DENDRITIC CYCLOTRIPHOSPHAZENE DERIVATIVE WITH HEXAXIS(ALKYLAZOBENZENE) SUBSTITUTION AS PHOTO-SENSITIVE TRIGGER

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Abstract – A dendritic cyclotriphosphazene derivative was synthesized by substitution with six alkylazobenzenes onto cyclotriphosphazene. Photo-induced trans-to-cis isomerization of the azobenzene moieties was discussed on each substituent. It was also investigated that the dendrimer acted as a photosensitive trigger for microenvironmental modification of chirally self-assembled organogels through the isomerization

INTRODUCTION

Photo-isomerization of azobenzene moieties has been frequently utilized in artificial systems because it induces changes in various properties: molecular volume, absorption spectrum, dipole moment, refractive index and conformational changes.[1] Photo-responsive azobenzene-containing triggers have been studied[2-5] to control release of drugs, orientation of liquid crystal molecules, electrical conductivity of films, and to induce self-organization of dye molecules. Under this aspect we synthesized a novel cyclotriphosphazene (CTP) derivative with six long-chain alkylated azobenzene groups: hexakis[p-(p'-dodecyloxy-phenylazo)phenoxy]cyclotriphosphazene (**1a**). The molecular design of **1a** is based on the fact that the molecular shape and volume can drastically change by isomerization of six photosensitive moieties immobilized onto a phosphazene core. Thus this molecule is very attractive as a photo-switchable trigger

for control of self-assembling systems. Indeed, **1a** underwent *trans*-to-*cis* isomerization in each azobenzene moiety to metamorphose into various molecular shapes with different molecular volumes. In this study, lipophilic L-glutamide lipid (**2**)[6] which works as a self-assembling organogelator[7,8] to provide unique chirality[9-11] was chosen as a preliminary model in order to obtain supramolecular structures with properties to be altered by the photo-isomerization of an azobenzene moiety. This paper describes how **1a** can work as a photosensitive trigger for microenvironmental modification of **2**-organogels through photo-isomerization of the azobenzene moieties.

RESULTS AND DISCUSSION

A hexa-substituted cyclotriphosphazene derivative (**1a**) was prepared *via* the procedure shown in Scheme 1: *p*-(*p*'-Dodecyloxyphenylazo)phenol (**3**) was prepared by a previously reported method.[12] Eight equimolars of **3** were mixed with cyclotriphosphazene in acetone and stirred at reflux temperature for 4 d, while the mono-substituted **1b** was prepared at room temperature for 24 h. In the case of **1b**, a negligible amount of by-products with a higher degree of substitution was also formed, but after recrystallization twice from acetonitrile, pure **1b** was obtained (one spot on TLC plate). The ^{31}P-NMR spectrum of **1b** consisted of an AB$_2$ spin system (ν_A = 13.30 ppm and ν_B = 23.30 ppm, J$_{PP}$ = 60.5 Hz), which is typical of a mono-substituted pentachlorocyclotriphosphazene derivative.[13] A hexa-substituted **1a** provided only one chemical shift at ν_A = 9.73 ppm.
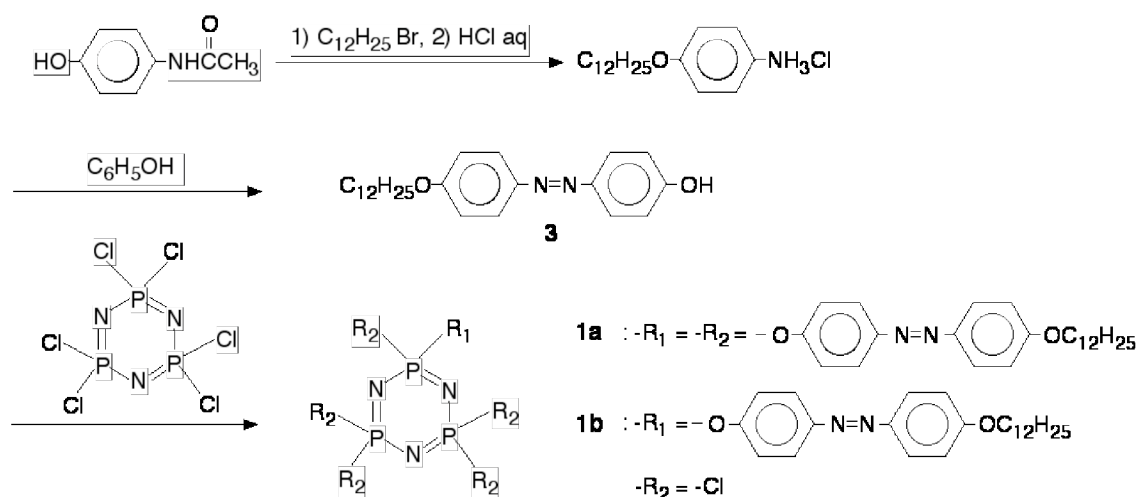
Scheme 1. Synthesis of dendritic cyclotriphosphazene derivative (**1a**)

1a in a solution state exhibited UV spectra, as is common for azobenzene-containing compounds.[14] It was also subjected to isomerization by UV-irradiation. However, it is very difficult to evaluate the conversion of isomerization because of the six azobenzene units. Therefore, the time course of the *trans*-to-*cis*

conversion of **1a** by UV-irradiation was monitored using the modified HPLC method previously reported by us.[13] The chromatogram seen in Figure 1a showed only one peak (**A**) at 13.0 min before UV-irradiation, while several small peaks were detected at shorter retention times. This main peak (**A**) can be assigned to **1a** with all *trans*-conformational azobenzenes because the UV-visible spectrum is exactly the same as that of the corresponding *trans*-azobenzene[15] (λ_{max} = 352 nm in the mobile phase). Therefore, this species **A** is abbreviated as $\mathbf{T_6C_0}$, where each number represents the *trans*- and *cis*-conformational azobenzenes, respectively. On the other hand, the chromatogram in Figure 1b shows that UV-irradiation for five sec yielded five new peaks (**B**, **C**, **D**, **E** and **F**) at 9.2, 9.6, 10.3, 11.0 and 11.9 min with decrease of the peak area of **A**. Further UV-irradiation yielded another new peak (**G**) at 8.6 min with complete disappearence of **A** (Figure 1c). UV-visible spectroscopy of peak (**G**) provided very important information on conformational analysis, because the spectrum pattern was very close to that of the corresponding *cis*-isomer (λ_{max} = 443 nm in the mobile phase) [14] without the *trans*-isomer. Therefore, the species (**G**) can be assigned to $\mathbf{T_0C_6}$. On the basis of this assignment, we can estimate that the peaks (**B**, **C**, **D**, **E** and **F**) are $\mathbf{T_5C_1}$, $\mathbf{T_4C_2}$, $\mathbf{T_3C_3}$, $\mathbf{T_2C_4}$ and $\mathbf{T_1C_5}$, respectively. This is supported by the following facts:

(1) a *cis*-isomer is relatively more polar than a *trans*-isomer. In a reversed-phase HPLC mode, a *cis*-isomer is eluted faster than a *trans*-isomer.[15,16] (2) The absorption ratio at 352 and 443 nm (Abs_{350}/Abs_{410}) in each peak decreases in descending order (**A**, **B**, **C**, **D**, **E**, **F**, **G**). This shows that the composition of a *trans* conformation is richer in the order from **A**, **B**, **C**, **D**, **E**, **F** to **G**. However, unfortunately, our assignment is not yet completed, because each isomers of $\mathbf{T_4C_2}$, $\mathbf{T_3C_3}$ and $\mathbf{T_2C_4}$ can take two isomers at least. Taking account of the possible number of trans conformations on both sides of a cyclotriphosphazene plane, $\mathbf{T_4C_2}$ may be configured either as 3 : 1 or 2 : 2 on each side. Similarly, possible configurations of 3 : 0 and 2 : 1 exist for $\mathbf{T_3C_3}$ and 2 : 0 and 1 : 1 for $\mathbf{T_2C_4}$, respectively.

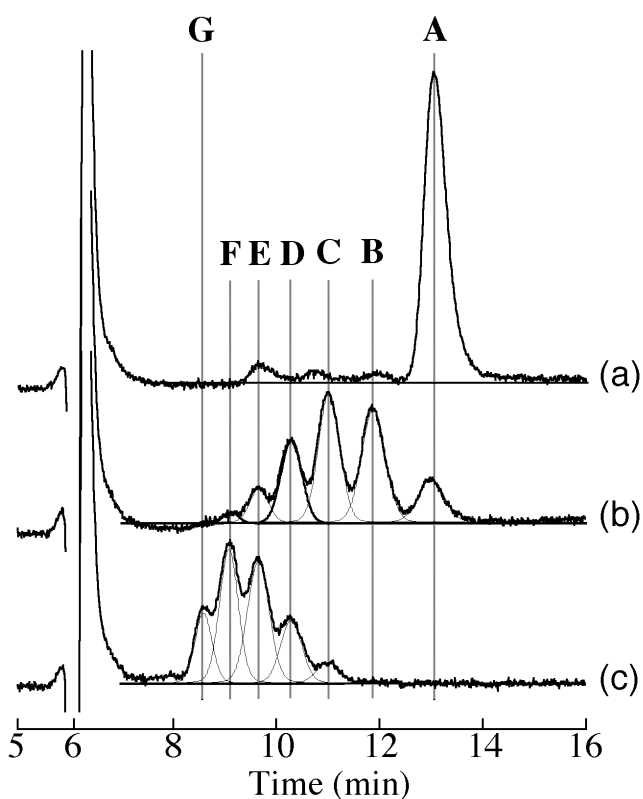As discussed above, **1a** can form various molecular shapes through *trans*-to-*cis*

Figure 1. Chromatographic analysis of *trans*-to-*cis* isomerization of **1a** at 35 °C in THF: (a) before, (b) after 5 sec and (c) 3 min irradiation with 350 nm light by high-pressure mercury lamp (distance: 30 cm). Column: ODS. Mobile phase: ethanol-THF = 75 : 25. Flow rate: 0.3 ml min^{-1}.

conformational changes. We estimate with the HyperChem calculation that **1a** with all *trans*-conformations is cylindrical but *cis*-conformation-including species are rather bulky and dendritic-like. Therefore, we would expect metamorphosis of **1a** to perturb molecular orientation locally if **1a** is assembled into a self-organized system. In this study, then, we investigated the effects of **1a** and mono-substituted **1b** on highly-ordered structures of self-assembled organogel systems with **2**.
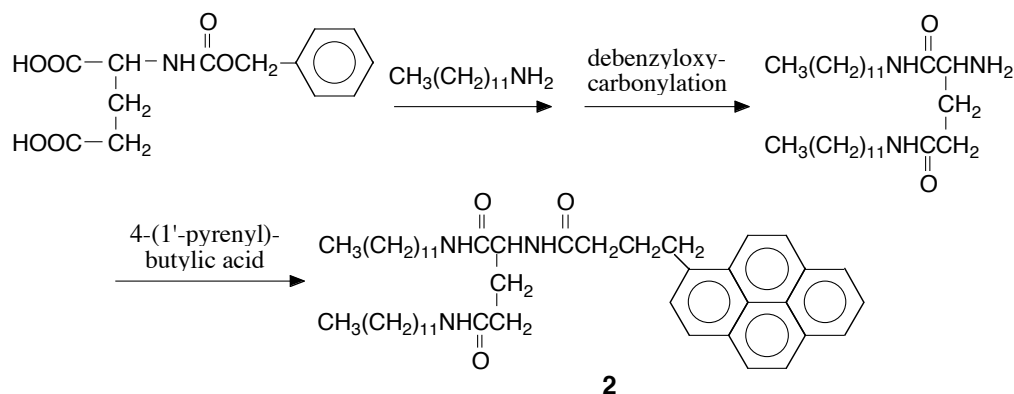
Scheme 2. Synthesis of lipophilic L-glutamide derivative (**2**) with a pyrenyl head group as a self-assembling organogelator

An L-glutamide derivative (**2**) produced organogels when dissolved in benzene at 70 ˚C and then cooled to 15 ˚C. As shown in the CD spectrum of Figure 2, the organogels provided very strong exciton coupling around 355 nm. This CD strength is much larger than that of a monomeric **2** in a solution state and thus such enhancement of chirality can be attributed to formation of highly-ordered assemblies[17] such as aqueous lipid bilayer membrane systems.[18] Further information is obtained by the facts that the λ_{max} is close to that of a pyrenyl group and the CD pattern is positive. The theory by M. Simonyi and co-workers[19] leads us to the estimation that the pyrenyl groups of **2** assemble through chiral arrangement with right-handed overlay in an organogel state. On the basis of this information, the critical aggregation concentration (cac) of **2** was determined to be 0.25 mM in benzene at 15 ˚C by the concentration-$[\theta]_{max}$ plots.[9] The following investigation was carried out with 0.5 mM (above cac) of **2** in benzene at 15 ˚C.

Figure 3 shows the effects of UV-irradiation on the CD strength of the **2** + **1a** mixed systems. The results for **1b** as a mono-substituted derivative are also included. UV-irradiation induced a *trans*-to-*cis* isomerization of **1a** and **1b** similarly to a system without **2**. On the other hand, the *trans*-to-*cis* isomerization was accompanied by reduction of the CD strengths of **2**. This indicates that the molecular orientation of **2** is disturbed by a *trans*-to-*cis* conformational change of **1a** and **1b**. However, there is a distinctly different effect between **1a** and **1b** in the concentration dependency. As can be seen in Figure 3, addition of only 15 mol-% of **1b** brought about almost complete CD disappearence (less than 5 %), but 10 % of the initial CD strength remained even with addition of 50 mol-% of **1a**.
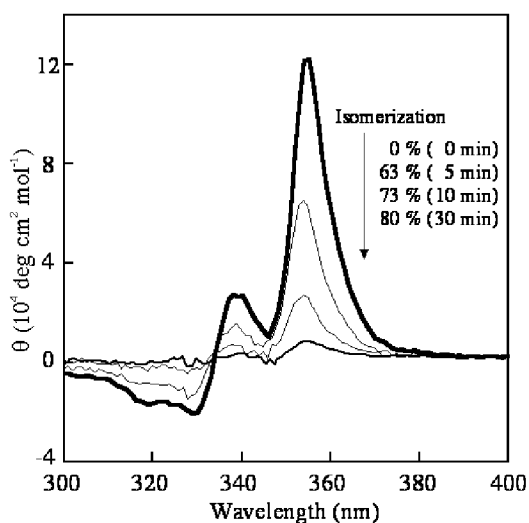
Figure 2. CD spectra of **1a** + **2** in benzene at 15 °C after the irradiation with 350 nm light (distance = 8 cm). [Azo unit] = 0.25 mM, [**2**] = 0.50 mM.
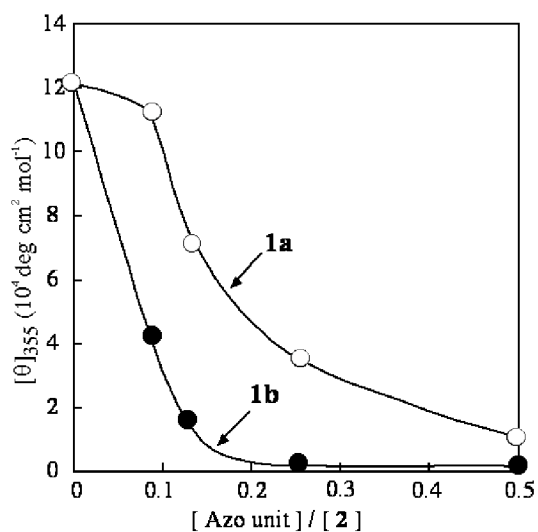
Figure 3. Effects of UV-iradiation on CD strength of **1a** + **2** and **1b** + **2** mixed systems in benzene at 15 °C after irradiation for 30 min. [**2**] = 0.50 mM.

This difference can be explained as schematically illustrated in Figure 4: in the case of **1a**, six azobenzene moieties are covalently connected on a rigid plane and thus morphological change of **1a** promotes disordering around boundary molecules, but **1b** destroys the whole orientation. These findings remind us of the possibility of **1a** as a photo-sensitive trigger such as a molecular channel agent.
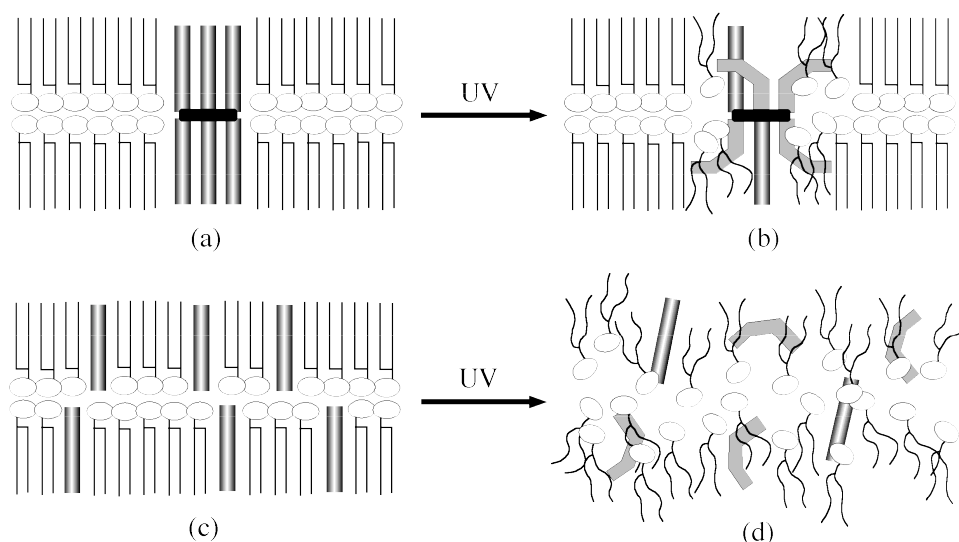

Figure 4. Proposed mechanisms of destruction of highly-ordered structures with photo-induced *trans*-to-*cis* isomerization: **1a** promotes local disordering (b) while **1b** induces total destruction (d).

We have discussed both mono- and hexa(alkylazobenzene)-substituted cyclo-triphosphazenes and it was found that the degree of the *trans*-to-*cis* isomerization in the azobenzene moieties can be controlled by

UV-irradiation and this morphological change can be used as a photo-sensitive trigger to induce microenvironmental disordering in highly-ordered systems.

EXPERIMENTAL

Measurements. ^{1}H-NMR spectra were recorded with a JEOL JNM-EX400 FT-NMR system operating at 400 MHz using solutions in $CDCl_3$ with TMS as internal reference. ^{31}P-NMR spectra were recorded with VARIAN AS400/54 superconducting magnet system operating at 162 MHz. Chemical shift positions were related to the external standard of 0.485 M triphenylphosphate in $CDCl_3$. Melting points were measured with Yanaco MP-J3. FT-IR spectra were recorded on a JASCO FT/IR-5M spectrophotometer with KBr disks. The HPLC system is composed of a JASCO PU-980 pump, a JASCO photodiode arrey detector (MD-2010 Plus) and a column heater (Sugai U-620 Type VP50). The samples were injected by a Reodyne Model 7125 injector. Chromatography was carried out at flow-rate 0.3 mL min^{-1} with Grand pack 120STC (Masis Inc.). Molecular modeling and molecular mechanics calculations were performed with MM$^+$ force field as implemented in the HyperChem software. The geometry optimizations were done *in vacuo*. The structure minimized with conjugate gradient method until the gradient is 0.05 kcal mol^{-1} Å^{-1}. UV-VIS spectra were measured with Hitachi U-2000 spectrophotometer. CD spectra were measured with a JASCO J-725 spectropolarimeter. **2** was dispersed in benzene at room temperature and then heated to be dissolved at 70 ˚C. The solution was rapidly added into a 1 mm quartz cell. The UV and CD spectral measurements were carried out after incubating at given temperature for 45 min. Photo-irradiation was carried out using a USHIO 450 W high pressure mercury lamp. Using a filter (Toshiba UV-D35 band pass filter), light with maximum wavelength of 350 nm was selected.

***p*-Dodecyloxyaniline hydrochloride**. *p*-Acetamidephenol (15 g, 0.10 mol) and potassium hydroxide (7.7 g, 0.12 mol) were dissolved in 150 mL of hot ethanol. 1-Bromododecane (25 g, 0.10 mol) was added to the solution, and the mixture was stirred at reflux temperature for 24 h. After addition of concentrated hydrochloric acid (60 mL), a white precipitate was found and then collected by filtration. *p*-Dodecyloxyaniline hydrochloride was obtained after recrystallization from ethanol and washed with ether and *n*-hexane (13.2 g, 42 %). mp 112-113 ˚C; IR (ν, cm^{-1}): 2917 (C-H), 2851 (C-H), 1473 (C-H), 1248 (C-O); ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 0.86-0.88 (3H, t, *J* = 6.8 Hz, CH_3), 1.26-1.44 (18H, m, CH_2), 1.67-1.89 (2H, m, CH_2), 3.91-3.95 (2H, t, *J* = 6.6 Hz, CH_2-O), 6.90-6.92 (2H, d, *J* = 8.8 Hz, aromatics), 7.43-7.45 (2H, d, *J* = 8.8 Hz, aromatics), 10.36 (3H, s, NH_3). Anal. Calcd for $C_{18}H_{32}NOCl$: C, 68.87; H, 10.28; N, 4.46. Found: C, 68.49; H, 10.21; N, 4.35.

***p*-(Dodecyloxyphenylazo)phenol** (**3**). *p*-Dodecyloxyaniline hydrochloride (12 g, 0.038 mol) was

dissolved in an acetone-water (1 : 1) mixture (300 mL) and concentrated hydrochloric acid (10 mL) was added to the solution. After addition of sodium nitrite (3.4 g, 0.050 mol), a mixture of phenol (6.0 g, 0.064 mol), sodium hydroxide (2.6 g, 0.064 mol) and sodium carbonate (23.7 g, 0.22 mol) in water (200 mL) was added to the solution and stirred at room temperature for 48 h. After further addition of concentrated hydrochloric acid, a red-orange precipitate was formed. These were collected by filtration, and dried *in vacuo*. *p*-(Dodecyloxyphenylazo)phenol was obtained after recrystallization from benzene (6.5 g, 45 %). mp 109-110 ˚C; IR (ν, cm^{-1}): 2918 (C-H), 2850 (C-H), 1583 (N=N), 1474 (C-H), 1247 (C-O); ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 0.86-0.90 (3H, t, J = 6.6 Hz, CH$_3$), 1.27-1.51 (18H, m, CH$_2$), 1.78-1.85 (2H, m, CH$_2$), 4.01-4.04 (2H, t, J = 6.4 Hz, CH$_2$-O), 6.92-6.94 (2H, d, J = 8.4 Hz, aromatics), 6.99-7.00 (2H, d, J = 8.8 Hz, aromatics), 7.82-7.88 (4H, m, aromatics). Anal. Calcd for C$_{24}$H$_{34}$N$_2$O$_2$: C, 75.35; H, 8.96; N, 7.32. Found: C, 74.36; H, 9.15; N, 7.25.

Hexakis[*p*-(*p'*-dodecyloxyphenylazo)phenoxy]cyclotriphosphazene (1a). A mixture of potassium hydroxide (2.1 g, 0.033 mol), *p*-(dodecyloxyphenylazo)phenol (5.0 g, 0.013 mol) and hexachloro-cyclotriphosphazene (0.56 g, 0.0016 mol) in acetone (200 mL) was stirred at reflux temperature for 96 h. The mixture was then filtrated and yielded yellow precipitate. **1a** was purified by washing the precipitate with hot acetone (3.2 g, 82 %). mp 172-173 ˚C; ^{31}P-NMR (CDCl$_3$, 162 MHz): δ 9.73; IR (ν, cm^{-1}): 2918 (C-H), 2850 (C-H), 1597 (N=N), 1584 (N=N), 1236 (C-O), 1168 (P-N); (s). ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 0.87-0.90 (18H, t, J = 6.8 Hz, CH$_3$), 1.28-1.50 (108H, m, CH$_2$), 1.82-1.86 (12H, m, CH$_2$), 4.02-4.05 (12H, t, J = 6.6 Hz, CH$_2$-O), 6.90-6.92 (12H, d, J = 8.8 Hz, aromatics), 7.10-7.12 (12H, d, J = 8.8 Hz, aromatics), 7.68-7.75 (24H, m, aromatics). Anal. Calcd for C$_{144}$H$_{198}$N$_{15}$O$_{12}$P$_3$: C, 71.30; H, 8.23; N, 8.67. Found: C, 70.89; H, 8.22; N, 8.26.

***p*-[*p'*-(Dodecyloxyphenylazo)phenoxy]pentachlorocyclotriphosphazene (1b)**. A mixture of hexachlorocyclotriphosphazene (2.7 g, 0.0079 mol), *p*-(dodecyloxyphenylazo)phenol (0.5 g, 0.0013 mol) and triethylamine (0.13 g, 0.0013 mol) in THF (100 mL) was stirred at rt for 24 h. The mixture was filtrated and the solvent was removed *in vacuo*, **1b** was obtained after twice recrystallization from acetonitrile (0.3 g, 33 %). mp 86.5-87.5 ˚C; IR (ν, cm^{-1}): 2921 (C-H), 2852 (C-H), 1602 (N=N), 1582 (N=N), 1216 (C-O), 1166 (P-N); ^{31}P-NMR (CDCl$_3$, 400 MHz): δ 12.96-13.71 (t, P-(AzoC$_{12}$)Cl), 23.36-23.73 (d, PCl$_2$). Anal. Calcd for C$_{24}$H$_{33}$N$_5$O$_2$Cl$_5$P$_3$: C, 42.41; H, 5.14; N, 10.10. Found: C, 41.6; H, 4.89; N, 10.10.

N^1, N^5-Didodecyl-L-glutamine. N^1, N^5-Didodecyl-N^2-benzyloxycarbonyl-L-glutamine (4.0 g, 8.3 mmol) was prepared by coupling *N*-benzyloxycarbonyl-L-glutamic acid with didodecylamine according to the previously reported procedure.[18] The didodecylamide was dissolved in ethanol (400 mL) with heating and Pd/C (0.4 g, 5 %) was added to the solution. H$_2$ gas was bubbled slowly into the solution for 6 h at 40 ˚C. After removal of the benzyl group, Pd/C was removed by filtration. The solution was concentrated and

dried *in vacuo*. The residue was recrystallized from methanol and dried *in vacuo* to give white powders. Yield 2.0 g (51 %). mp 110-115 ˚C; IR (ν, cm^{-1}): 3324 (N-H), 2917 (C-H), 1632 (C=O), 1528 (H-N-C=O); ^{1}H-NMR (CDCl$_3$): ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.88 (6H, t, J = 6.8 Hz, CH$_3$), 1.26 (36H, m, -CH$_2$-), 1.50 (4H, m, -CH$_2$-), 1.95 (2H, m, -CH$_2$-), 2.31 (2H, m, -CH$_2$CONH-), 3.23 (4H, m, -CH$_2$-), 3.41 (1H, t, J = 6.8 Hz, -CH-), 6.11 (1H, br, NH), 6.81 (1H, br, NH), 7.26 (1H, br, N-H). Anal. Calcd for C$_{29}$H$_{59}$N$_3$O$_2$: C, 72.3; H, 12.3; N, 8.7. Found: C, 71.8; H, 12.2; N, 8.5.

N^1,N^5-Didodecyl-N^2-[4-(1-pyrenylbutyroyl)]-L-glutamine (2). 4-(1-Pyrenyl)butyric acid (0.37 g, 1.3 mmol) and N,N'-didodecyl-L-glutamine (0.60 g, 1.2 mmol) was dissolved in CHCl$_3$ (70 mL) and the mixture was stirred at 0 ˚C. Triethylamine (58 mL, 0.41 mol) and diethyl cyanophosphate (0.48 g, 0.45 mol) were added to the mixture. After being stirred for 1 day at rt, the solution was washed with 0.2N-NaOH three times, 0.2N-HCl three times and water. After dried with sodium sulfate, the solution was concentrated *in vacuo*, and the residue was recrystallized from methanol to produce a pale yellow solid (0.89 g, 93 %). mp 190-195 ˚C; IR (ν, cm^{-1}): 3284 (N-H), 2918 (C-H), 2851 (C-H), 1631 (C=O), 1541 (H-N-C=O); ^{1}H-NMR (CDCl$_3$, 400 MHz): δ = 0.87 (6H, t, J = 6.8 Hz, CH$_3$), 1.21 (36H, m, CH$_2$), 1.46 (4H, m, -CH$_2$-), 1.93 (2H, m, -CH$_2$-), 2.18-2.45 (4H, m, -NHCOCH$_2$CH$_2$-), 2.39 (2H, t, J = 6.4 Hz, -CH$_2$CONH-), 3.20 (4H, m, -CH$_2$NHCO-), 3.36 (2H, m, -CH$_2$-pyrene), 4.34 (1H, m, -CH-), 5.96 (1H, br, NH), 6.81 (1H, br, NH), 7.05 (1H, br, NH), 8.05 (9H, m, pyrene). Anal. Calcd for C$_{49}$H$_{73}$N$_3$O$_3$: C, 78.2; H, 9.8; N, 5.6. Found: C, 77.5; H, 9.6; N, 5.4.

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