanes.[39] Self-association behavior of PAMs and related macrocycles is also sensitive to the polarity of the solvent.[7c,12] Moreover, a remarkable solvophobic effect on the intramolecular association of linear oligomers of *m*-

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(35) However, the ^{1}H NMR chemical shifts of 8mer **3c** having the polyether chains did not exhibit concentration dependence in $CDCl_3$.
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(37) All NMR and osmometric data and some UV spectra are listed in the Supporting Information.
(38) Cram, D. J.; Choi, H.-J.; Bryant, J. A.; Knobler, C. B. *J. Am. Chem. Soc.* **1992**, *114*, 7748−7765.
(39) Smithrud, D. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 339−343.

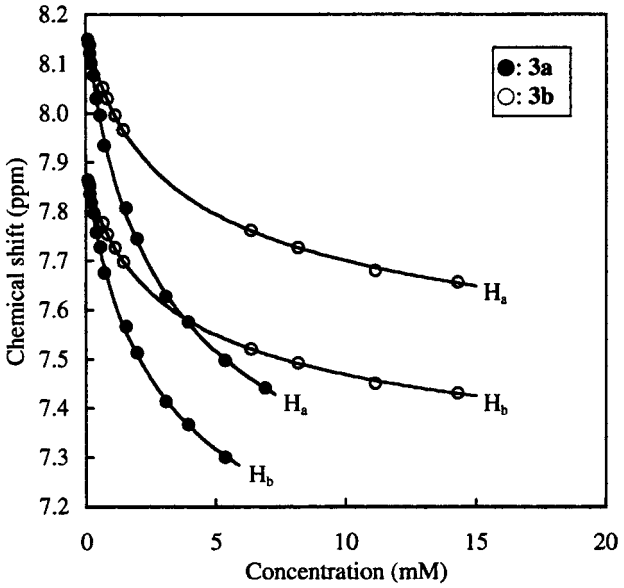


Figure 1. Concentration dependence of ^{1}H NMR chemical shifts for *exo*-annular aromatic protons (H_a) and *endo*-annular aromatic protons (H_b) of **3a** and **3b** in $CDCl_3$ at 30 °C.

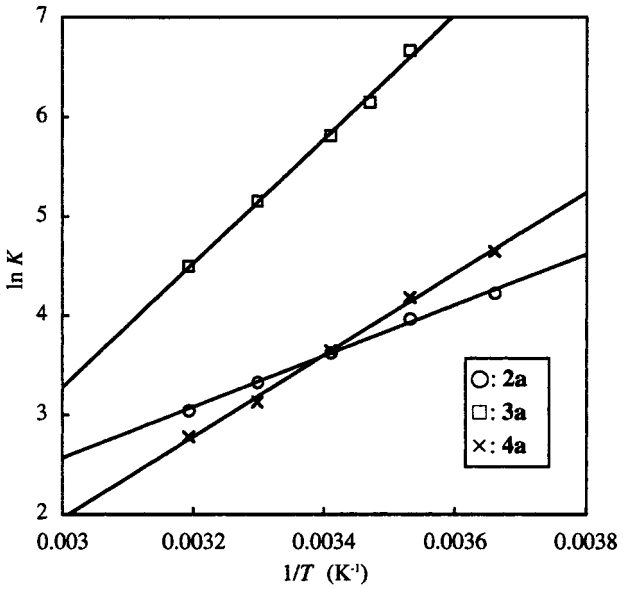


Figure 2. van't Hoff plots for self-association of DBMs **2a**, **3a**, and **4a** in $CDCl_3$.

Table 1. Dimerization Constants and Thermodynamic Parameters for Self-Aggregation of DBMs **2a**−**c**, **3a**−**c**, and **4a** and PAM **14a** in $CDCl_3$ at 303 K[a]

compd	K_2 (M^{-1})	ΔG (kJ·mol^{-1})	ΔH (kJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})
2a	27.9 ± 0.7	−8.38 ± 0.07	−21 ± 1	−42 ± 2
2b	28.7 ± 2.4	−8.46 ± 0.22	−24 ± 1	−50 ± 3
2c	19.9 ± 1.3	−7.53 ± 0.17	−15 ± 1	−26 ± 2
3a	173 ± 17	−13.0 ± 0.3	−52 ± 2	−128 ± 6
3b	150 ± 4	−12.6 ± 0.1	−39 ± 2	−88 ± 6
3c	42.7 ± 1.4	−9.45 ± 0.08	−31 ± 1	−71 ± 3
4a	22.8 ± 0.9	−7.88 ± 0.10	−34 ± 1	−86 ± 4
14a[b]	39	−9.3	−21 ± 0.8	−39 ± 3

[a] Determined on the basis of the dimerization model by the NMR method. [b] Calculated from the data in ref 7b.

phenylacetylene, forming helical structures in polar solvents, has been reported by Moore and co-workers.[7c,40] We examined the effect of polar solvents such as deuterated acetone, aceto-

Table 2. Association Constants and the Corresponding Free Energies for Self-Aggregation of DBMs **2c** and **3c** in Polar Solvents at 303 K[a]

DBM	solvent	K_E (M^{-1})	ΔG (kJ·mol^{-1})
2c	CD_3COCD_3	19100 ± 1900	−24.8 ± 0.3
	$CD_3CN/CDCl_3$ = 3/7	184 ± 14	
	$CD_3CN/CDCl_3$ = 5/5	1150 ± 70	
	$CD_3CN/CDCl_3$ = 6/4	1990 ± 150	
	$CD_3CN/CDCl_3$ = 7/3	3170 ± 260	
	$CD_3CN/CDCl_3$ = 8/2	8070 ± 1190	
	CD_3CN[b]	27000	−26
	$CD_3OD/CDCl_3$ = 2/8	111 ± 3	
	$CD_3OD/CDCl_3$ = 3/7	307 ± 6	
	$CD_3OD/CDCl_3$ = 5/5	2260 ± 140	
	$CD_3OD/CDCl_3$ = 7/3	13000 ± 1000	
	CD_3OD[b]	150000	−30
3c	$CD_3OD/CDCl_3$ = 1/9	102 ± 4	
	$CD_3OD/CDCl_3$ = 2/8	316 ± 16	
	$CD_3OD/CDCl_3$ = 3/7	1050 ± 80	
	$CD_3OD/CDCl_3$ = 4/6	2610 ± 550	
	CD_3OD[b]	580000	−33

[a] Determined on the basis of the infinite association model by the NMR method. [b] Extrapolated to pure solvent from the plot of ΔG vs solvent composition shown in Figure 3.

nitrile, and methanol on the association of DBMs **2c** and **3c** bearing ester groups of triglyme monomethyl ether. Unfortunately, because of significant peak broadening, the dilution experiment was not carried out for **3c** in CD_3COCD_3 and CD_3CN. Since **2c** and **3c** were not soluble in neat CD_3CN and CD_3OD at the NMR concentration level, the NMR experiments were carried out in mixed solvent systems, $CD_3CN/CDCl_3$ and $CD_3OD/CDCl_3$, of several different compositions. Although the chemical shift data fit nicely to the theoretical curves derived from eq 1 for dimerization, the data were analyzed by the infinite (isodesmic) association model, assuming the formation of higher aggregates shown in Scheme 1, since the VPO analysis clearly indicated the formation of higher aggregates as described later. The least-squares curve fitting was thus carried out with eq 2 ,

$$\delta = \delta_m + (\delta_a - \delta_m)\left(1 + \frac{1 - \sqrt{4K_E C_t + 1}}{2K_E C_t}\right) \qquad (2)$$

assuming $K_2 = K_3 = K_4 = ... = K_n = K_E$, in which δ_a is the average chemical shift of the aggregates.[41] As expected, **2c** and **3c** exhibited an increasing tendency to self-associate with an increasing portion of the polar solvent relative to $CDCl_3$ (Table 2), indicating that the aggregate formation was enhanced by the solvophobic interactions. The linear relationship between the free energy of association versus the composition of the polar solvent in $CDCl_3$ was observed as shown in Figure 3, from which K_E in neat CD_3CN and CD_3OD was estimated by extrapolation. Similar effect of the solvent composition on the conformation of linear phenylacetylene oligomers was reported.[40b] Comparison of the association constants summarized in Table 2 with those in Table 1 clearly indicates that the self-aggregation

(40) (a) Nelson, J. C.; Saven, J. G.; Moore, J. S.; Wolynes, P. G. *Science* **1997**, *277*, 1793−1796. (b) Prince, R. B.; Saven, J. G.; Wolynes, P. G.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 3114−3121.

(41) Since all the NMR dilution data fit nicely to the assumptions of both eqs 1 and 2, we did not examine the model in which the association constant for dimerization (K_2) is different from those for the formation of higher aggregates ($K_2 \neq K_E$).[34] A case has recently been found in the aggregation of an imine-containing PAM, in which NMR data did not fit the $K_2 = K_E$ model but fit the $K_2 \neq K_E$ model; personal communication from Prof. Moore.

Table 3. Association Constants and Thermodynamic Parameters for Self-Aggregation of DBMs **2a**,**c**, **3a**,**c**, and **4a** and PAM **14b** in Aromatic Solvents at 303 K[a]

compd	solvent	K_E (M^{-1})	ΔG (kJ·mol^{-1})	ΔH (kJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})
2a	toluene-d_8/$CDCl_3$ = 1/9	63.6 ± 4.1			
	toluene-d_8/$CDCl_3$ = 2/8	75.3 ± 6.2			
	toluene-d_8/$CDCl_3$ = 3/7	83.9 ± 4.4			
	toluene-d_8/$CDCl_3$ = 4/6	98.9 ± 12.2			
	toluene-d_8/$CDCl_3$ = 5/5	115 ± 26			
	toluene-d_8[b]	240	−14		
2c	toluene-d_8[c]	163 ± 11	−12.8 ± 0.2	−28 ± 1	−51 ± 2
3a	toluene-d_8[c]	210000	−31	−120 ± 10	−300 ± 30
	o-xylene-d_{10}[c]	19000	−25	−100 ± 10	−260 ± 30
3c	toluene-d_8[c]	30000	−26	−90 ± 3	−210 ± 10
4a	toluene-d_8	340 ± 70	−14.7 ± 0.6	−120 ± 20	−330 ± 50
14b	benzene-d_6[d]	1200	−18		

[a] Determined on the basis of the infinite association model by the NMR method. [b] Extrapolated to pure solvent from the plot of ΔG vs solvent composition. [c] Extrapolated from the association constants determined at higher temperatures. [d] Data from ref 7c at room temperature (not specified).

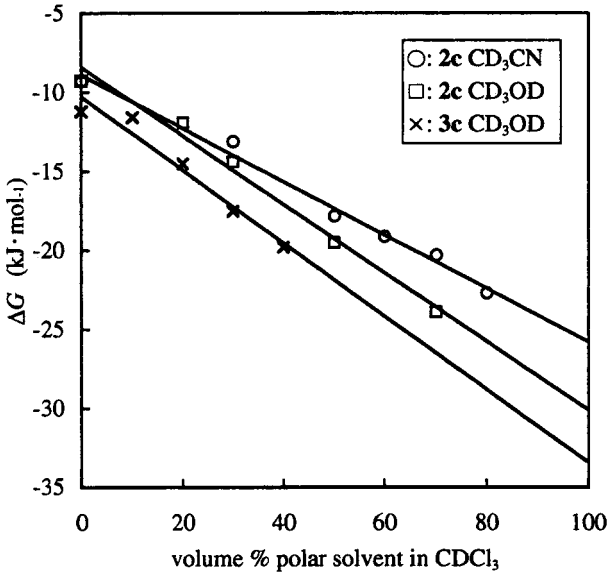


Figure 3. Relationship between ΔG of aggregation of DBMs **2c** and **3c** and the composition of the polar solvents in $CH_3CN/CHCl_3$ and $CH_3OH/CHCl_3$ systems.

of DBMs is remarkably enhanced by the solvophobic interactions.[42]

As for the effect of aromatic solvents on the association behavior of PAMs, Moore reported that PAM **14a** did not show concentration-dependent chemical shifts in benzene-d_6.[7b] However, in the subsequent paper, its derivative **14b** bearing polyether chains was reported to aggregate more strongly in benzene-d_6 than in $CDCl_3$.[7c] Enhancement of self-aggregation in an aromatic solvent was also noted by Yamaguchi and coworkers for chiral macrocycles.[15] We had also been aware of the unexpected aggregation behavior of DBMs in aromatic solvents.[43] Because of the low solubility in benzene, the NMR dilution experiments were undertaken in toluene-d_8 for **2a**,**c**, **3a**,**c** and **4a**. For **3a**, self-aggregation was also examined in *p*-xylene-d_{10}. The data were treated with eq 2, assuming the infinite association, since the VPO analysis for **2c** and **3c** strongly indicated the formation of aggregates larger than dimers in toluene (vide infra).[37] In the case of **3a** and **3c**, it was not possible to measure the precise chemical shifts at 30 °C owing to the significant peak broadening. Therefore, the measurements were carried out at several different temperatures to elucidate thermodynamic parameters in order to make direct comparison of the association propensities possible (see Supporting Information for the van't Hoff plots). Since DBMs **2a** was much less soluble in toluene-d_8 than in $CDCl_3$, its association constant at 30 °C was estimated by extrapolating from the data in toluene-d_8/$CDCl_3$ mixtures of several different compositions (see Supporting Information for the plot of ΔG vs solvent composition), as in the case of the dilution experiments in polar solvents. The results are summarized in Table 3. As shown, the association was remarkably enhanced in the aromatic solvents compared to that in $CDCl_3$, which we had not expected at the outset.

Besides the NMR method, self-aggregation of solutes is frequently analyzed on the basis of the molal osmotic coefficient (ϕ) determined by vapor pressure osmometry (VPO).[34] Since the mosmotic measurements are colligative and count moles in solution, this method may sense aggregates which do not exhibit upfield shift in the NMR spectra. Moreover, there exist problems in the use of NMR for the investigation of higher aggregation behavior due to the oversimplification of the analysis models, significant line broadening, and the concentration limits arising from solubility and sensitivity. To check the reliability of the results obtained by the NMR experiments, we examined the association behavior of **2a** ($CHCl_3$, 40 °C), **2c** ($CHCl_3$, 40 °C; toluene, 60 °C; acetone 40 °C), **3a** ($CHCl_3$, 40 °C), and **3c** ($CHCl_3$, 40 °C; toluene, 60 °C; acetone 40 °C) by VPO.

In the VPO measurements, osmotic coefficient (ϕ), activity coefficient (γ), and monomer concentration (m_1) were calculated for each sample solution with use of the coefficients of the sixth order polynominal, which were obtained by curve fitting, using the experimental data, stoichiometric molal concentration (m_s), and colligative molal concentration (m_c), to the polynominal equation (see the Experimental Section).[37] For analysis of the data, we employ two models, the equal K model,[44] which assumes $K_2 = K_3 = K_4 = ... = K_n = K_E$ and $K_{n+1} = 0$, and the $K_2 \neq K$ model,[45] which assumes $K_2 \neq K$ together with a few different hypotheses regarding the relationship between the association constants for the formation of higher aggregates. In

(42) Although the definitions of K_2 and K_E are different, comparison of eqs 1 and 2 indicates K_E can formally be regarded to be twice as large as K_2.
(43) Araki, S.; Adachi, K.; Nagano, A.; Kawabata, K.; Utsumi, N.; Sonoda, M.; Hirose, K.; Tobe, Y. *XI International Symposium on Supramolecular Chemistry*, July 30 to August 4, 2000, Fukuoka, Japan: Abstract of papers, p 411.
(44) Ts'o, P. O.; Chan, S. I. *J. Am. Chem. Soc.* **1964**, *86*, 4176−4181.
(45) Rossotti, F. J. C.; Rossotti, H. *J. Phys. Chem.* **1961**, *65*, 930−934.

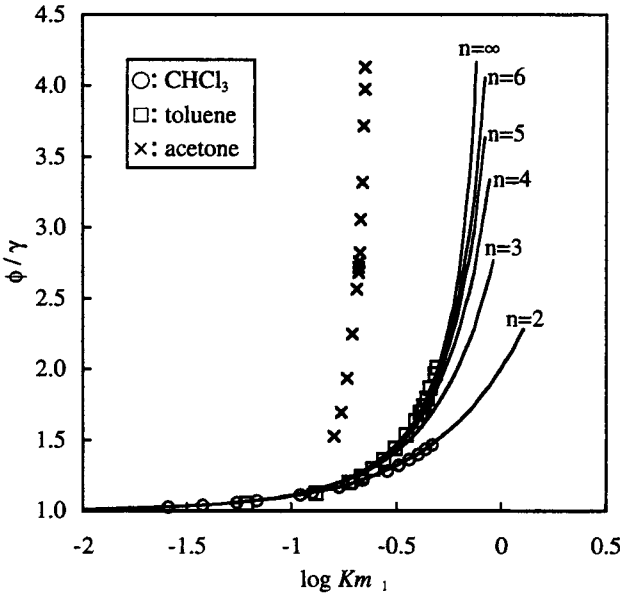


Figure 4. Master curves of $[1 - (Km_1)^n]/(1 - Km_1)$ vs log Km_1 and data plots for determination of association constants of DBM **2c** in chloroform at 40 °C, toluene at 60 °C, and acetone at 40 °C according to the equal *K* model.

Table 4. Association Constants for Self-Aggregation of DBMs **2a**,**c** and **3a**,**c** Determined by the VPO Method on the Basis of the Equal *K* Model

DBM	solvent	temp (°C)	K_2 or K_E (*n*) (M^{-1})
2a	$CHCl_3$	40	K_2: 146
2c	$CHCl_3$	40	K_2: 45
	toluene	60	K_E: 139 ($n = \infty$)
3a	$CHCl_3$	40	K_E: 350 ($n = 6$)
3c	$CHCl_3$	40	K_2: 428

the first model, on the basis of eq 3, which relates ϕ/γ to *K* and m_1, the master curves are plotted for $[1 - (K_E m_1)^n]/(1 - K_E m_1)$ versus log $K_E m_1$ for different *n* ($n = 1$, 2, 3, 4, 5, 6, and ∞) of the monomer units in the largest aggregate present in a solution.

$$\frac{\phi}{\gamma} = \frac{1 - (K_E m_1)^n}{1 - K_E m_1} \tag{3}$$

Fitting a plot of the experimentally obtained ϕ/γ versus log m_1 to the plots yielded log *K* as the translation along the abscissa.[44] As examples, Figure 4 shows plots of the data for **2c** in chloroform, toluene, and acetone. As can be seen, the data in $CHCl_3$ fit the master curve of $n = 2$, yielding $K_2 = 44.8\ M^{-1}$, while the data in toluene fit the curve of $n = \infty$, furnishing $K_E = 139\ M^{-1}$. Importantly, this analysis allowed the elucidation of the mode of association, i.e., dimerization or further aggregation. The results are summarized in Table 4. The aggregation of **2a**, **2c**, and **3c** in chloroform was confirmed to form dimers mainly, while **2a** forms higher aggregates ($n = \infty$) in toluene. The aggregation of **3a** in chloroform is an intermediate case, which forms up to hexamer ($n = 6$) with a comparable association constant to that obtained by the NMR method.[42] However, taking into account the difference between the temperature of the measurements, the association constants determined by VPO method are, in general, considerably larger than the corresponding data determined by NMR.[46]

As shown in Figure 4, the plot for **2c** in acetone did not fit any of the master curves. Similarly, the data for **3c** in toluene and acetone did not fit the theoretical curves based on the equal *K* model. For these case, extremely large K_E ($>10^4$) was determined by the NMR method. It turned out that the data fit to the $K_2 \neq K$ model developed by Rossotti.[45] In this model, four different hypotheses I−IV are considered, which relate the association constants for the formation of higher aggregates as shown in eqs 4, 6, 8, and 10, respectively. For each model, *T*, defined in eq 12, is related to m_1 in eqs 5, 7, 9, and 11, respectively.

Hypothesis (I): $$K_3 = K_4 = K_5 = ... = K_n = K_E \tag{4}$$

$$T = \sum_2^\infty n(Km_1)^{n-1} = \frac{Km_1(2 - Km_1)}{(1 - Km_1)^2} \tag{5}$$

Hypothesis (II):

$$K_3 = \frac{1}{2}K,\ K_4 = \frac{2}{3}K,\ K_5 = \frac{3}{4}K,\ ...,\ K_n = \frac{n-2}{n-1}K \tag{6}$$

$$T = \sum_2^\infty \frac{(Km_1)^{n-1}}{n-1} = \frac{Km_1}{1 - Km_1} - \ln(1 - Km_1) \tag{7}$$

Hypothesis (III):

$$K_3 = \frac{1}{2}K,\ K_4 = \frac{1}{3}K,\ K_5 = \frac{1}{4}K,\ ...,\ K_n = \frac{1}{n-1}K \tag{8}$$

$$T = \sum_2^\infty \frac{n(Km_1)^{n-1}}{(n-1)!} = e^{Km_1}(1 + Km_1) - 1 \tag{9}$$

Hypothesis (IV):

$$K_3 = 2K,\ K_4 = \frac{3}{2}K,\ K_5 = \frac{4}{3}K,\ ...,\ K_n = \frac{n-1}{n-2}K \tag{10}$$

$$T = \sum_2^\infty n(n-1)(Km_1)^{n-1} = \frac{2Km_1}{(1 - Km_1)^3} \tag{11}$$

$$T = \frac{K(m_s - m_1)}{K_2 m_1} \tag{12}$$

The master curves are plotted for log *T* versus log Km_1 by using eqs 5, 7, 9, and 11. Fitting a plot of experimentally obtained log $[(m_s - m_1)/m_1]$ versus log m_1 to the master plots gave log *K* as the translation along the abscissa and $\log(K/K_2)$ as the translation along the ordinate. As an example, Figure 5 shows a plot for **2c** in acetone. The data fit best to model IV among the hypotheses I−IV, furnishing $K_2 = 552\ M^{-1}$ and $K = 3370\ M^{-1}$. Since, in general, the data fit best to hypothesis IV, K_2 and *K* shown in Table 5 were calculated with this model.[47] Table 5 also lists the higher aggregation constants, K_3, K_4, and K_∞ calculated from eq 10, to show clearly the respective binding constants. At first glance, it is rather surprising that, compared to the large K_E determined by NMR, the association constants (K_2 and *K*) determined by the $K_2 \neq K$ model are

(46) The problems which would reduce the reliability of the analysis based on NMR would not apply in the monomer−dimer models. Accordingly, we do not have explanations at this moment for the relatively large discrepancy between the association constants determined by NMR and VPO.

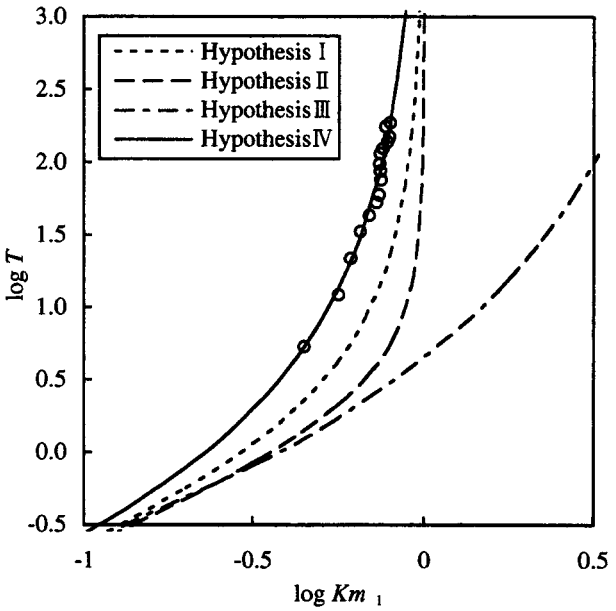


Figure 5. Master curves of log T vs log Km_1 and a data plot for determination of the association constant of DBM **2c** in acetone at 40 °C according to the $K_2 \neq K$ model.

Table 5. Association Constants for Self-Aggregation of DBMs **2c** and **3a**,**c** Determined by the VPO Method on the Basis of the $K_2 \neq K$ Model[a]

DBM	solvent	temp (°C)	K_2 (M^{-1})	K (M^{-1})	K_3 (M^{-1})	K_4 (M^{-1})	K_∞ (M^{-1})
2c	toluene	60	111	104	208	156	104
	acetone	40	552	3370	6740	5060	3370
3a	$CHCl_3$	40	566	342	682	513	342
3c	toluene	60	350	2580	5160	3870	2580
	acetone	40	1180	3170	6340	4760	3170

[a] Analyzed on the basis of the hypothesis (IV).

considerably smaller. However, when taking the difference between the temperature into account, it becomes apparent that the discrepancy is moderate. Namely, with the difference of 30 °C between the temperature of the NMR and VPO measurements,[48] one can roughly estimate $K_3 = 16000\ M^{-1}$ and $K_4 = 12000\ M^{-1}$ and so on for the aggregation of **2c** in acetone, which are still smaller than but in the same order as that determined by the NMR method ($K_E = 28000\ M^{-1}$). The data for **2c** in toluene and those for **3a** in $CHCl_3$ were also analyzed by this model to give the results consistent with those obtained by the equal K model, i.e., $K_2 \approx K$. It should be pointed out that the analysis of self-aggregation by VPO thus revealed the unique aggregation behavior of DBMs in acetone and toluene, which was not elucidated by the NMR method.

To elucidate the effect of the macrocyclic structure on the aggregation property of DBMs **2a**,**c** and **3a**,**c**, the aggregation behavior of the corresponding linear tetramers **11a**,**c** and hexamers **13a**,**c** was also investigated by NMR and VPO. In $CDCl_3$ and toluene-d_8, none of the linear oligomers exhibit concentration dependence of the chemical shifts, indicating the critical importance of the macrocyclic structure of DBMs for the self-aggregation in apolar and aromatic solvents. On the other hand, **11c** and **13c** aggregate in polar solvents although much less strongly than DBMs.[49] The association constants K_2 and K_E were determined by NMR and VPO in CD_3COCD_3 (or acetone), CD_3CN, and $CD_3OD/CDCl_3 = 7/3$. Owing to the broadening of the NMR peaks, the data for **13c** in CD_3CN were not obtained. Since the VPO data of 4mer **11c** fit well the dimerization curve ($n = 2$) of the equal K model, the NMR data were analyzed assuming the dimer formation (eq 1). On the other hand, the VPO data of 6mer **13c** fit the master plot of infinite aggregation ($n = \infty$) for the equal K model. This was confirmed by the $K_2 \neq K$ model, which gave comparable K_2 and K. The NMR data for **13c** were, therefore, treated with the infinite association model (eq 2). The results are listed in Table 6. Comparison of the data in Table 6 with those in Tables 2, 4, and 5 indicates that the aggregation propensity of the linear oligomers **11c** and **13c** is much less than that of the corresponding DBMs **2c** and **3c**. It is worth noting, however, that the aggregation of liner oligomers is observed only in polar solvents, indicating that the aggregation is solvophobically driven.

The electronic spectrum is another proof for the investigation of $\pi-\pi$ stacking interactions, since electronic interactions between the chromophores cause spectral changes, in most cases a hypochromic shift.[50] The absorption spectra of DBMs **2c** and **3c** and liner oligomers **11c** and **13c** were recorded in $CHCl_3$, $CH_3CN/CHCl_3 = 9/1$ and $CH_3OH/CHCl_3 = 9/1$ in a concentration ranging from ca. 1×10^{-6} to 5×10^{-5} M. Under these conditions, little concentration dependence was observed in the spectra of **2c** and **3c** in $CHCl_3$ and those of **11c** and **13c** in all solvents. On the other hand, the spectra of **2c** and **3c** in polar solvents exhibit remarkable hypochromic shift with slight hypsochromic shift of the abosorption bands at 280−340 nm, as a result of strong aggregation. Figure 6 shows the spectra of **2c** in $CH_3OH/CHCl_3 = 9/1$ as an example.[37]

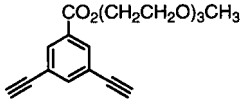
Discussion

General Features of Self-Association of DBMs. Owing to the limitations due to solubility, peak broadening in NMR, and the sensitivity limit of the VPO reading particularly when extremely large aggregates were formed, it was not possible to obtain the data which would allow direct comparison of all association constants determined by different methods under

(47) The difference between hypotheses I and IV are the relationship between the higher association constants, either constant (I), gradually increasing (II) to $K_\infty = K$, rapidly dropping to $K_\infty = 0$ (III), or gradually decreasing $K_\infty = K$ (IV). The difference must be due to the steric and electrostatic interactions in the step-by-step formation of higher aggregates as discussed in ref 47a. In all the cases we examined, hypothesis II gave the worst fit to the experimental data, excluding the possibility of this model. Although the model IV gave the best fit in most cases, a similarly good fit was obtained with hypotheses I and III in some cases. With the available data, it is not possible to explain why hypothesis IV gave better fits. However, hypothesis IV also turns out to be satisfactory in the analysis of aggreagation reported in the literature using Rossotti's model. For example, see: (a) Ghosh, A. K.; Mukerjee, P. *J. Am. Chem. Soc.* **1970**, *92*, 6408−6412. (b) Klofutar, C.; Paljk, S.; Abram, V. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3065−3069.

(48) By lowering the temperature by 10 °C, we assume a 1.5 times increase of association constants.

(49) The monomer unit **15** did not show concentration dependence of the NMR chemical shift in the same polar solvents, suggesting that at least a few diethynylbenzene units are necessary to effect aggregation.



15

The preparation of **15** is described in the Supporting Information.

(50) For example: Diederich, F. *Cyclophanes*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, 1991; pp 19−21.

Table 6. Association Constants for Self-Aggregation of Linear Oligomers **11c** and **13c** in Polar Solvents at 303 K

compd	solvent	method (model for data analysis)	K_2, K_E (n), or K (M^{-1})
11c	CD_3COCD_3	NMR (dimer model)	K_2: 9.12 ± 0.38
	acetone	VPO (equal K model)	K_2: 38.2
	CD_3CN	NMR (dimer model)	K_2: 22.0 ± 6.9
	$CD_3OD/CDCl_3$ = 7/3.	NMR (dimer model)	K_2: 28.0 ± 1.9
13c	CD_3COCD_3	NMR (infinite association model)	K_E: 86.1 ± 5.6
	acetone	VPO (equal K model)	K_E: 107 ($n = \infty$)
	acetone	VPO ($K_2 \neq K$ model))	K_2: 75.6, K_2: 105
	$CD_3OD/CDCl_3$ = 7/3	NMR (infinite association model)	K_E: 841 ± 43

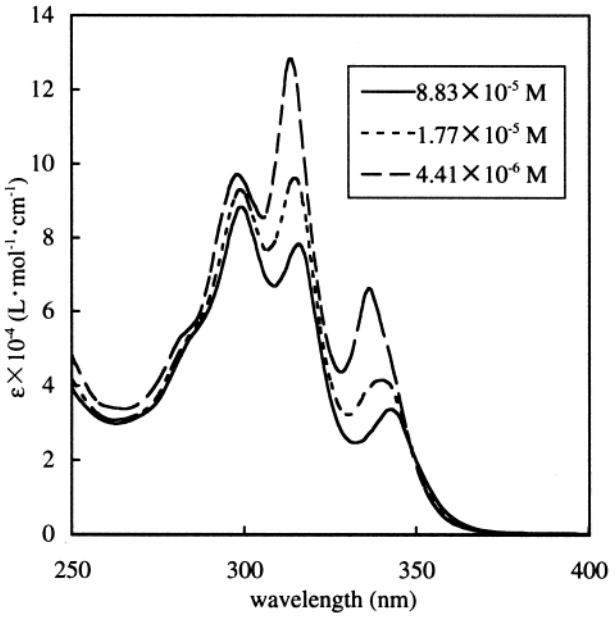


Figure 6. UV spectra of DBM **2c** in $CH_3OH/CHCl_3$ = 9/1 at 30 °C.

different conditions. Qualitatively the data derived from the NMR method agree with those from VPO. However, there exist discrepancies between the data derived by the two methods; the VPO method tends to give larger association constants than those from the NMR method when the extent of aggregation is small.[46] On the contrary, VPO tends to give smaller association constants than those from NMR when large aggregates are formed with large association constants. The latter may be due to the problem in the use of NMR for analysis of higher aggregation as described before.

The analysis of self-aggregation by VPO revealed unique aggregation behavior of DBMs **2c** in acetone and **3c** in toluene and acetone, which was not obtained from the NMR method as long as the infinite association model was used. Namely, the osmotic data can only be analyzed by the $K_2 \neq K$ model, and it appeared the association constants for infinite association (K_3, K_4, and K_∞) are several times larger than the dimerization constant (K_2), indicating that the formation of the higher aggregates is more favorable than that of the dimers due to the solvophobic interactions. In other words, the aggregation is enhanced by the formation under these conditions, suggesting a nucleation mechanism. These results demonstrate that the methods and models for analysis are critical for investigation of aggregations particularly when extensive aggregation takes place.

Like self-association of PAMs[7] and the related macrocycles,[12,15] the driving forces of self-association of DBMs are attributed to $\pi-\pi$ stacking and solvophobic interactions between the planar macrocyclic framework of DBMs for the following reasons. (1) There is no functional group capable of forming a hydrogen bond. (2) Polar solvents remarkably enhance the propensity toward aggregation. (3) In the NMR spectra, the upfield shift of the aromatic protons was observed due to the influence of the ring current of the aromatic rings of the neighboring molecules. Only the aromatic protons show remarkable concentration-dependent chemical shifts. The chemical shifts of the aliphatic protons did not move in the same concentration range. (4) Hypochomic shift of the UV spectra was observed in polar solvents, when the degree of aggregation was high. (5) Linear oligomers **11a**,**c** and **13a**,**c** did not show a concentration-dependent chemical shift in apolar solvents. Polyether esters **11c** and **13c** aggregate only weakly in polar solvents. Accordingly, the cyclic array of aromatic rings is indispensable for the self-association.

Self-Association in Chloroform. As mentioned above, DBMs and PAMs showed qualitatively similar self-association behavior in $CDCl_3$. The common features are as follows: (1) As shown in Table 1, the dimerization of DBMs in $CDCl_3$ is enthalpy driven ($\Delta H < 0$) and entropy opposed ($\Delta S < 0$). (2) In the series of DBMs having the same functional group and a different ring size, cyclic 6mers **3a**−**c** show the most negative ΔH values, indicating that cyclic 6mers self-associate most strongly due to the $\pi-\pi$ stacking interaction. The smaller association force of 4mers **2a**−**c** than that of **3a**−**c** is ascribed to the smaller number of possible $\pi-\pi$ stacking interaction sites. The less negative ΔH value of 8mer **4a** than that of 6mer **3a** is ascribed to the nonplanar geometry and the conformational flexibility of **4a**. Molecular modeling[51] for model hydrocarbon **4d** with the AM1 method indicates the presence of a number of stable nonplanar conformers within a small energy difference (<0.2 kJ·mol^{-1}).[18b] On the contrary, the calculated geometry of the parent 6mer **3d** adopts a planar conformation.[18b] (3) The effect of the length of the alkyl chain is negligible. On the other hand, the aggregation propensity of the polyether esters **2c** and **3c** is lower than that of the alkyl esters, presumably because the polyether moieties are better solvated by chloroform than the hydrocarbon chain. In other words, the nonpolar hydrocarbon chain may facilitate, to some extent, the aggregation of DBMs due to solvophobic interactions between the alkyl chains and the solvent.

Comparison of the association constants and thermodynamic parameters in $CDCl_3$ of DBM **3a** and those of PAM **14a**, having the same number of aromatic rings, reveals several remarkable differences between their association properties. (1) First, the association of **3a** is enthalpically more favored than that of **14a**. For example, the association constant of **3a** is more than four times larger than that of **14a** at 30 °C. This implies that the butadiyne units are a more effective activator for $\pi-\pi$ stacking

(51) *SPARTAN*, verson 5.0 program package; Wavefunctin, Inc.: Irvine, CA.

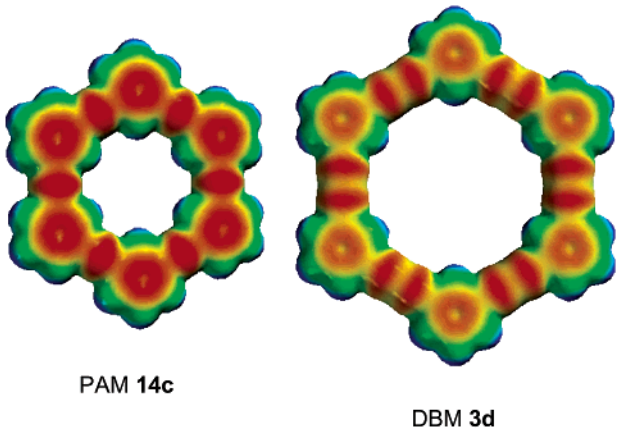


Figure 7. Calculated electrostatic potentials on the van der Waals molecular surfaces of model compounds **3d** and **14c**, based on HF/3-21G single point calculations for the geometries optimized by semiempirical AM1 calculations. The potentials are drawn in the same color scale, with red indicating more negative electrostatic potentials and blue more positive potentials.

interactions than the acetylene units. Since it has been well-documented that an electron-withdrawing group activates an aromatic ring toward $\pi-\pi$ stacking interactions,[7,22c] the activating effect of the butadiyne units is attributed to the strong electron-withdrawing effect of this group. Indeed, as shown in Figure 7, the electrostatic potentials of the model compound **3d** and **14c** on the basis of the molecular orbital calculations (AM1//3-21G) indicate that the aromatic rings of **3d** are more electron-deficient than those of **14c**. (2) DBM 6mers **3a**−**c** and 8mer **4a** show large negative ΔS values compared to PAM **14a**. In general, the reported entropy of association of two components in an apolar solvent ranges from about −46 to −63 $J\cdot mol^{-1}\cdot K^{-1}$.[52] Unusually large negative ΔS values observed for **3a**,**b** and **4a** may be indicative of some ordering of the alkyl chains in solution due to solvophobic interactions. (3) Moore reported that the values of ΔH and ΔS could not be obtained for flexible PAM having seven phenylacetylene units (heptameric PAM) by the van't Hoff plot because of the change in proportion of conformers at different temperatures.[7b] On the contrary, DBM 8mer **4a** exhibits the straight van't Hoff plot as shown in Figure 2. Probably the population of the conformers of **4a** does not change significantly over the temperature range of the measurements.

Self-Association in Polar Solvents and in Aromatic Solvents. As expected, DBMs self-associate in polar solvents much more strongly than in an apolar solvent, chloroform. An estimate of the association constant (K_E) of **2c** and **3c** for infinite association in methanol extends to the order of 10^6 M^{-1} according to the analysis based on NMR. Since the degree of aggregation is estimated to be considerably large, nanotubular aggregates of DBMs must be formed.[19] Although precise comparison is not possible, the association constant of DBM **3c** in polar solvents seems to be larger than that of PAM **14b**, due to the larger solvophobic area of the former. It should be pointed out that linear oligomers **11c** and **13c** aggregate only in polar solvents. This suggests that, owing to solvophobic interactions, the backbone of these compounds may coil to adopt a pseudocyclic conformer that induces aggregation by stacking interactions like those of DBMs.

It is intuitively reasonable to assume that aromatic solvents suppress $\pi-\pi$ stacking interactions between aromatic solutes because such interactions between the solute and solvent would prevail over those between solutes.[53] On the contrary, like PAM **14b**[7c] and the related chiral macrocycles,[15] DBMs **2a**,**b** and **3a**,**c** turned out to self-associate in aromatic solvents, toluene and *o*-xylene. Moreover, whereas the association constants of 4mers **2a** and **2c** in toluene are in the same order of magnitude as those in chloroform, 6mers **3a** and **3c** exhibit much larger association constants in aromatic solvents than in chloroform. The ΔH term in toluene-d_8 determined by the NMR method is about twice as favorable as that in $CDCl_3$. Although the role of the aromatic solvents in the present system is not clear, the large cavities of 6mers, through which the solvent molecules can penetrate freely, may be responsible for this unusual behavior.

Conclusion

We synthesized the novel rigid diethynylbenzene macrocycles (DBMs), which showed self-association properties in solution to form dimers and higher aggregates owing to $\pi-\pi$ stacking interactions. The size of the DBMs is critical to this behavior; cyclic hexamers having planar and rigid macrocyclic framework exhibit the strongest tendency to self-associate. By comparing the association behaviors of the DBMs and PAMs, it is revealed that the buta-1,3-diyne units promote $\pi-\pi$ stacking interactions effectively owing to their electron-withdrawing effect. In polar solvents, the association of DBMs is much enhanced due to the solvophonic effect compared to that in an apolar solvent (chloroform), and in aromatic solvents, DBMs aggregate more strongly than in chloroform for a reason that is not clarified. In these solvents, the degree of aggregation is large enough to form nanotubular aggregates. The analysis of self-aggregation by VPO revealed unique aggregation behavior of DBMs in acetone and toluene, suggesting a nucleation mechanism.

Experimental Section

General. ^1H NMR spectra were recorded at 270, 300, or 400 MHz and ^{13}C NMR spectra at 67.5, 75, or 100 MHz on a JEOL JNM-AL-400, a Varian Mercury 300, or a JEOL JNM-GSX-270 in $CDCl_3$ and with Me_4Si or residual solvent as an internal standard at 30 °C unless otherwise stated. IR spectra were recorded as a KBr disk or a neat film on a JASCO FTIR-410 and Raman spectra on a Bio-Rad Ft-Raman II spectrometer. Electronic spectra were recorded on a HITACHI U-3310 spectrometer. Mass spectral analyses were performed on a JEOL JMS-DX303HF spectrometer or a JEOL JMS-700 spectrometer for EI, FAB, and FD ionization. For most of the MALDI-TOF mass measurements, a Shimadzu/Kratos AXIMA-CFR spectrometer was employed. Elemental analyses were performed on a Perkin-Elmer 2400II analyzer. Vapor pressure osmometry was conducted with a HITACHI 117 vapor pressure osmometer. Melting points were measured with a hot-stage apparatus and are uncorrected. Column chromatography and TLC were performed with Merck silica gel 60 (70−230 mesh ASTM) and Merck silica gel 60 F_{254}, respectively. Flash chromatography was performed with Fuji Silysia silica gel (BW-300). Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph using 600-mm × 20-mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as an eluent. All reagents were obtained from commercial suppliers and used as received. Solvents were dried (drying agent in parentheses) and distilled prior to use: THF ($LiAlH_4$ followed by sodium benzophenone ketyl), benzene (CaH_2), $CDCl_3$ (P_4O_{10}), and

(52) Bryant, J. A.; Ericson, J. L.; Cram, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 1255−1256.
(53) Sanders, G. M.; van Dijk, M.; van Veldhuizen, A.; van der Plas, H. C.; Hofstra, U.; Schaafsma, T. J. *J. Org. Chem.* **1988**, *53*, 5272−5281.

pyridine (KOH). All reactions which required anhydrous conditions were conducted under a dry nitrogen atmosphere.

TIPS-Protected 2mer 6a. To a solution of $Cu(OAc)_2$ (8.28 g, 45.6 mmol) in pyridine (800 mL) was added a solution of **5a**[29] (9.75 g, 22.2 mmol) in pyridine (100 mL). After the solution was stirred for 4 h, additional $Cu(OAc)_2$ (4.14 g, 22.8 mmol) was added. After an additional 19 h of stirring, the solvent was removed and the green residue was passed through a short plug of alumina. After removed of the solvent under reduced pressure, purification by flash chromatography afforded **6a** as a pale yellow solid (8.32 g, 89%): mp 52−54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 1.5 Hz, 4H), 7.77 (t, J = 1.5 Hz, 2H), 4.33 (t, J = 6.8 Hz, 4H), 1.78 (quintet, J = 6.8 Hz, 4H), 1.45−1.29 (m, 20H), 1.14 (s, 42H), 0.89 (t, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.92 (s), 139.39 (d), 133.44 (d), 132.83 (d), 131.24 (s), 124.52 (s), 122.17 (s), 104.59 (s), 93.39 (s), 80.33 (s), 74.81 (s), 65.80 (t), 31.83 (t), 29.28 (t), 29.22 (t), 28.71 (t), 26.05 (t), 22.69 (t), 18.70 (d), 14.14 (q), 11.35 (q); IR (KBr) 2154, 1726, 1221, 968, 882, 768, 677 cm^{-1}; MS (FAB) m/z 875 (M^+ + H), 831 (M^+ + H − i-Pr), 719 (M^+ + H − $CO_2C_8H_{17}$). Anal. Calcd for $C_{56}H_{82}O_4Si_2$: C, 76.83; H, 9.44. Found: C, 77.11; H, 9.56.

TIPS-Protected 2mer 6b. To a solution of $Cu(OAc)_2$ (3.30 g, 18.0 mmol) in pyridine (300 mL) was added a solution of **5b**[29] (5.00 g, 9.08 mol) in pyridine (70 mL). After being stirred for 4 h, the mixture was worked up as described for the reaction of **6a**. Purification by flash chromatography afforded **6b** as a pale yellow solid (4.77 g, 96%): mp 48−49 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.09 (d, J = 1.7 Hz, 4H), 7.78 (m, 2H), 4.33 (t, J = 6.8 Hz, 4H), 1.78 (quintet, J = 6.8 Hz, 4H), 1.46−1.25 (br s, 52H), 1.13 (s, 42H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 164.87 (s), 139.37 (d), 133.42 (d), 132.81 (d), 131.24 (s), 124.52 (s), 122.17 (s), 104.59 (s), 93.36 (s), 80.32 (s), 74.82 (s), 65.76 (t), 31.97 (t), 29.75 (t), 29.71 (t), 29.70 (t), 29.64 (t), 29.57 (t), 29.42 (t), 29.33 (t), 28.72 (t), 26.04 (t), 22.75 (t), 18.69 (d), 14.16 (q), 11.35 (q); IR (KBr) 2150, 1720, 1220, 890, 670 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ϵ) 337 (4.39), 313 (4.49), 294 (4.33), 296 (4.78), 259 (4.80) nm; MS (FAB) m/z 1099 (M^+ + H), 1054 (M^+ + H − i-Pr). Anal. Calcd for $C_{72}H_{114}O_4Si_2$: C, 78.63; H, 10.45. Found: C, 78.70; H, 10.81.

TIPS-Protected 2mer 6c. A suspension of CuCl (4.95 g, 50.0 mmol) and tetramethylethylenediamine (TMEDA) (1.98 g, 17.0 mmol) in acetone (80 mL) was stirred at room temperature for 30 min. The blue skim of this mixture was used as a catalyst. To an oxygen-saturated solution of **5c**[29] (501 mg, 1.06 mmol) in acetone (8 mL) was added a solution of the above catalyst (0.4 mL). The mixture was stirred at room temperature for 24 h while oxygen was bubbled through a glass tube immersed into the solution. Additional catalyst (0.2 mL) was added, and the solution was stirred for an additional 21 h. After addition of 1 N HCl (1 mL) and water (20 mL), most of the acetone was evaporated in vacuo and the residue was extracted with ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure to give a crude product. Purification by silica gel chromatography afforded **6c** as a pale yellow oil (458 mg, 92%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12−8.10 (m, 4H), 7.78 (t, J = 1.5 Hz, 2H), 4.51−4.48 (m, 4H), 3.86−3.83 (m, 4H), 3.74−3.64 (m, 12H), 3.55−3.52 (m, 4H), 3.37 (s, 6H), 1.14−1.13 (m, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.82 (s), 139.56 (d), 133.52 (d), 132.94 (d), 130.88 (s), 124.55 (s), 122.19 (s), 104.47 (s), 93.43 (s), 80.22 (s), 74.82 (s), 71.90 (t), 70.67 (t), 70.61 (t), 70.58 (t), 69.02 (t), 64.57 (t), 58.94 (q), 18.60 (d), 11.22 (q); IR (neat) 2156, 1729, 1220, 890, 670 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ϵ) 337 (4.39), 313 (4.49), 294 (4.33), 296 (4.78), 259 (4.80) nm; MS (FAB) m/z 965 (M^+ + Na), 943 (M^+ + H).

Partial Deprotection of 6a: 2mer 7a and Singly-Protected 2mer 8a. To a solution of TIPS-protected acetylene **6a** (3.04 g, 3.48 mmol) in THF (107 mL) and water (4.2 mL) was added dropwise 3.6 mL of a solution of tetrabuthylammonium fluoride (TBAF) in THF (1.0 M). After being stirred at room temperature for 70 min, the mixture was poured to ice water and extracted with $CHCl_3$. The extract was washed with water and brine and dried over $MgSO_4$. Removal of the solvent in vacuo afforded crude products. Purification by flash chromatography afforded **7a** (763 mg, 39%), **8a** (1.25 g, 50%), and the starting material **6a** (207 mg).

7a: white solid; mp 89−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (t, J = 1.5 Hz, 2H), 8.13 (t, J = 1.5 Hz, 2H), 7.79 (t, J = 1.5 Hz, 2H), 4.33 (t, J = 6.8 Hz, 4H), 3.16 (s, 2H), 1.77 (quintet, J = 6.8 Hz, 4H), 1.46−1.30 (m, 20H), 0.89 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.71 (s), 139.33 (d), 133.64 (d), 133.47 (d), 131.40 (s), 123.19 (s), 122.33 (s), 81.46 (d), 80.18 (s), 79.16 (s), 74.93 (s), 65.86 (t), 31.84 (t), 29.28 (t), 29.21 (t), 28.69 (t), 26.05 (t), 22.70 (t), 14.15 (q); IR (KBr) 3257, 2114, 1720, 1307, 1223, 897, 771, 709, 669 cm^{-1}; MS (FAB) m/z 562 (M^+), 433 (M^+ − OC_8H_{17}), 321(M^+ + H − OC_8H_{17} − C_8H_{17}), 248 (M^+ − $(CO_2C_8H_{17})_2$). Anal. Calcd for $C_{38}H_{42}O_4$: C, 81.11; H, 7.52. Found: C, 81.01; H, 7.42.

8a: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 1.5 Hz, 1H), 8.12 (t, J = 1.5 Hz, 1H), 8.10 (m, 2H), 7.78 (m, 2H), 4.33 (t, J = 6.6 Hz, 2H), 4.32 (t, J = 6.6 Hz, 2H), 3.17 (s, 1H), 1.77 (m, 4H), 1.45−1.29 (m, 20H), 1.14 (s, 21H), 0.89 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.74 (s), 164.54 (s), 139.29 (d), 139.21 (d), 133.52 (d), 133.39 (d), 133.37 (d), 132.76 (d), 131.32 (s), 131.21 (s), 124.48 (s), 123.15 (s), 122.31 (s), 122.08 (s), 104.54 (s), 93.32 (s), 81.41 (d), 80.37 (s), 80.01 (s), 79.15 (s), 74.98 (s), 74.76 (s), 65.76 (t), 65.71 (t), 31.81 (t), 31.79 (t), 29.25 (t), 29.19 (t), 28.68 (t), 28.67 (t), 26.02 (t), 22.66 (t), 18.65 (d), 14.10 (q), 11.31 (q); IR (neat) 3306, 2158, 1727, 1219, 768, 678 cm^{-1}; MS (FAB) m/z 719 (M^+ + H), 675 (M^+ − i-Pr), 563 (M^+ + H − i-Pr − C_8H_{17}).

Partial Deprotection of 6b: 2mer 7b and Singly-Protected 2mer 8b. To a solution of TIPS-protected acetylene **6b** (50 mg, 0.046 mmol) in THF (1.5 mL) and water (0.2 mL) was added dropwise 0.046 mL of a solution of TBAF (1.0 M) in THF and the solution was stirred at room temperature. The reaction was monitored by HPLC and another TBAF solution (each 0.04 mL portion) was added seven times at 30-min intervals. After 4 h, the reaction mixture was worked up as described for the reaction of **6a**. Purification by flash chromatography afforded **7b** (8 mg, 22%), **8b** (17 mg, 40%), and the starting material **6b** (11 mg).

7b: white solid; mp 87−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 1.5 Hz, 2H), 8.13 (t, J = 1.5 Hz, 2H), 7.78 (t, J = 1.5 Hz, 2H), 4.33 (t, J = 6.8 Hz, 4H), 3.20 (s, 2H), 1.77 (quintet, J = 6.8 Hz, 4H), 1.46−1.25 (m, 52H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.66 (s), 139.31 (d), 133.62 (d), 133.44 (d), 131.37 (s), 123.18 (s), 122.32 (s), 81.45 (d), 80.17 (s), 79.16 (s), 74.95 (s), 65.83 (t), 31.97 (t), 29.74 (t), 29.71 (t), 29.64 (t), 29.55 (t), 29.41 (t), 29.32 (t), 28.69 (t), 26.04 (t), 22.74 (t), 14.16 (q); IR (KBr) 3270, 1720, 1208, 895 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ϵ) 335 (4.28), 311 (4.31), 292 (4.15), 246 (4.62) nm; MS (FAB) m/z 786 (M^+), 393 (M^+ − $C_2C_6H_3$-$(CO_2C_{16}H_{33})(C_2H)$). Anal. Calcd for $C_{54}H_{74}O_4$: C, 82.40; H, 9.47. Found: C, 82.52; H, 9.75.

8b: white solid; mp 56−57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, J = 1.5 Hz, 1H), 8.13 (t, J = 1.5 Hz, 1H), 8.10 (m, 2H), 7.78 (t, J = 1.5 Hz, 2H), 4.330 (t, J = 6.6 Hz, 2H), 4.326 (t, J = 6.6 Hz, 2H), 3.16 (s, 1H), 1.77 (m, 4H), 1.45−1.25 (m, 52H), 1.14 (s, 21H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.85 (s), 164.66 (s), 139.37 (d), 139.29 (d), 133.58 (d), 133.44 (d), 133.44 (d), 132.82 (d), 131.36 (s), 131.25 (s), 124.53 (s), 123.18 (s), 122.38 (s), 122.12 (s), 104.57 (s), 93.38 (s), 81.46 (d), 80.42 (s), 80.04 (s), 79.14 (s), 75.00 (s), 74.77 (s), 65.81 (t), 65.77 (t), 31.97 (t), 29.75 (t), 29.72 (t), 29.70 (t), 29.64 (t), 29.57 (t), 29.41 (t), 29.32 (t), 28.72 (t), 28.69 (t), 26.04 (t), 22.74 (t), 18.69 (d), 14.16 (q), 11.34 (q); IR (KBr) 3299, 2164, 1730, 1221, 899, 767, 677, 631 cm^{-1}; MS (FAB) m/z 943 (M^+), 899 (M^+ − i-Pr − H), 675 (M^+ − i-Pr − $C_{16}H_{33}$), 393 (M^+ − $C_2C_6H_3$-$(CO_2C_{16}H_{33})(C_2TIPS)$). Anal. Calcd for $C_{63}H_{94}O_4Si$: C, 80.20; H, 10.04. Found: C, 80.42; H, 9.84.

Partial Deprotection of 6c: 2mer 7c and Singly-Protected 2mer 8c. To a solution of TIPS-protected acetylene **6c** (320 mg, 0.339 mmol)

in THF (12 mL) and water (0.6 mL) was added dropwise 0.34 mL of a solution of TBAF (1.0 M) in THF. After being stirred at room temperature for 1.5 h, the reaction mixture was worked up as described for the reaction of **6a** except that ether was employed instead of $CHCl_3$ for extraction. Purification by flash chromatography afforded the products **7c** (51 mg, 24%) and **8c** (122 mg, 46%), and the starting material **6c** (84 mg) was recovered.

7c: pale yellow solid; mp 60−61 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17−8.15 (m, 4H), 7.78 (t, J = 1.6 Hz, 2H), 4.51−4.48 (m, 4H), 3.86−3.82 (m, 4H), 3.73−3.64 (m, 12H), 3.56−3.53 (m, 4H), 3.37 (s, 6H), 3.17 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.61 (s), 139.48 (d), 133.73 (d), 133.55 (d), 131.02 (s), 123.22 (s), 122.33 (s), 81.32 (d), 80.08 (s), 79.28 (s), 74.93 (s), 71.88 (t), 70.64 (t), 70.57 (t), 70.55 (t), 68.97 (t), 64.60 (t), 58.93 (q); IR (KBr) 3257, 2222, 2104, 1725, 1307, 1223, 897, 771, 709, 669 cm^{-1}; MS (FAB) *m*/*z* 631 (M^+ + H), 511 (M^+ − $O(CH_2CH_2O)_2CH_3$). Anal. Calcd for $C_{36}H_{38}O_{10}$: C, 68.56; H, 6.07. Found: C, 68.21; H, 6.03.

8c: pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17−8.14 (m, 2H), 8.13−8.11 (m, 2H), 7.80−7.78 (m, 2H), 4.51−4.47 (m, 4H), 3.86−3.82 (m, 4H), 3.74−3.64 (m, 12H), 3.56−3.53 (m, 4H), 3.372 (s, 3H), 3.370 (s, 3H), 3.16 (s, 1H), 1.14 (br s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.86 (s), 164.67 (s), 139.61 (d), 139.52 (d), 133.74 (d), 133.59 (d), 132.99 (d), 131.05 (d), 130.91 (s), 124.59 (s), 123.24 (s), 122.43 (s), 122.16 (s), 104.48 (s), 93.50 (s), 81.36 (d), 80.37 (s), 79.98 (s), 79.24 (s), 75.02 (s), 74.78 (s), 71.92 (t), 70.68 (t), 70.59 (t), 69.04 (t), 69.00 (t), 64.63 (t), 64.59 (t), 58.97 (q), 18.60 (d), 11.31 (q); IR (neat) 3306, 2158, 1727, 1219, 768, 678 cm^{-1}; MS (FAB) *m*/*z* 787 (M^+ + H), 667 (M^+ − $O(CH_2CH_2O)_2CH_3$).

2mer **8c** was also prepared by transesterification of **8a**. Thus, to a stirred solution of **8a** (2.46 g, 2.78 mmol) and triethylene glycol monomethyl ether (56.0 g, 341 mmol) were added K_2CO_3 (3.84 g, 27.8 mmol) and 18-crown-6 ether (0.367 g, 1.39 mmol). After the mixture was stirred at room temperature for 9 h, the solvent was removed with an evaporator to give a mixture of **8c**, two isomers of monoexchanged 2mers, and **8a** (recovered). Purification by flash chromatography afforded **8c** as a pale yellow oil (1.50 g, 56%).

TIPS-Protected Linear 4mer 10a. The catalyst was prepared by stirring a suspension of CuCl (4.95 g, 50.0 mmol) and TMEDA (1.98 g, 17.0 mmol) in acetone (80 mL) at room temperature for 30 min. To an oxygen-saturated solution of **8a** (7.58 g, 10.5 mmol) in acetone (100 mL) was added a solution of the above catalyst (80 mL). The mixture was stirred at room temperature for 48 h while oxygen was bubbled through a glass tube immersed into the solution. The reaction mixture was worked up as described for the synthesis of **6c**. Purification by flash chromatography afforded **10a** as a pale yellow oil (6.65 g, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 1.5 Hz, 4H), 8.10 (t, J = 1.5 Hz, 4H), 7.81 (t, J = 1.5 Hz, 2H), 7.79 (t, J = 1.5 Hz, 2H), 4.34 (t, J = 6.8 Hz, 4H), 4.33 (t, J = 6.8 Hz, 4H), 1.78 (quintet, J = 6.8 Hz, 8H), 1.46−1.14 (m, 40H), 1.14 (s, 42H), 0.92−0.88 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.78 (s), 164.41 (s), 139.41 (d), 139.34 (d), 133.90 (d), 133.47 (d), 132.80 (d), 131.57 (s), 131.24 (s), 124.51 (s), 122.66 (s), 122.52 (s), 122.02 (s), 104.53 (s), 93.41 (s), 80.65 (s), 80.13 (s), 79.78 (s), 75.34 (s), 75.20 (s), 74.70 (s), 65.93 (t), 65.78 (t), 31.87 (t), 31.86 (t), 29.30 (t), 28.23 (t), 28.73 (t), 26.08 (t), 22.72 (t), 18.72 (d), 14.17 (q), 11.37 (q); IR (neat) 2160, 1730, 1590, 1260, 766, 677 cm^{-1}; MS (MALDI-TOF) *m*/*z* 1497.9 (M^+ + Cu), 1458.0 (M^+ + Na).

Linear 4mer 11a. To a solution of TIPS-protected acetylene **10a** (261 mg, 0.173 mmol) in THF (4 mL) and water (1 mL) was added dropwise 2 mL of a solution of TBAF (1.0 M) in THF. After being stirred at room temperature for 8 h, the reaction mixture was worked up as described for the synthesis of **7a** and **8a**. Purification by flash chromatography afforded **11a** (190 mg, 98%) as a white solid: mp 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.13 (m, 8H), 7.81 (t, J = 1.5 Hz, 2H), 7.79 (t, J = 1.5 Hz, 2H), 4.34 (t, J = 6.9 Hz, 4H), 4.33 (t, J = 6.6 Hz, 4H), 3.17 (s, 2H), 1.81−1.74 (m, 8H), 1.46−1.30 (m, 40H), 0.94−0.85 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.66 (s), 164.46 (s), 139.47 (d), 139.32 (d), 133.98 (d), 133.67 (d), 133.47 (d), 131.60 (s), 131.40 (s), 123.20 (s), 122.63 (s), 122.56 (s), 122.26 (s), 100.55 (s), 81.43 (d), 80.40 (s), 79.90 (s), 79.13 (s), 75.28 (s), 75.20 (s), 74.88 (s), 65.95 (t), 65.85 (t), 31.85 (t), 29.28 (t), 29.21 (t), 28.69 (t), 26.05 (t), 22.70 (t), 14.15 (q); IR (KBr) 3260, 2150, 2110, 1730, 1260, 894, 768, 672 cm^{-1}; MS (MALDI-TOF) *m*/*z* 1185.5 (M^+ + Cu), 1145.3 (M^+ + Na).

TIPS-Protected Linear 4mer 10c. The catalyst was prepared by srirring a suspension of CuCl (1.00 g, 10.1 mmol) and TMEDA (391 mg, 3.37 mmol) in acetone (20 mL) at room temperature for 30 min. To an oxygen-saturated solution of **8c** (3.85 g, 4.89 mmol) in acetone (50 mL) was added a solution of the above catalyst (2.9 mL). The mixture was stirred at room temperature for 6 h while oxygen was bubbled through a glass tube immersed into the solution. Additional catalyst (1.5 mL) was added, and the solution was stirred for an additional 26 h. The reaction mixture was worked up as described for the synthesis of **6c**. Purification by silica gel chromatography afforded **10c** as a pale yellow oil (3.61 g, 94%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21−8.19 (m 4H), 8.14−8.11 (m, 4H), 7.83 (t, J = 1.5 Hz, 2H), 7.80 (t, J = 1.5 Hz, 2H), 4.52−4.48 (m, 8H), 3.86−3.83 (m, 8H), 3.74−3.64 (m, 24H), 3.57−3.52 (m, 8H), 3.38 (s, 6H), 3.37 (s, 6H), 1.14 (br s, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.85 (s), 164.47 (s), 139.69 (d), 139.62 (d), 134.12 (d), 134.05 (d), 133.64 (d), 132.99 (d), 131.28 (s), 130.92 (s), 124.59 (s), 122.74 (s), 122.60 (s), 122.10 (s), 104.46 (s), 93.52 (s), 80.58 (s), 80.05 (s), 79.70 (s), 75.35 (s), 75.20 (s), 74.71 (s), 71.93 (t), 71.90 (t), 70.68 (t), 70.61 (t), 69.03 (t), 68.97 (t), 64.72 (t), 64.59 (t), 58.91 (q), 18.60 (d), 11.22 (q); IR (neat) 2156, 1730, 1585, 1260, 766, 677 cm^{-1}; MS (MALDI-TOF) *m*/*z* 1593.7 (M^+ + Na).

Linear 4mer 11c. To a solution of TIPS-protected acetylene **10c** (3.61 g, 2.30 mmol) in THF (115 mL) and water (5 mL) was added dropwise 11.5 mL of a solution of TBAF (1.0 M) in THF. After being stirred at room temperature for 2 h, the reaction mixture was worked up as described for the synthesis of **7a** and **8a**. Purification by flash chromatography afforded **11c** (2.49 mg, 86%) as a pale yellow solid: mp 81−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 1.5 Hz, 4H), 8.17 (t, J = 1.5 Hz, 2H), 8.16 (t, J = 1.5 Hz, 2H), 7.84 (t, J = 1.5 Hz, 2H), 7.81 (t, J = 1.5 Hz, 2H), 4.52−4.48 (m, 8H), 3.86−3.83 (m, 8H), 3.75−3.65 (m, 24H), 3.57−3.53 (m, 8H), 3.38 (s, 6H), 3.37 (s, 6H), 3.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.66 (s), 164.47 (s), 139.71 (d), 139.55 (d), 134.13 (d), 133.83 (d), 133.62 (d), 131.29 (s), 131.07 (s), 123.27 (s), 122.69 (s), 122.62 (s), 122.31 (s), 81.35 (d), 80.33 (s), 80.06 (s), 79.84 (s), 79.30 (s), 75.30 (s), 75.23 (s), 74.90 (s), 71.93 (t), 70.70 (t), 70.61 (t), 69.00 (t), 64.74 (t), 64.65 (t), 58.99 (q); IR (KBr) 3290, 3260, 3080, 2875, 2224, 2111, 1727, 1585, 1455, 1435, 1263, 1219, 1114, 897, 765, 673 cm^{-1}; MS (MALDI-TOF) *m*/*z* 1281.9 (M^+ + Na). Anal. Calcd for $C_{72}H_{74}O_{20}$: C, 68.67; H, 5.92. Found: C, 68.30; H, 6.10.

Monobrominated 2mer 9a. In a flask covered with aluminum foil, **8a** (12.3 g, 17.1 mmol) was dissolved in acetone (450 mL), and then $AgNO_3$ (0.87 g, 5.1 mmol) and *N*-bromosuccinimide (NBS) (4.27 g, 24.0 mmol) were added. After being stirred at room temperature for 50 min, the mixture was diluted with water and extracted with $CHCl_3$. The extract was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, purification by flash chromatography afforded **9a** as a pale yellow oil (13.2 g, 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (m, 1H), 8.09 (m, 3H), 7.78 (m, 1H), 7.73 (m, 1H), 4.33 (t, J = 6.6 Hz, 2H), 4.32 (t, J = 6.6 Hz, 2H), 1.77 (m, 4H), 1.44−1.29 (m, 20H), 1.14 (s, 21H), 0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.89 (s), 164.66 (s), 139.38 (d), 139.14 (d), 133.48 (d), 133.33 (d), 132.83 (d), 131.41 (s), 131.26 (s), 124.53 (s), 123.73 (s), 122.43 (s), 122.10 (s), 104.56 (s), 93.42 (s), 80.48 (s), 80.01 (s), 78.11 (s), 75.04 (s), 74.75 (s), 65.86 (t), 65.80 (t), 52.60 (s), 31.85 (t), 29.28 (t), 29.21 (t), 28.71 (t), 28.69 (t), 26.05 (t), 22.70 (t), 18.70 (d), 14.15 (q), 11.35 (q); IR (neat) 2204, 2160, 1728, 1221, 896, 768, 678 cm^{-1};

MS (FAB) *m*/*z* 799, 797 ($M^+ + H$), 755, 753 ($M^+ - i$-Pr), 669, 667 ($M^+ - OC_8H_{17}$).

Monobrominated 2mer 9b. In a flask covered with aluminum foil, **8b** (366 mg, 0.39 mmol) was dissolved in acetone (10 mL) with warming at 45 °C. To the solution were added $AgNO_3$ (26 mg, 0.16 mmol) followed by NBS (76 mg, 0.43 mmol) and the mixture was stirred at 45 °C. After 1 h, additional NBS (33 mg, 0.18 mmol) was added and the solution was stirred for an additional 1 h. The reaction mixture was worked up as described for the reaction of **8a**. Purification by flash chromatography afforded **9b** as a pale yellow solid (356 mg, 90%): mp 49−50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 1.5 Hz, 1H), 8.10 (m, 3H), 7.78 (t, J = 1.5 Hz, 1H), 7.73 (t, J = 1.5 Hz, 1H), 4.33 (t, J = 6.8 Hz, 2H), 4.32 (t, J = 6.6 Hz, 2H), 3.19 (m, 4H), 1.43−1.25 (m, 52H), 1.14 (s, 21 H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.88 (s), 164.65 (s), 139.38 (d), 139.14 (d), 133.48 (d), 133.32 (d), 132.82 (d), 131.41 (s), 131.26 (s), 124.53 (s), 123.73 (s), 122.43 (s), 122.11 (s), 104.57 (s), 93.41 (s), 80.48 (s), 80.01 (s), 78.11 (s), 75.05 (s), 74.76 (s), 65.85 (t), 65.79 (t), 52.59 (s), 31.98 (t), 29.76 (t), 29.73 (t), 29.71 (t), 29.65 (t), 29.57 (t), 29.56 (t), 29.42 (t), 29.33 (t), 28.72 (t), 28.70 (t), 26.04 (t), 22.75 (t), 18.71 (d), 14.17 (q), 11.35 (q); IR (KBr) 2206, 2160, 1727, 1223, 897, 768, 677 cm^{-1}; MS (FAB) *m*/*z* 1024, 1022 ($M^+ + H$), 981, 979 ($M^+ + H - i$-Pr), 755, 753 ($M^+ + H - CO_2C_{16}H_{33}$). Anal. Calcd for $C_{63}H_{93}O_4BrSi$: C, 74.01; H, 9.17. Found: C, 74.10; H, 9.40.

Monobrominated 2mer 9c. In a flask covered with aluminum foil, **8c** (122 mg, 0.155 mmol) was dissolved in acetone (3 mL), and then $AgNO_3$ (7.9 mg, 0.046 mmol) and NBS (38.7 mg, 0.217 mmol) were added. After being stirred at room temperature for 1 h, the reaction mixture was worked up as described for the synthesis of **9a** except that ether was employed instead of $CHCl_3$ for extraction. Purification by flash chromatography afforded **9c** as a pale yellow oil (101 mg, 75%): ^{1}H NMR (270 MHz, $CDCl_3$, 30 °C) δ 8.15 (t, J = 1.6 Hz, 1H), 8.12−8.10 (m, 3H), 7.78 (t, J = 1.6 Hz, 1H), 7.74 (t, J = 1.6 Hz, 1H), 4.51−4.47 (m, 4H), 3.85−3.81 (m, 4H), 3.73−3.63 (m, 12H), 3.55−3.52 (m, 4H), 3.37 (s, 3H), 3.36 (s, 3H) 1.138−1.133 (m, 21H);^{13}C (67.5 MHz, $CDCl_3$, 30 °C) δ 164.72 (s), 164.47 (s), 139.50 (d), 139.23 (d), 133.54 (d), 133.50 (d), 133.35 (d), 132.89 (d), 130.98 (s), 130.82 (s), 124.49 (s), 123.69 (s), 122.38 (s), 122.06 (s), 104.41 (s), 93.44 (s), 80.36 (s), 79.90 (s), 77.98 (s), 75.04 (s), 74.76 (s), 71.91 (t), 71.89 (t), 70.67 (t), 70.60 (t), 70.59 (t), 70.58 (t), 70.57 (t), 69.02 (t), 68.98 (t), 64.62 (t), 64.57 (t), 58.97 (q), 52.68 (s), 18.65 (q), 11.28 (t); IR (neat) 3070, 2942, 2865, 2202, 2155, 1727, 1586, 1460, 1434, 1256, 1112, 895, 767, 677 cm^{-1}; MS (FAB) *m*/*z* 867, 865 ($M^+ + H$), 747, 745 ($M^+ - O(CH_2CH_2O)_2CH_3$).

TIPS-Protected Linear 6mer 12a. A flask was charged with linear 2mer **7a** (50 mg, 0.090 mmol), bromide **9a** (150 mg, 0.190 mmol), $Pd_2(dba)_3$·$CHCl_3$ (4.6 mg, 0.0045 mmol), CuI (0.85 mg, 0.0045 mmol), and benzene (3 mL). After being stiired at room temperature for 5 min, *i*-Pr_2NH (0.030 mL) was added dropwise and the mixture was stirred at room temperature for 45 min. After completion of the reaction, the mixture was concentrated in vacuo and the residue was subjected to flash chromatography on silica gel to afford **12a** as a yellow oil (67 mg, 38%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (m, 8H), 8.10 (m, 4H), 7.81 (m, 4H), 7.79 (t, J = 1.7 Hz, 2H), 4.34 (t, J = 6.6 Hz, 8H), 4.33 (t, J = 6.6 Hz, 4H), 1.78 (m, 12H), 1.44−1.30 (m, 60H), 1.14 (s, 42H), 0.90 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.85 (s), 164.47 (s), 164.44 (s), 139.45 (d), 139.38 (d), 133.51 (d), 133.91 (d), 133.51 (d), 132.83 (d), 131.60 (s), 131.59 (s), 131.26 (s), 124.54 (s), 122.69 (s), 122.58 (s), 122.54 (s), 122.04 (s), 104.54 (s), 93.43 (s), 80.66 (s), 80.16 (s), 80.12 (s), 80.09 (s), 79.78 (s), 75.34 (s), 75.24 (s), 75.19 (s), 74.70 (s), 65.95 (t), 65.79 (t), 31.85 (t), 31.83 (t), 29.29 (t), 29.21 (t), 28.71 (t), 28.69 (t), 26.06 (t), 26.04 (t), 22.70 (t), 18.69 (t), 14.16 (d), 14.14 (q), 11.34 (q); IR (neat) 2235, 2160, 1730, 1256, 895, 767, 676 cm^{-1}; MS (MALDI-TOF) *m*/*z* 2057.7 ($M^+ + Cu$), 2017.8 ($M^+ + Na$).

TIPS-Protected Linear 6mer 12b. A flask was charged with linear 2mer **7b** (23 mg, 0.029 mmol), bromide **9b** (90 mg, 0.088 mmol), $Pd_2(dba)_3$·$CHCl_3$ (6 mg, 0.006 mmol), CuI (0.95 mg, 0.0050 mmol), and benzene (1.4 mL). After being stirred at room temperature for 5 min, *i*-Pr_2NH (0.041 mL) was added dropwise and the mixture was stirred at room temperature for 45 min. After completion of the reaction, the mixture was concentrated in vacuo and the residue was subjected to flash chromatography on silica gel to afford **12b** as a brown oil (34 mg, 44%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (m, 8H), 8.10 (m, 4H), 7.81 (m, 4H), 7.78 (t, J = 1.7 Hz, 2H), 4.34 (m, 12H), 1.78 (m, 12H), 1.46−1.25 (m, 156H), 1.14 (s, 42H), 0.87 (t, J = 6.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.85 (s), 164.48 (s), 164.45 (s), 139.46 (d), 139.39 (d), 134.00 (d), 133.91 (d), 133.51 (d), 132.83 (d), 131.60 (s), 131.59 (s), 131.26 (s), 124.54 (s), 122.70 (s), 122.60 (s), 122.55 (s), 122.05 (s), 104.55 (s), 93.43 (s), 80.66 (s), 80.15 (s), 80.11 (s), 80.09 (s), 79.77 (s), 75.35 (s), 75.24 (s), 74.71 (s), 65.95 (t), 65.79 (t), 31.97 (t), 29.75 (t), 29.71 (t), 29.65 (t), 29.56 (t), 29.42 (t), 29.32 (t), 28.72 (t), 28.69 (t), 26.04 (t), 22.75 (t), 22.74 (t), 18.70 (d), 14.17 (q), 11.35 (q); IR (neat) 2228, 2160, 1730, 1256, 896, 768, 677 cm^{-1}; MS (MALDI-TOF) *m*/*z* 2691.3 ($M^+ + Na$).

TIPS-Protected Linear 6mer 12c. A flask was charged with linear 2mer **7c** (1.78 g, 2.83 mmol), bromide **9c** (5.14 g, 5.94 mmol), $Pd_2(dba)_3$·$CHCl_3$ (141 mg, 0.141 mmol), CuI (26 mg, 0.141 mmol), and benzene (150 mL). After being stirred at room temperature for 5 min, *i*-Pr_2NH (0.95 mL) was added dropwise and the mixture was stirred at room temperature for 45 min. After completion of the reaction, the mixture was concentrated in vacuo and the residue was subjected to flash chromatography on silica gel to afford **12c** as a yellow oil (1.91 g, 31%): ^{1}H NMR (270 MHz, $CDCl_3$, 30 °C) δ 8.20−8.19 (m, 8H), 8.12 (t, J = 1.6 Hz, 2H), 8.11 (t, J = 1.6 Hz, 2H), 7.84 (t, J = 1.6 Hz, 2H), 7.83 (t, J = 1.6 Hz, 2H), 7.79 (t, J = 1.6 Hz, 2H), 4.52−4.48 (m, 12H), 3.86−3.83 (m, 12H), 3.73−3.63 (m, 36H), 3.56−3.53 (m, 12H), 3.377 (s, 12H), 3.370 (s, 6H), 1.140−1.135 (m, 42H); ^{13}C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 164.72 (s), 164.38 (s), 139.63 (d), 139.54 (d), 134.09 (d), 133.51 (d), 132.93 (d), 131.23 (s), 131.21 (s), 130.85 (s), 127.70 (s), 124.54 (s), 122.69 (s), 122.58 (s), 122.54 (s), 122.04 (s), 104.42 (s), 97.19 (s), 93.50 (s), 80.58 (s), 80.07 (s), 80.02 (s), 79.70 (s), 75.35 (s), 75.24 (s), 75.19 (s), 74.71 (s), 71.94 (t), 71.92 (t), 70.70 (t), 70.68 (t), 70.62 (t), 70.61 (t), 70.59 (t), 69.05 (t), 68.99 (t), 64.75 (t), 64.61 (t), 59.01 (q), 59.00 (q), 18.68 (q), 11.30 (d); IR (neat) 3069, 2943, 2865, 2223, 2155, 1728 1584, 1434, 1258, 1217, 1113, 896, 765, 675 cm^{-1}; MS (MALDI-TOF) *m*/*z* 2222.1 ($M^+ + Na$).

Linear 6mer 13a. To a solution of TIPS-protected acetylene **12a** (2.11 g, 1.06 mmol) in THF (50 mL) and water (0.25 mL) was added dropwise 53 mL of a solution of TBAF/acetic acid (0.2 M/0.3 M) in THF during 30 min. To complete the reaction, an additional 21.2 mL of a solution of TBAF/acetic acid (0.5 M/0.75 M) in THF was added over 10 min. After the mixture was stirred at room temperature for further 30 min, 5.0 g of silica gel was added at 0 °C and the solvent was removed in vacuo. The residue was loaded on the top of a silica gel chromatography column and subsequent flash chromatography afforded **13a** as a pale yellow solid (1.74 g, 97%): mp 89−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (m, 8H), 8.15 (m, 2H), 8.13 (m, 2H), 7.82 (m, 4H), 7.79 (m, 2H), 4.34 (m, 12H), 3.17 (s, 2H), 1.78 (m, 12H), 1.44−1.30 (m, 60H), 0.90 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.68 (s), 164.48 (s), 139.48 (d), 139.33 (d), 134.00 (d), 133.68 (d), 133.48 (d), 131.60 (s), 131.40 (s), 123.21 (s), 122.64 (s), 122.59 (s), 122.56 (s), 122.27 (s), 81.44 (d), 80.40 (s), 80.13 (s), 79.91 (s), 79.19 (s), 75.28 (s), 75.23 (s), 75.20 (s), 74.89 (s), 65.97 (t), 65.86 (t), 31.86 (t), 29.29 (t), 29.22 (t), 28.69 (t), 26.06 (t), 22.71 (t), 14.16 (q); IR (KBr) 3255, 2217, 1728, 1258, 892, 766, 672 cm^{-1}; MS (MALDI-TOF) *m*/*z* 1745.7 ($M^+ + Cu$), 1705.8 ($M^+ + Na$). Anal. Calcd for $C_{114}H_{122}O_{12}$: C, 81.30; H, 7.30. Found: C, 81.31; H, 7.47.

Linear 6mer 13b. To a solution of TIPS-protected acetylene **12b** (1.57 g, 0.59 mmol) in THF (57 mL) and water (0.15 mL) was added dropwise 12.9 mL of a solution of TBAF/acetic acid (0.1 M/0.15 M) in THF over 10 min. To complete the reaction, an additional 12.9 mL

of a solution of TBAF/acetic acid (0.1 M/0.15 M) in THF was added duoverring 10 min. After being stirred at room temperature for further 2 h, the reaction mixture was worked up according to the above procedure. Purification by flash chromatography afforded **13b** as a pale yellow solid (1.34 g, 97%): mp 44−47 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (m, 8H), 8.15 (m, 2H), 8.13 (m, 2H), 7.81 (m, 4H), 7.78 (m, 2H), 4.33 (m, 12H), 3.16 (s, 2H), 1.78 (m, 12H), 1.44−1.25 (m, 156H), 0.87 (t, J = 6.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.64 (s), 166.44 (s), 139.46 (d), 139.32 (d), 133.98 (d), 133.66 (d), 133.45 (d), 131.59 (s), 131.38 (s), 123.20 (s), 122.64 (s), 122.58 (s), 122.27 (s), 81.43 (d), 80.39 (s), 80.11 (s), 79.90 (s), 79.19 (s), 75.30 (s), 75.25 (s), 74.91 (s), 65.95 (t), 65.84 (t), 31.97 (t), 29.75 (t), 29.71 (t), 29.65 (t), 29.56 (t), 29.41 (t), 29.32 (t), 28.69 (t), 26.04 (t), 22.75 (t), 14.17 (q); IR (KBr) 3307, 2217, 1729, 1257, 894, 766, 673 cm^{-1}; MS (MALDI-TOF) *m*/*z* 2377.9 (M^+ + Na). Anal. Calcd for $C_{162}H_{218}O_{12}$: C, 82.54; H, 9.32. Found: C, 82.49; H, 9.54.

Linear 6mer 13c. To a solution of TIPS-protected acetylene **12c** (332 mg, 0.150 mmol) in THF (7.5 mL) and water (0.3 mL) was added dropwise 0.75 mL of a solution of TBAF (1 M) in THF. After being stirred at room temperature for 4.5 h, the reaction mixture was worked up as described for the synthesis of **7a** and **8a**. Purification by flash chromatography followed by preparative HPLC afforded **13c** as a pale yellow solid (195 mg, 67%): mp 72−73 °C;^{1}H NMR (270 MHz, $CDCl_3$) δ_8.20 (t, J = 1.5 Hz, 8H), 8.17 (t, J = 1.6 Hz, 2H), 8.15 (t, J = 1.6 Hz, 2H), 7.84 (t, J = 1.6 Hz, 2H), 7.83 (t, J = 1.6 Hz, 2H), 7.80 (t, J = 1.6 Hz, 2H), 4.52−4.47 (m, 12H), 3.86−3.82 (m, 12H), 3.71−3.64 (m, 36H), 3.56−3.52 (m, 12H), 3.38 (s, 12H), 3.37 (s, 6H), 3.16 (s, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 164.56 (s), 164.38 (s), 139.64 (d), 139.48 (d), 134.10 (d), 133.73 (d), 133.56 (d), 131.24 (s), 131.01 (s), 123.22 (s), 122.65 (s), 122.59 (s), 122.57 (s), 122.27 (s), 81.35 (s), 80.33 (s), 80.07 (s), 80.05 (s), 80.04 (s), 79.83 (s), 79.28 (s), 75.31 (s), 75.26 (s), 75.23 (s), 74.91 (s), 71.95 (t), 71.94 (t), 70.71 (t), 70.65 (t), 70.64 (t), 69.01 (t), 64.76 (t), 64.67 (t), 59.03 (q); IR (KBr) 3252, 3072, 2875, 2223, 2109, 1726 1585, 1433, 1261, 1112, 891, 764, 672 cm^{-1}; MS (MALDI-TOF) *m*/*z* 1910.0 (M^+ + Na). Anal. Calcd for $C_{108}H_{110}O_{30}$: C, 68.70; H, 5.87. Found: C, 68.44; H, 5.75.

Cyclization of Linear 4mer 11a: DBMs 2a and 4a. To a solution of $Cu(OAc)_2$ (8.88 g, 48.9 mmol) in 2 L of pyridine/benzene (3:2, v/v) was added dropwise a solution of **11a** (3.67 g, 3.20 mmol) in 500 mL of the same solvent with a Hershberg dropping funnel over 7 h. After additional stirring at room temperature for 6 d, the solvent was removed in vacuo and the green residue was passed through a short plug of SiO_2 and the solvent was removed to afford crude products. Purification by flash chromatography followed by preparative HPLC afforded **2a** (1.53 g, 43%) and **4a** (310 mg, 9%).

2a: mp 218−220 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, 1.1 mM) δ 8.02 (t, J = 1.6 Hz, 4H), 7.96 (d, J = 1.6 Hz, 8H), 4.32 (t, J = 6.8 Hz, 8H), 1.78 (quintet, J = 6.8 Hz, 8H), 1.50−1.26 (m, 40H), 0.91 (t, J = 7.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 164.34 (s), 144.51 (d), 131.46 (s), 131.08 (d), 122.69 (s), 81.92 (s), 76.26 (s), 65.89 (t), 31.90 (t), 29.53 (t), 29.28 (t), 28.69 (t), 26.10 (t), 22.74 (t), 14.19 (q); IR (KBr) 2216, 1727, 1270, 892, 767, 721, 670 cm^{-1}; Raman 2222 cm^{-1}; UV ($CHCl_3$, 25 °C) λ_{max} (log ϵ) 338 (5.08), 315 (5.23), 296 (4.96), 281 (4.73), 265 (4.61) nm; MS (FAB) *m*/*z* 1121.4 (M^+ + H).

4a: mp 208−209 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, 3.4 mM) δ 8.12 (d, J = 1.6 Hz, 16H), 7.75 (t, J = 1.6 Hz, 8H), 4.31 (t, J = 6.7 Hz, 16H), 1.77 (quintet, J = 6.7 Hz, 16H), 1.43−1.26 (m, 80H), 0.90 (t, J = 6.7 Hz, 24H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 163.78 (s), 138.20 (d), 133.69 (d), 130.91 (s), 122.34 (s), 80.18 (s), 75.70 (s), 65.72 (t), 31.90 (t), 29.36 (t), 29.27 (t), 28.61 (t), 26.08 (t), 22.73 (t), 14.18 (q); IR (KBr) 2223, 1728, 1256, 893, 766, 674 cm^{-1}; UV ($CHCl_3$, 25 °C) λ_{max} (log ϵ) 337 (5.31), 315 (5.41), 296 (5.29), 276 (5.37), 263 (5.37) nm; MS (MALDI-TOF) *m*/*z* 2263.9 (M^+ + Na).

Cyclization of 2mer 7b: DBMs 2b and 4b. To a solution of $Cu(OAc)_2$ (900 mg, 4.9 mmol) in 500 mL of pyridine/benzene (3:2, v/v) was added dropwise a solution of **7b** (390 mg, 0.5 mmol) in 50 mL of the same solvent over 72 h. After additional stirring at room temperature for 3 h, the reaction mixture was worked up as described for the synthesis of **2a** and **4a**. Purification by flash chromatography followed by preparative HPLC afforded **2b** (40 mg, 10%) and **4b** (8 mg, 2%).

2b: mp 133−134 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 30 °C, 8.54 mM) δ 7.94 (t, J = 1.6 Hz, 4H), 7.86 (d, J = 1.6 Hz, 8H), 4.29 (t, J = 6.8 Hz, 8H), 1.77 (qunitet, J = 6.8 Hz, 8H), 1.53−1.26 (m, 104H), 0.88 (t, J = 6.6 Hz, 12H);^{13}C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 164.50 (s), 144.66 (d), 131.60 (s), 131.22 (d), 122.78 (s), 81.94 (s), 76.24 (s), 65.89 (t), 31.93 (t), 29.72 (t), 29.67 (t), 29.63 (t), 29.54 (t), 29.37 (t), 29.31 (t), 28.63 (t), 26.01 (t), 22.69 (t), 14.10 (q); IR (KBr) 2217, 1729, 1250, 893, 766, 720, 672 cm^{-1}; UV ($CHCl_3$, 25 °C) λ_{max} (log ϵ) 339 (5.15), 315 (5.31), 296 (5.02), 281 (4.73), 242 (5.00) nm; MS (FD) *m*/*z* 1570 (M^+ + H).

4b: mp 156−157 °C; ^{1}H NMR (270 Hz, $CDCl_3$, 30 °C) δ 8.16 (d, J = 1.0 Hz, 16H), 7.81 (t, J = 1.0 Hz, 8H), 4.33 (t, J = 6.7 Hz, 16H), 1.75 (quintet, J = 6.7 Hz, 16H), 1.53−1.25 (m, 208H), 0.87 (t, J = 6.6 Hz, 24H); IR (KBr) 2224, 1728, 1257, 893, 766, 672 cm^{-1}; UV ($CHCl_3$, 25 °C) λ_{max} (log ϵ) 338 (5.16), 315 (5.26), 296 (5.13), 276 (5.19) nm; MS (MALDI-TOF) *m*/*z* 3139.45 (M^+ + H).

Cyclization of Linear 4mer 11c: DBMs 2c and 4c. To a solution of $Cu(OAc)_2$ (5.10 g, 28.1 mmol) in 765 mL of pyridine/benzene (3:2, v/v) was added dropwise a solution of **11c** (2.36 g, 1.87 mmol) in 765 mL of the same solvent over 74 h. After additional stirring at room temperature for 3 h, the reaction mixture was worked up as described for the synthesis of **2a** and **4a**. Purification by preparative HPLC afforded **2c** (1.00 g, 43%) and **4c** (331 mg, 14%) both as pale yellow solid.

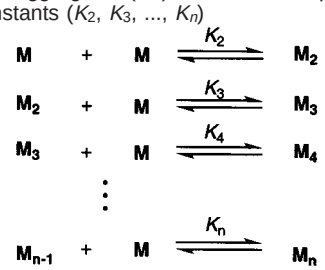
2c: dec at 145 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 30 °C, 2.3 mM) δ 8.06 (t, J = 1.5 Hz, 8H), 8.04 (d, J = 1.5 Hz, 4H), 4.51−4.48 (m, 8H), 3.86−3.83 (m, 8H), 3.74−3.65 (m, 24H), 3.57−3.54 (m, 8H), 3.39 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) δ 164.04 (s), 144.47 (d), 130.92 (s), 131.88 (d), 122.59 (s), 81.76 (s), 76.35 (s), 71.94 (t), 70.64 (t), 70.58 (t), 68.86 (t), 64.58 (t), 58.99 (q); IR (KBr) 2216, 1727, 1261, 892, 767, 721, 670 cm^{-1}; MS (MALDI-TOF) *m*/*z* 1279.4 (M^+ + Na). Anal. Calcd for $C_{72}H_{72}O_{20}$: C, 68.78; H, 5.77. Found: C, 68.60; H, 5.68.

4c: dec at 109 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 30 °C, 2.7 mM) δ 8.19 (d, J = 1.6 Hz, 16H), 7.83 (t, J = 1.5 Hz, 8H), 4.52−4.48 (m, 16H), 3.86−3.83 (m, 16H), 3.74−3.65 (m, 48H), 3.59−3.53 (m, 16H), 3.37 (s, 24H); ^{13}C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 164.34 (s), 139.75 (d), 134.03 (d), 131.25 (s), 122.58 (s), 80.05 (s), 75.26 (s), 71.98 (t), 70.74 (t), 70.66 (t), 69.03 (t), 64.79 (t), 59.06 (q); IR (KBr) 2360, 1726, 1261, 1111, 893, 766, 674 cm^{-1}; MS (MALDI-TOF) *m*/*z* 2535.7 (M^+ + Na).

Transesterification of 2a: DBM 2e. To a stirred solution of octyl ester **2a** (18 mg, 1.6 μmol) and 1-butanol (1.5 mL, 16 mmol) in 3 mL of toluene were added K_2CO_3 (11 mg, 8.1 μmol) and 18-crown-6 ether (2 mg, 8.1 μmol). After the mixture was stirred at 60 °C for 16 h, the solvent was removed with an evaporator. Purification by flash chromatography followed by preparative HPLC afforded butyl ester **2e** as a white solid (10 mg, 71%): dec at 247 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 40 °C, 0.55 mM) δ 8.07 (t, J = 1.6 Hz, 4H), 8.03 (d, J = 1.6 Hz, 8H), 4.35 (t, J = 6.9 Hz, 8H), 1.77 (quintet, J = 6.9 Hz, 8H), 1.48 (m, 8H), 1.00 (t, J = 7.4 Hz, 12H); IR (KBr) 2219, 1726, 1249, 892, 766, 671 cm^{-1}; MS (MALDI-TOF) *m*/*z* 896.1 (M^+).

Cyclization of Linear 6mer 13a: DBM 3a. To a solution of $Cu(OAc)_2$ (5.39 g, 29.7 mmol) in 1.6 L of pyridine/benzene (3:2, v/v) was added dropwise a solution of **13a** (1.0 g, 0.59 mmol) in 400 mL of the same solvent over 53.5 h. After additional stirring at room temperature for 2.5 h, the reaction mixture was worked up as described for the synthesis of **2a** and **4a**. Purification by flash chromatography followed by preparative HPLC afforded **3a** as a pale yellow solid (270 mg, 27%): dec at 255 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C, 14.9 mM) δ 7.23 (br s, 12H), 7.07 (br s, 6H), 4.02 (br s, 12H), 1.69 (m,

Scheme 2. Equilibrium between Monomer (M), Dimer (M_2), Trimer (M_3), and Higher Aggregates (M_n) and the Corresponding Association Constants (K_2, K_3, ..., K_n)



12H), 1.40 (m, 60H), 0.97 (t, $J = 6.7$ Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, 14.9 mM) δ 163.21 (s), 138.34 (d), 132.40 (d), 130.29 (s), 122.02 (s), 79.84 (s), 75.72 (s), 65.48 (t), 32.00 (t), 29.48 (t), 29.34 (t), 28.49 (t), 26.14 (t), 22.82 (t), 14.26(q); IR (KBr) 2223, 1728, 1249, 893, 766, 673 cm^{-1}; Raman 2223 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ϵ) 338 (5.21), 315 (5.30), 296 (5.08), 278 (4.93) nm; MS (MALDI-TOF) *m*/*z* 1680.54 (M^+). Anal. Calcd for $C_{114}H_{120}O_{12}$: C, 81.40; H, 7.19. Found: C, 81.22; H, 7.26.

Cyclization of Linear 6mer 13b: DBM 3b. To a solution of $Cu(OAc)_2$ (5.16 g, 28.4 mmol) in 1.6 L of pyridine/benzene (3:2, v/v) was added dropwise a solution of **13b** (1.4 g, 0.58 mmol) in 400 mL of the same solvent over 48 h. After additional stirring at room temperature for 24 h, the reaction mixture was worked up as described for the synthesis of **2a** and **4a**. Purification by flash chromatography followed by preparative HPLC afforded **3b** as a pale yellow solid (202 mg, 15%): mp 178−180 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 30 °C, 12.1 mM) δ 7.69 (br s, 12H), 7.46 (br s, 6H), 4.20 (t, $J = 6.4$ Hz, 12H), 1.77 (m, 12H), 1.42−1.27 (m, 156H), 0.88 (t, $J = 6.6$ Hz, 18H); ^{13}C NMR (67.5 MHz, $CDCl_3$, 30 °C, 12.1 mM) δ 163.87 (s), 139.16 (d), 133.11 (d), 130.98 (s), 122.41 (s), 80.06 (s), 75.71 (s), 65.73 (t), 31.94 (t), 29.76 (t), 29.70 (t), 29.65 (t), 29.42 (t), 29.39 (t), 28.60 (t), 26.05 (t), 22.70 (t), 14.10 (q); IR (KBr) 2217, 1730, 1255, 891, 765, 720, 671 cm^{-1}; UV ($CHCl_3$, 25 °C) λ_{max} (log ϵ) 338 (5.24), 315 (5.32), 296 (5.10), 278 (4.95), 243 (5.11) nm; MS (MALDI-TOF) *m*/*z* 2376.73 (M^+ + Na), 2353.71 (M^+). Anal. Calcd for $C_{162}H_{216}O_{12}$: C, 82.61; H, 9.24. Found: C, 82.50; H, 9.39.

Cyclization of Linear 6mer 13c: DBM 3c. To a solution of $Cu(OAc)_2$ (150 mg, 0.826 mmol) in 25 mL of pyridine/benzene (3:2, v/v) was added dropwise a solution of **13c** (595 mg, 0.529 mmol) in 25 mL of the same solvent over 48 h. After additional stirring at room temperature for 24 h, the reaction mixture was worked up as described for the synthesis of **2a** and **4a**. Purification by flash chromatography followed by preparative HPLC afforded **3c** as a pale yellow solid (67 mg, 65%): dec at 242 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, $J =$ 1.6 Hz, 12H), 7.77 (t, $J = 1.6$ Hz, 6H), 4.49−4.46 (m, 12H), 3.86−3.83 (m, 12H), 3.75−3.67 (m, 36H), 3.66−3.54 (m, 12H), 3.39 (s, 18H); ^{13}C NMR (67.5 MHz, $CDCl_3$, 30 °C) δ 163.62 (s), 139.12 (d), 132.98 (d), 130.52 (s), 122.32 (s), 79.93 (s), 75.74 (s), 71.97 (t), 70.65 (t), 70.62 (t), 70.60 (t), 68.80 (t), 64.51 (t), 59.01 (q); IR (KBr) 3067, 2874, 2222, 1727, 1584, 1444, 1259, 1112, 890, 764, 673 cm^{-1}; MS (MALDI-TOF) *m*/*z* 1907.7 (M^+ + Na). Anal. Calcd for $C_{108}H_{108}O_{30}$: C, 68.78; H, 5.77. Found: C, 68.44; H, 5.75.

Analysis of Self-Association by ^{1}H NMR Spectra.[37] For treatment of the experimental NMR data, the sum of deviations between the chemical shifts (δ_{calcd}) calculated according to eq 1 for the dimer model or eq 2 for the infinite association model and those of experimental chemical shifts (δ_{obs}) were calculated, and K_2 (or K_E), δ_m, and δ_d (or δ_a) were optimized to reduce the sum of deviations by using the "solver" function implemented in the Excel program.[54] The same curve fitting was also performed by the IGOR program.[55] The obtained K_2 (or K_E), δ_m, and δ_d (or δ_a) values are consistent with each other. The standard deviations for the calculated values were estimated by using the IGOR or SOLVSTAT[56] macro of Excel.

Analysis of Self-Association by Vapor Pressure Osmometry.[37] In the VPO measurements, the osmotic coefficient (ϕ) is related to activity coefficient (γ) in the following eqs 13 and 14 according to the Gibbs−Duhem equation:

$$\phi = \frac{m_c}{m_s} = 1 + am_s + bm_s^2 + cm_s^3 + dm_s^4 + em_s^5 + fm_s^6 \quad (13)$$

$$\ln \gamma = 2am_s + \frac{3}{2}bm_s^2 + \frac{4}{3}cm_s^3 + \frac{5}{4}dm_s^4 + \frac{6}{5}em_s^5 + \frac{7}{6}fm_s^6 \quad (14)$$

where m_s is stoichiometric molal concentration and m_c is colligative molal concentration. Using eq 13, the experimental data obtained for samples of several (typically 15−16) different concentrations ranging from ca. 10^{-2} to 10^{-4} M are fitted to the sixth order polynominal, from which the monomer concentrations ($m_1 = \gamma m_s$) for each sample solution were calculated. In the equal K model,[44] eq 3 which relates ϕ/γ to K and m_1 is derived from the following eqs 15 and 16.

$$m_c = m_1 + m_2 + m_3 + ... + m_n = m_1 + K_2m_1^2 + K_2K_3m_1^3 + ... + K_2K_3...K_nm_1^n \quad (15)$$

$$\frac{m_c}{m_1} = 1 + Km_1 + K_2m_1^2 + ... + K^{n-1}m_1^{n-1} \quad (16)$$

Fitting a plot of the experimentally obtained ϕ/γ versus log m_1 to the master curves, which were plotted for $[1 - (Km_1)^n]/(1 - Km_1)$ versus log Km_1 for different n ($n = 1, 2, 3, 4, 5, 6$, and ∞), yielded log K as the translation along the abscissa.

In the second model ($K_2 \neq K$),[45] for each hypothesis I−IV, T defined in eq 12 is related to log m_1 as eqs 5, 7, 9, and 11. Fitting a plot of experimentally obtained $\log[(m_s - m_1)/m_1]$ versus log m_1 to the master curves of log T versus log Km_1 for eqs 5, 7, 9, and 11 gave log K as the translation along the abscissa and $\log(K/K_2)$ as the translation along the ordinate. Since, in general, the data fit best to the model IV among the models I−IV, K_2 and K shown in Table 5 were calculated by using this model.

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Supporting Information Available: Synthesis of **2e**, **5a**,**b**, and **15**, determination of association constants of DBMs **2a**−**c**, **3a**−**c**, and **4a**, the linear oligomers **11c** and **13c** by ^{1}H NMR spectra and VPO, and UV spectra of **2c** and **3c** in polar solvents (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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