J. Am. Chem. Soc. 1986, 108, 325-327

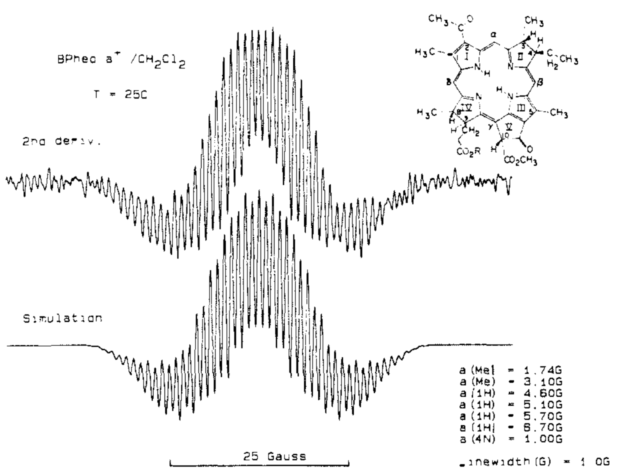

Figure 2. (Top) Second-derivative ESR spectrum of BPheo a$^+$ in CH$_2$Cl$_2$ at 25 °C obtained by computer averaging.[13] (Bottom) Simulation that demonstrates that two methyl groups, four large protons, and four nitrogens determine the spectral pattern observed.

of BPheo a$^+$ agree within 2% with those observed in the alcoholic solvent, indicating that hydrogen bonding has little effect on the spin distributions of the radicals (Table I). (Comparison of BChl a$^+$ in CH$_2$Cl$_2$ and CH$_3$OH is complicated by the formation of aggregates in CH$_2$Cl$_2$).

The combination of (1) and (2) suggests therefore that oxygen ligation of the Mg in BChls and/or hydrogen bonding of the oxygen peripheral groups do not significantly alter the spin profiles of BChl a$^+$ in vitro and, by extrapolation, the profiles of the primary donors P870$^+$ and P960$^+$ in vivo.

(3) Computer signal averaging yields[3] a partially resolved solution ESR spectrum of BPheo a$^+$ with 40 or more lines (Figure 2). This spectrum provides a sensitive test for the assignments of the ENDOR coupling constants. A satisfactory facsimile of the experimental BPheo a$^+$ spectrum is obtained with a computer simulation (Figure 2) that assumes two methyl groups with a_H = 1.74 (1-CH$_3$) and 3.10 G (5-CH$_3$), four protons with a_H = 4.6, 5.1, 5.7, and 6.7 G (β protons on rings II and IV), and four nitrogens with a_N = 1.0 G (approximated from the sole N splitting that is resolved).[13] These results thus support the ENDOR assignments and the similar spin profiles predicted by MO calculations for the BPheo and BChl cations.[3,4,10,14]

(4) Changes in the coupling constants of BPheo a$^+$ can be induced near the "freezing" point of CH$_3$OH/CH$_2$Cl$_2$ mixtures (Figure 1, T = 153-163 K)). However, only the β protons of rings II and IV are significantly affected. The effect observed is attributable to conformational changes[4,11] (twisting) of the flexible saturated rings[17] induced by the glassy matrix. Analogous variations in rings IV or II have been observed in X-ray structures of single crystals of methyl bacteriopheophorbides a and d.[17] Similar conformational effects could be induced by packing and protein interactions in vivo and may explain some of the ESR and ENDOR variations observed in different photosynthetic bacteria.[1-5] It is intriguing to speculate further that some conformational rearrangements accompany electron transfer[18] and alter both the distances and the relative orientations of BChl donors and acceptors in vivo and thereby help to regulate forward and back electron flow.[19]

Acknowledgment. This work was supported by the Division of Chemical Sciences, US Department of Energy, Washington, DC, under Contract DE-AC02-76CH00016. We thank Arthur Forman for the simulation in Figure 2.

Registry No. BPheoa$^{+\cdot}$, 60686-68-2.

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First Realization of Threefold Fluxionality in Polycyclic Conjugated Hydrocarbon-Metal Complexes: Synthesis and Dynamic NMR Study of [Pd(η^3-phenalenyl)(tmeda)]$^+$PF$_6^-$ and Its Methyl Derivative

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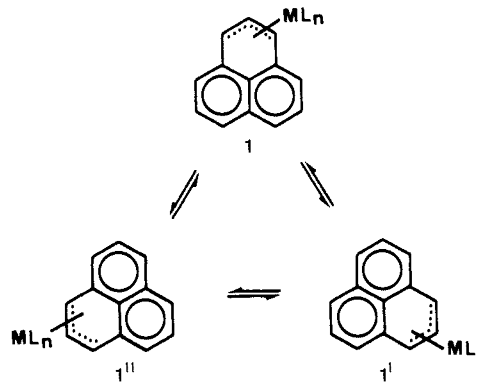
A major goal of current research in the area of dynamic behaviors in organometallic chemistry is the synthesis of new metal complexes that exhibit migration of an ML$_n$ unit from one ring to another in a polycyclic conjugated hydrocarbon ligand.[1-3] A case in point would be the phenalenyl-ML$_n$ system.[4-7] If the ML$_n$ unit in an η^3-phenalenyl complex **1** migrates around the phenalenyl skeleton through the pathway of **1** ⇄ **1′** ⇄ **1″**, such a stereochemical nonrigid behavior provides a novel example of a 3-fold fluxionality in the metal complexes of polycyclic conjugated hydrocarbon.[8,9] We now report the first realization of such a



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[1] Much experimental information for this type of process is confined to simple cyclic polyene complexes. (a) Cotton, F. A. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 10. (b) Faller, J. W. *Adv. Organomet. Chem.* **1977**, *16*, 211. (c) Deganello, G. "Transition Metal Complexes of Cyclic Polyolefins"; Academic Press: New York, 1979. (d) Fedorov, L. A. *Russ. Chem. Rev.* **1973**, *42*, 678.

[2] For a leading review and theoretical treatment of the interring migration of an ML$_n$ unit in polycyclic hydrocarbon-metal complexes, see: Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396 and references cited therein. **Note Added In Proof.** After submittion of this paper Silvesta and Albright (*J. Am. Chem. Soc.* **1985**, *107*, 6829) have reported some aspects of the haptotropic shift in phenalenium-ML$_2$ complex.

[3] (a) For the migration of a Cr(CO)$_3$ group between two nonadjacent six-membered rings, see: Cunningham, S. D.; Öfele, K.; Willeford, B. R. *J. Am. Chem. Soc.* **1983**, *105*, 3724. (b) Crabtree, R. H.; Parnell, C. P. *Organometallics* **1984**, *3*, 1727.

[4] (a) η^1-σ- and η^6-π-: Lin, S.; Boudjouk, P. *J. Organomet. Chem.* **1980**, *187*, C11. (b) η^2-π-: Woell, J. B.; Boudjouk, P. *J. Organomet. Chem.* **1979**, *172*, C43.

[5] η^3-allyl-: Keasey, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1978**, 142.

[6] (a) Nakasuji, K.; Yamaguchi, M.; Murata, I.; Tatsumi, K; Nakamura, A. *Chem. Lett.* **1983**, 1489; (b) *Organometallics* **1984**, *3*, 1257.

[7] For the postulated intermediacy of an (η^3-phenalenyl)rhodium complex, see: Paquette, L. A.; Grée, R. *J. Organomet. Chem.* **1978**, *146*, 319. For the thermally and photochemically induced sigmatropic shifts of the trimethylsilyl group in 1-(trimethylsilyl)phenalene, see: Butcher, J. A., Jr.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 3997.

[8] For attempts to detect such a behavior, see ref 5 and 6.

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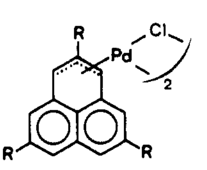
behavior.

We have recently prepared the acetylacetonate (acac) complex Pd(η^3-phenalenyl)(acac) (**1**, ML_n = Pd(acac)) and characterized it by its ^{1}H NMR spectrum.[6] Unfortunately, however, the complex was too labile to detect such fluxionality at elevated temperatures. Accordingly, in order to enhance the thermal stability, we prepared the *N,N,N′,N′*-tetramethylethylenediamine (tmeda) complex [Pd(η^3-phenalenyl)(tmeda)]$^+$PF$_6^-$ (**3a**), from bis(μ-chloro)bis(η^3-phenalenyl)palladium (**2a**)[11] by ligand exchange. Thus, a suspension of **2a** in acetone was treated with 2 equiv of TMEDA and KPF$_6$ under nitrogen for 0.5 h to afford **3a** as yellow needles, mp 183 °C dec, which is fairly stable in contrast to **1**, ML_n = Pd(acac). ^{1}H and ^{13}C NMR data[12] at room temperature unambiguously support the coordination site of the structure **1**.



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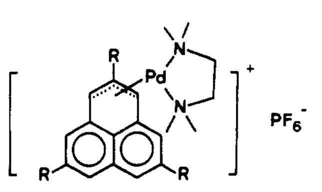

3

a, R = H; **b**, R = CH$_3$

As the temperature is raised, the two sets of signals (an ABC system (6 H) at δ 7.97, 7.93, and 7.40 and an XY$_2$ system (3 H) at δ 6.23 and 6.04) in the ^{1}H NMR spectra (100 MHz) become broad and change to a broad A$_2$B-like pattern (δ_A 7.32, δ_B 7.04) at 160 °C, the chemical shifts of which are very close to the weighted average (δ 7.31 and 7.00) of six α- (1, 3, 4, 6, 7, and 9) and three β-protons (2, 5, and 8) of the phenalenyl skeleton. In the ^{13}C NMR spectrum (100 MHz) at 102 °C, the two signals for the allylic carbons (δ 74.85 for C$_1$ and C$_3$, δ 99.33 for C$_2$) were broaden and hidden under the signal noise. Although decomposition occurred at higher temperatures,[13] both the ^{1}H and ^{13}C NMR spectral behaviors were found to be reversible within the above temperature range. These results strongly suggest a stereochemical nonrigidity between structurally equivalent species. A most likely possibility responsible for these observations is the 3-fold degenerate interring migration, $\mathbf{1} \rightleftarrows \mathbf{1'} \rightleftarrows \mathbf{1''}$.

In the dynamic NMR spectroscopy, the signals with a smaller chemical shift separation coalesce at a lower temperature. To attain a coalescence temperature low enough to be observed before decomposition of the complex, we introduced methyl groups as a suitable probe. For this substitution, the three β-positions of the phenalenyl system were selected to minimize electronic and steric perturbations caused by the substituents and to maintain the D_{3h} symmetry of the ligand. Thus, the symmetrical trimethyl complex **3b**[14] was prepared from 2,5,8-trimethylphenalene[15] through **2b**[16] by a similar procedure as that described above. The ^{1}H NMR signals of the methyl groups overlapped with those of the TMEDA ligand. However, the ^{13}C NMR (50 MHz) signals of the methyl groups situated at the respective coordinated and uncoordinated rings for **3b** showed fairly small separation by only 32.96 Hz. Figure 1 shows a comparison of the observed and computer-simulated ^{13}C dynamic NMR spectra of the methyl region of **3b**, in which the two signals arising from the methyl groups on the allyl (δ 21.67) and the naphthalene moieties (δ 21.02) coalesce at 92.1 °C and finally change to a sharp single line on further temperature increase. The activation parameters obtained by the complete line-shape analysis[17] are E_a = 21.6 ± 0.4 kcal/mol, $\Delta H^‡$ = 20.9 ± 0.4 kcal/mol, $\Delta G^‡$ = 21.4 ± 0.1 kcal/mol, and $\Delta S^‡$ = −1.3 ± 0.3 eu (90.0 °C).[18]

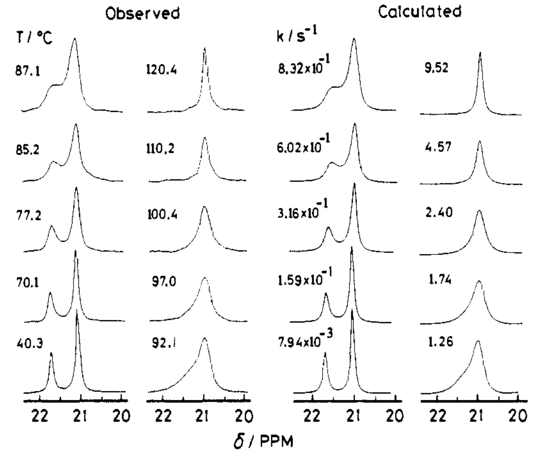

Figure 1. Observed and calculated 50-MHz ^{13}C NMR spectra of methyl region for **3b** at several temperatures (exchange rates).

To conclude, although it is difficult to define the rigorous migration pathway, the available evidence described in this paper reveals that the 3-fold fluxional behavior in **3** does occur.[20] The unique topological features associated with the phenalenyl non-

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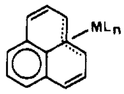
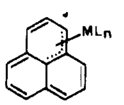
(9) In the case of η^3-phenalenyl complexes, both **1** and an alternate isomer



i



ii

i are expected to contain relatively low energies from the topology of the nonbonding phenalenyl orbital. A less stable isomer ii can also be drawn on the basis of a simple valence bond treatment.[6] These features of η^3-phenalenyl complexes may contribute to relatively low activation energy for the dynamic behavior,[10] if it occurs intramolecularly.

(10) These are born out by the comparison of the total energies (i and ii are less stable than **1** by 1.2 and 15.7 kcal/mol, respectively) calculated by the extended Hückel molecular orbital method. See ref 6.

(11) This complex is very likely an η^3-complex as shown in **2a**, but the evidence in support of the coordination site is not conclusive. See ref 4b and 6.

(12) **3a**: ^{1}H NMR (400 MHz, in Me$_2$SO-d_6) δ 7.97 (2 H, H-6,7), 7.93 (2 H, H-4,9), 7.40 (2 H, H-5,8, $J_{4,5} = J_{8,9}$ = 7.8, $J_{5,6} = J_{7,8}$ = 7.2, $J_{4,6} = J_{7,9}$ = 0.8 Hz), 6.23 (1 H, H-2), 6.04 (2 H, H-1,3, $J_{1,2} = J_{2,3}$ = 6.4 Hz), 2.6–2.5 (4 H, m, NCH$_2$), 2.75, 2.26 (12 H, each s, NCH$_3$); ^{13}C NMR (100 MHz, in Me$_2$SO-d_6) δ 133.72 (C-3a, -6a, -9a), 125.71 (C-3b), 122.40, 126.78, 129.02 (C-4.9; -5.8; -6,7), 99.33 (C-2), 74.85 (C-1,3), 60.29 (NCH$_2$), 51.64, 49.21 (NCH$_3$). Anal. Calcd for $C_{19}H_{25}F_6N_2PPd$: C, 42.83; H, 4.73; N, 5.26. Found: C, 42.85; H, 4.71; N, 5.28.

(13) The formation of a slight amount of phenalenone was observed by ^{1}H NMR.

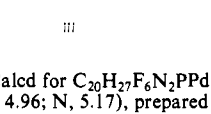
(14) **3b**: yellow microcrystals, mp 206–207 °C dec (from CH$_2$Cl$_2$–hexane); ^{1}H NMR (100 MHz, CD$_2$Cl$_2$) δ 7.53 (2 H, br s, H-4,9 or -6,7), 7.47 (2 H, br s, H-6,7 or -4,9), 5.50 (2 H, s, H-1,3), 2.76, 2.26 (12 H, each s, NCH$_3$), 2.54 (6 H, s, 5,8-CH$_3$), 2.50 (4 H, br s, NCH$_2$), 2.44 (3 H, s, 2-CH$_3$); ^{13}C NMR (50.0 MHz, Me$_2$SO-d_6) δ 137.58 (C-5,8), 133.28 (C-3a,9a), 133.13 (C-6a), 124.03, 122.04 (C-4,9; -6,7), 120.73 (C-3b), 113.50 (C-2), 73.63 (C-1,3), 59.45 (NCH$_2$), 51.13, 48.24 (NCH$_3$), 21.67 (2-CH$_3$), 21.02 (5,8-CH$_3$) (at 34.5 °C). Anal. Calcd for $C_{22}H_{31}F_6N_2PPd$: C, 45.96; H, 5.44; N, 4.87. Found: C, 45.89; H, 5.47; N, 4.78.

(15) 2,5,8-Trimethylphenalene was prepared according to the route described in the literature, with some modifications: Wolinska-Mocydlarz, J.; Canonne, P.; Leitch, L. C. *Synthesis* **1974**, 566.

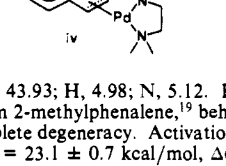
(16) **2b** was prepared by using the reported method for bis(μ-chloro)bis(η^3-indenyl)palladium. See ref 6b.

(17) Yamoto, O.; Hayamizu, K.; Nakanishi, H.; Yanagisawa, M. *J. Nat. Chem. Lab. Ind.* (*Jpn. 1903–1979*) **1974**, *69*, 14.

(18) A mixture of [Pd(η^3-2-methylphenalenyl)(tmeda)]$^+$PF$_6^-$, iii, and iv



iii



iv

(Anal. Calcd for $C_{20}H_{27}F_6N_2PPd$: C, 43.93; H, 4.98; N, 5.12. Found: C, 43.79; H, 4.96; N, 5.17), prepared from 2-methylphenalene,[19] behaves similarly, although this mixture lacks complete degeneracy. Activation parameters: E_a = 23.8 ± 0.7 kcal/mol, $\Delta H^‡$ = 23.1 ± 0.7 kcal/mol, $\Delta G^‡$ = 21.6 ± 0.1 kcal/mol, $\Delta S^‡$ = 4.1 ± 1.9 eu at 90.0 °C.

(19) Boekelheide, V.; Larrabee, C. E. *J. Am. Chem. Soc.* **1950**, *72*, 1240.

(20) There is, to our knowledge, no precedent for the stereochemical nonrigid behaviors of polycyclic conjugated hydrocarbon–metal complexes, activation parameters of which were determined by dynamic NMR spectroscopy.

bonding MO[6] may be crucial for detecting such fluxionality. Attention to the nonbonding MO's of odd alternant polycyclic hydrocarbon ligands will open the way to explore further examples of stereochemical nonrigid behaviors.

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Ordering of Metal Chelates on the Basis of Bilayer Assembly

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We report herein strong intermetallic interactions of Cu(II) chelates formed at the surface of bilayer aggregates.

Synthetic bilayer membranes are two-dimensional arrays of molecules and are useful vehicles for ordering of part or whole molecules because of their structural flexibility. The molecular ordering produces various interesting properties. For instance, efficient energy migration among chromophores was implied in ammonium bilayers that contained anthracene[1] and carbazole[2] units, and large enhancements due to extensive dipolar coupling were observed in circular dichroism of chiral bilayer membranes.[3-5] These unique characteristics should be similarly applicable to preparation of ordered arrays of metal chelates.

Simon and others carried out extensive investigations on micellar and liquid-crystalline metal complexes[6,7] and found, among other results, a remarkable enhancement of the dioxygen stability constant for micellar cobaltous complexes.[8] We examined previously the interaction of metal ions with ligands at the bilayer surface, which caused subsequent changes of membrane physical states.[9,10] In these cases, however, the direct interaction of metal ions is not observed.

We prepared a single-chain amphiphile ($C_6AzoC_{10}\cdot 14N_4$)[11] that contains the azobenzene moiety in the hydrophobic part and a cyclic tetramine (cyclam) as the hydrophilic head. The azobenzene unit was selected as reporter group, since its absorption spectra were shown to correlate with the membrane physical state[13,14] (Chart I).

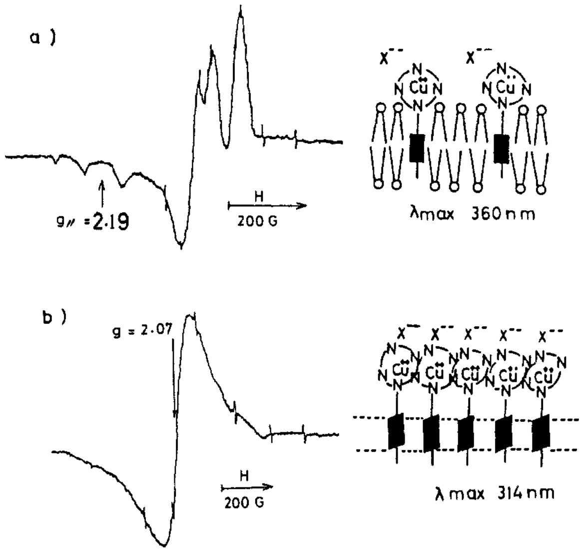


Figure 1. ESR spectra and schematic illustrations of Cu(II) chelates in the bilayer assembly. The ESR samples were prepared by quenching of aqueous bilayer dispersions by liquid nitrogen. (a) [$2C_{16}N^+2C_1$] = 0.1 M; [$C_6AzoC_{10}\cdot 14N_4$] = [$CuCl_2$] = 1.0 mM. (b) [$C_6AzoC_{10}\cdot 14N_4$] = [$CuCl_2$] = 1.0 mM; [KCl] = 1.0 M.

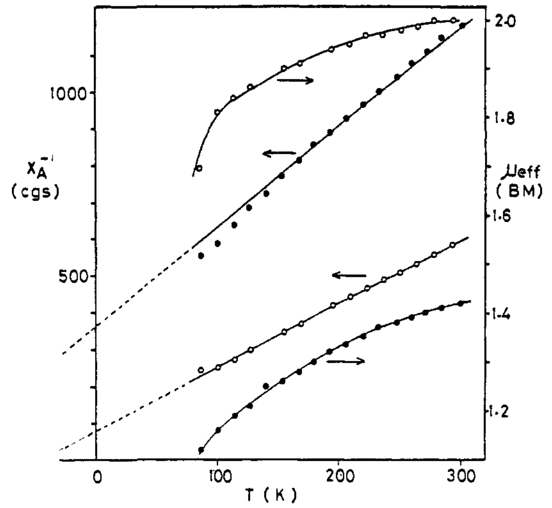
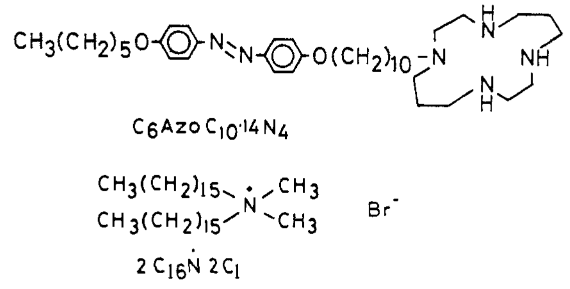


Figure 2. Temperature dependence of the magnetic property of bilayer powders: (○) [$(C_6AzoC_{10}\cdot 14N_4)_{1.0}Cu]Cl_2$; (●) [$(C_AzoC_{10}\cdot 14N_4)_{1.0}Cu]SO_4$.

Chart I



The azobenzene amphiphile was dispersed in deionized water by sonication (Branson Cell Disruptor, 2 min, 40 W) together with

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(1) Shimomura, M.; Hashimoto, H.; Kunitake, T. *Chem. Lett.* **1982**, 1285-1288.

(2) Kunitake, T.; Shimomura, M.; Hashiguchi, Y.; Kawanaka, T. *J. Chem. Soc., Chem. Commun.* **1985**, 833-835.

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(4) Kunitake, T.; Nakashima, N.; Morimitsu, K. *Chem. Lett.* **1980**, 1347-1350.

(5) Nakashima, N.; Morimitsu, K.; Kunitake, T. *Bull. Chem. Soc. Jpn.* *57*, **1984**, 3253-3257.

(6) Le Moigne, J.; Simon, J. *J. Phys. Chem.* **1980**, *84*, 170-177.

(7) Markovitsi, D.; Mathis, A.; Simon, J.; Wittman, J. C.; Le Moigne, J. *Mol. Cryst. Liq. Cryst.* **1980**, *64*, 121-125.

(8) Simon, J.; Le Markovitsi, D.; Dayantis, J. *J. Am. Chem. Soc.* **1980**, *102*, 7247-7252.

(9) Shimomura, M.; Kunitake, T. *J. Am. Chem. Soc.* **1982**, *104*, 1757-1759.

(10) Kunitake, T.; Shimomura, M.; Iida, K.; Okahata, Y.; Kano, K.; Ogawa, T. *Nippon Kagaku Kaishi* **1983**, 893-900.

(11) The azobenzene amphiphile was prepared from the corresponding bromide[12,13] and cyclam: NMR ($CDCl_3$) δ 0.93 (t, 3, CCH_3), 1.33 (m, 29, CCH_2C), 2.80 (m, 18, NCH_2), 4.03 (t, 4, OCH_2), 4.31 (m, 3, N-H), 6.95 (d, 4, aromatic), 7.85 (d, 4, Ar). Anal. Calcd for $C_{38}H_{64}N_6O_2\cdot 3H_2O$: C, 66.05; H, 10.21; N, 12.16. Found: C, 66.41; H, 9.63; N, 11.96.

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(13) Shimomura, M.; Ando, R.; Kunitake, T. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 1134-1143.

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