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PAPER

# Water-supported organized structures based on wedge-shaped amphiphilic derivatives of dipyrrolyldiketone boron complexes†

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Wedge-shaped amphiphilic derivatives of 1,3-dipyrrolyl-1,3-propanedione boron complexes, with one or no aliphatic chains attached at one aryl moiety and three hydrophilic chains at the other, exhibited formation of assembled structures in aqueous solutions. UV/vis, fluorescence and DLS analyses suggested that the wedge-shaped amphiphiles exist in assembled modes in the solution state, and TEM measurements revealed that a balance of hydrophobic and hydrophilic moieties in the amphiphiles is crucial for the formation of organized structures in aqueous solutions as evidenced by the formation of spherical and cylindrical micelles.

## Introduction

Biotic systems, such as protein folding, DNA double helices and membranes consisting of lipid bilayers, are fabricated based on supramolecular assemblies in an aqueous solution.[1] In these aqueous solutions, the noncovalent interactions between hydrophobic moieties within the assemblies and those between hydrophilic sites and water molecules result in the organized structures.[2] A similar structural ordering in the solution state has been reported in artificial systems, where various amphiphilic molecules bearing both hydrophilic and hydrophobic moieties have been used as components of ordered aggregates.[3–6] Among the building subunits for supramolecular assemblies, π-conjugated systems with hydrophilic chains (and hydrophobic aliphatic chains) have been shown to be effective synthons for the supramolecular assembly of nanoscale architectures as a result of stacking of hydrophobic π-planes, especially, in aqueous solutions. For example, Lee *et al.* reported the formation of nanofibers and nanosheets by the self-assembly of oligophenylene derivatives and their analogs; these nanoassemblies act as liquid crystals and supramolecular gels, as well as micelles and multilayer vesicles.[3] Fukushima and Aida *et al.* also reported the self-assembly of amphiphilic hexabenzocoronenes into π-electronic discrete nanotubular objects.[4] Furthermore, Würthner *et al.* achieved shape-dependent control of the morphology of nanoaggregates by judicious control of the shapes of amphiphilic perylene bisimides.[5] Dynamic structural changes of the amphiphilic aggregates as a result of ambient conditions are also fascinating from the point of view of their potential applications as soft materials in aqueous solutions. It is, therefore, recognized that organized structures that can be modulated by external physical and chemical stimuli[6] such as temperature[6c] and solvents[6d] could find application as versatile actuators, activated in aqueous solutions and related solvents.

It has also been recognized that, among various acyclic planar π-conjugated molecules, $BF_2$ complexes of 1,3-dipyrrolyl-1,3-propanediones (*e.g.*, **1a–c** and **2a–d**, Fig. 1a)[7–10] may act as scaffoldings in the formation of dimension-controlled organized structures based on π–π stacking interactions and also exhibit anion-binding behaviours.[11] For example, single crystals of α-phenyl-substituted **1a** along with unsubstituted and benzo-substituted derivatives, in which no aliphatic and hydrophilic chains are attached, showed solid-state electronic and optical properties including charge-carrier mobilities. These properties were found to be modulated by polymorphs of the crystals, peripheral substituents and anion binding followed by the inclusion of counter cations.[9h] Introduction of aliphatic chains provided anion-responsive supramolecular organogels[9a,f,g] and thermotropic liquid crystals[9f] as observed in octyloxy- and hexadecyloxy-substituted **1b,c**. Furthermore, amphiphilic π-conjugated molecules **2a–d** substituted by three aliphatic and hydrophilic triethylene glycol (TEG) or hexaethylene glycol (HEG) chains at each aryl ring were found to form organized structures in aqueous solutions.[9d] Regular and cryogenic transmission electron microscopies (TEM) were used to

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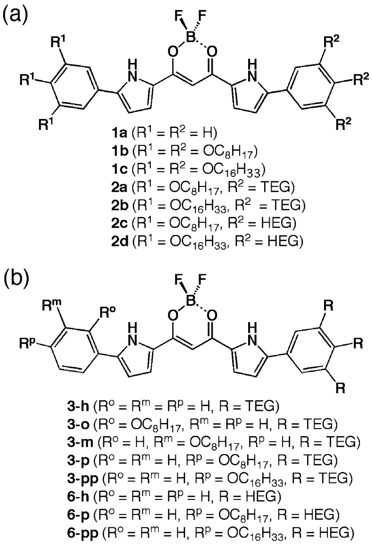

**Fig. 1** (a) α-Phenyl-substituted **1a** and hexasubstituted derivatives **1b,c** and **2a–d** of dipyrrolyldiketone $BF_2$ complexes and (b) wedge-shaped derivatives **3** and **6**. TEG and HEG represent methoxy triethylene glycol and methoxy hexaethylene glycol, respectively.

elucidate the fabrication of vesicles[12] based on the formation of H-aggregated bilayers. The water-assisted aggregates are stable and sustainable under external stimuli such as anions, whereas extraction by immiscible organic solvents or removal of water transforms the assemblies to other stacking modes such as J-type aggregates. In these hexasubstituted amphiphiles, relatively larger organized structures like vesicles can be constructed owing to the suitable numbers of both aliphatic and hydrophilic chains. These studies illustrate that the morphologies of the organized structures may be controlled by the number of substituents. It is recognized that small numbers of hydrophilic chains located on the outside of the amphiphilic assemblies are not appropriate for the formation of organized structures in aqueous solutions owing to low solubilities,[9d] and, therefore, in this study, the supramolecular assembly behaviours of wedge-shaped amphiphiles **3** and **6** (Fig. 1b), which have hydrophilic chains and one or no aliphatic chain, are examined.

## Results and discussion

Wedge-shaped amphiphilic derivatives **3** and **6** (Fig. 1b) were synthesized according to previously reported procedures,[9d] by treatment of equivalent amounts of two pyrrole derivatives, α-phenyl- or monoalkoxy-substituted aryl-pyrroles[9a,e] and hydrophilic tris-(methoxy triethylene glycol (TEG))- or tris-(methoxy hexaethylene glycol (HEG))-substituted arylpyrroles,[9d] with malonyl chloride, followed by boron complexation by $BF_3{\cdot}OEt_2$. Tris-TEG-substituted derivatives were prepared, in which the aryl ring has no substituents **3-h**, an octyloxy-substituent at the *ortho*-, *meta*- and *para*-position **3-o**, **3-m** and **3-p**, respectively, and a hexadecyloxy-substituent at the *para*-position **3-pp**, along with the corresponding tris-HEG-substituted derivatives **6-h**, **6-p** and **6-pp** (the *ortho*- and *meta*-substituted derivatives were not prepared). Chemical identification of these wedge-shaped amphiphiles was conducted using $^1$H NMR and MALDI-TOF-MS. Fascinatingly, in contrast to solid-state **3-p** and **3-pp**, amphiphiles **3-h**, **3-o**, **3-m**, **6-h**, **6-p** and **6-pp** are liquids at room temperature, suggesting that it is difficult to construct ordered structures of these derivatives in the absence of solvent. The liquid states were confirmed by synchrotron radiation X-ray diffraction (XRD) measurements (BL40B2 at SPring-8), which exhibited broad patterns. UV/vis absorption spectra suggested that all of the wedge-shaped amphiphiles are dispersed as monomers in $CH_2Cl_2$ and $CH_3OH$ ($1 \times 10^{-5}$ M). In $CH_2Cl_2$, the absorption maxima ($\lambda_{max}$) of **3-h**, **3-o**, **3-m**, **3-p**, **3-pp**, **6-h**, **6-p** and **6-pp** are observed at 509, 516, 510, 519, 520, 510, 519 and 519 nm, respectively, whereas fluorescence emission maxima ($\lambda_{em}$) and corresponding quantum yields ($\Phi_F$ in the parentheses) excited at each $\lambda_{max}$ are 550 (0.64), 550 (0.91), 551 (0.67), 560 (0.84), 561 (0.90), 551 (0.50), 559 (0.80) and 560 (0.80) nm, respectively. Similarly, in $CH_3OH$, the $\lambda_{max}$ and $\lambda_{em}$ ($\Phi_F$) are 502 and 544 (0.23) nm for **3-h**, 509 and 550 (0.41) nm for **3-o**, 503 and 547 (0.26) nm for **3-m**, 511 and 557 (0.34) nm for **3-p**, 511 and 556 (0.37) nm for **3-pp**, 502 and 544 (0.25) nm for **6-h**, 512 and 556 (0.41) nm for **6-p** and 512 and 557 (0.40) nm for **6-pp**. The amphiphiles are soluble in aqueous solutions as a result of the formation of aggregates, the details of which are discussed in a subsequent section.

Initially, the effect of variations in the position of the substituents on the organization of the structures of the amphiphiles in aqueous solutions was examined using **3-o**, **3-m** and **3-p** along with **3-h** as a reference. The $\lambda_{max}$ and $\lambda_{em}$ ($\Phi_F$) are 487 and 553 (0.010) nm for **3-h**, 490 and 666 (0.032) nm for **3-o**, 494 and 650 (0.034) nm for **3-m** and 470 and 663 (0.010) nm for **3-p** (Fig. 2). The relatively broad and blue-shifted absorption bands and broad and red-shifted emission bands with significantly reduced emission quantum

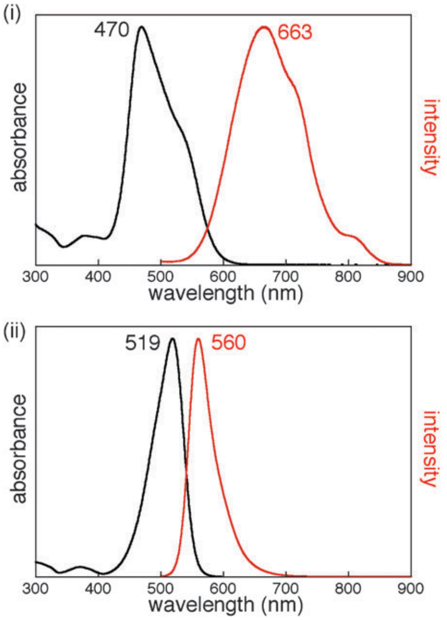

**Fig. 2** Normalized UV/visible absorption (black line) and fluorescence emission (red line) spectra of **3-p** ($1 \times 10^{-5}$ M) in (i) water and (ii) $CH_2Cl_2$. Fluorescence was observed by excitation at each absorption maximum ($\lambda_{max}$).

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yields ($\Phi_F < 0.04$) suggest the formation of assembled structures comprising H-like aggregates in aqueous solutions. These spectral features are also in sharp contrast to the behaviour observed in polar protic solvents like $CH_3OH$. Furthermore, as compared with the absorption bands of **3-o** and **3-m** that have shoulders, 460 and 526 nm for **3-o** and 518 nm for **3-m**, as a result of the presence of J-like or related aggregates, **3-p** exhibits the formation of more stable H-aggregates than the others, presumably because of the symmetrical geometry of the *para*-substituent. Focusing on the *para*-substituted amphiphiles, which seem to be stable and suitable for a more detailed discussion, the aggregation behaviours of **3-pp**, **6-p** and **6-pp** as well as **6-h** as a reference were investigated in order to examine the effects of variations in the lengths of the alkyl chain and hydrophilic chains on the aggregation behaviour. In aqueous solutions, the $\lambda_{max}$ and $\lambda_{em}$ ($\Phi_F$) are 460 and 665 (0.011) nm for **3-pp**, 486 and 559 (0.029) nm for **6-h**, 489 and 651 (0.017) nm for **6-p** and 491 and 659 (0.016) nm for **6-pp**. From these observations, it can be deduced that the wedge-shaped amphiphiles **3-pp**, **6-p** and **6-pp** also form H-like aggregates in a manner similar to **3-p**. Compared to the derivatives substituted with an aliphatic chain, **3-h** and **6-h** show blue-shifted emissions at 553 and 559 nm, suggesting that the alkyl chain plays an essential role in the construction of stable H-like aggregates. Solvent-dependent formation of aggregates was suggested by the changes in the UV/vis absorption spectra in mixed water–$CH_3OH$ solvents. Increasing the ratio of water induces a red-shift in the absorption spectrum which is derived from H-like aggregates. This suggests that the amphiphiles show a transition from dispersed monomers to H-aggregates at appropriate water ratios of *ca*. 40–50% in $1 \times 10^{-5}$ M solution. On the other hand, **3-h** and **6-h** showed transitions at higher water ratios of *ca*. 80% presumably because they cannot form stable H-aggregates.

The formation of organized structures exhibits a strong dependence on the initial conditions. The TEG-substituted amphiphiles **3-h**, **3-o**, **3-m**, **3-p** and **3-pp**, which exist as dispersed monomers in $CH_2Cl_2$, cannot be extracted with water. From this observation, it can be deduced that the monomers are stable in $CH_2Cl_2$ and do not form aggregates upon extraction with water. Conversely, these amphiphiles exist as metastable H-aggregates in aqueous solutions and cannot be completely extracted using $CH_2Cl_2$ (Fig. 3), suggesting that the initial conditions are crucial to the fabrication of organized structures. Among the amphiphiles, the majority of **3-o** and **3-m** can be extracted into $CH_2Cl_2$ by sonication, even though small amounts are soluble in aqueous solutions. Furthermore, from spectroscopic analysis it can be elucidated that the H-aggregates of the wedge-shaped amphiphiles in aqueous solutions were supported by water molecules. In fact, solid-state spectra of the films of the amphiphiles cast from aqueous solutions ($1 \times 10^{-4}$ M) followed by drying show bands with $\lambda_{max}$ of 526, 537, 523, 526, 532, 516, 532 and 537 nm for **3-h**, **3-o**, **3-m**, **3-p**, **3-pp**, **6-h**, **6-p** and **6-pp**, respectively, which are red-shifted compared to those of the monomeric states in $CH_2Cl_2$, suggesting the formation of J-aggregates in the absence of water molecules.

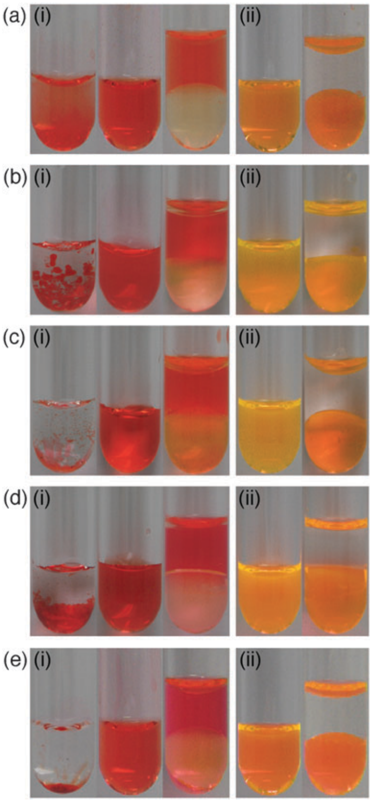

**Fig. 3** Photographs of the extraction processes of (a) **3-h**, (b) **3-o**, (c) **3-m**, (d) **3-p** and (e) **3-pp**: (i) aqueous solutions before shaking (left), two phases of water and $CH_2Cl_2$ (right) extracted from aqueous solutions (center) and (ii) two phases of water and $CH_2Cl_2$ (right) extracted from $CH_2Cl_2$ solution (left). Initial concentrations are $1 \times 10^{-4}$ M.

The sizes of the aggregates were elucidated by dynamic light scanning (DLS) in aqueous solutions ($1 \times 10^{-5}$ M) at 20 °C. Amphiphile **3-o** showed peaks consistent with a diameter of 20 nm in addition to larger aggregates, whereas the peaks observed for **3-m** were dispersed, suggesting the absence of ordered structures. On the other hand, **3-p** and **3-pp** showed relatively discrete peaks at 40 and 33 nm, respectively, suggesting the formation of stable aggregates. Similarly, **3-h** also showed a peak at 45 nm. The data also show that the introduction of HEG chains may provide fairly disordered soluble aggregates along with monomers or small aggregates with diameters of 10–20 nm in aqueous solutions, as evidenced by the dispersed peaks. At higher temperatures of 70 or 80 °C, more discrete peaks appeared as a result of the changes in the assembled structures induced by dehydration around hydrophilic chains, the details of which will be examined in the near future. Although the values obtained from the DLS measurements depend on the shapes of the organized structures, they are not always the same as the actual sizes. Nonetheless, we can safely conclude that the wedge-shaped amphiphiles fabricate nanometre-scale assemblies in aqueous solutions.

The exact structures of the aggregates formed by the wedge-shaped amphiphiles were elucidated using TEM (Fig. 4). As reported in the previous work,[9d] although cryo-TEM was more appropriate for examination of organized structures in

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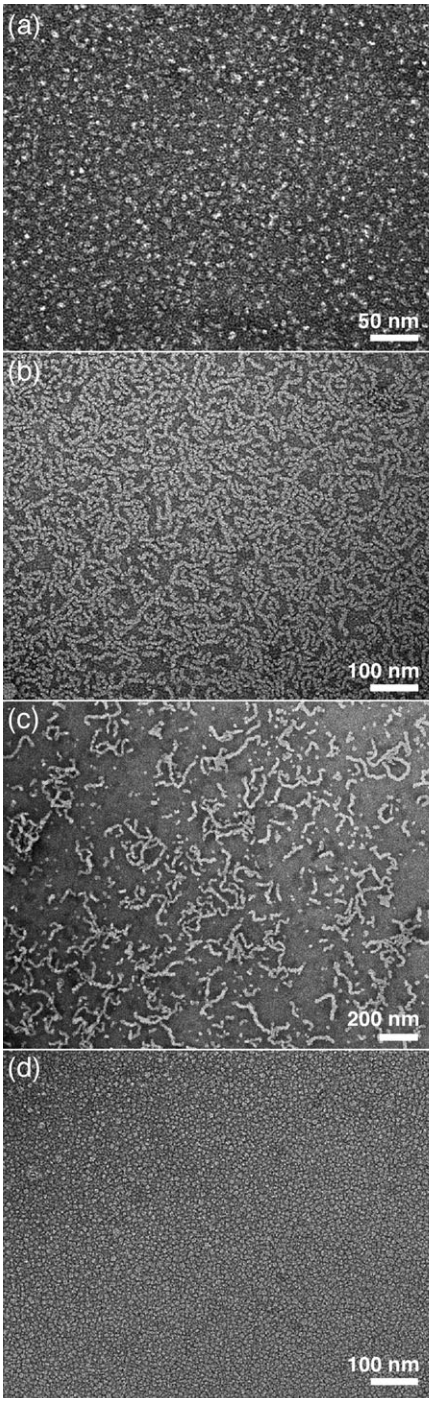

**Fig. 4** TEM images of amphiphiles (a) **3-o**, (b) **3-p**, (c) **3-pp** and (d) **6-p** from aqueous solutions ($1 \times 10^{-5}$ M) with $UO_2(OAc)_2$ staining.

solutions, TEM measurements of the dried samples were also found to reveal the morphologies of organized structures even after removal of the aqueous solvent. This result suggests that the shapes of the assemblies were maintained even though the packing modes at the molecular level are changed from H- to J-aggregates. The TEM measurements show that amphiphile **3-o** afforded spherical micelles with a diameter of 5 nm (Fig. 4a), whereas **3-p** formed cylindrical micelles with a diameter of 10 nm and averaged lengths of 50–100 nm (Fig. 4b). In addition, **3-pp** also formed cylindrical micelles of various lengths of up to *ca*. 400 nm with a diameter of 20 nm (Fig. 4c). In contrast to vesicles from hexasubstituted **2a**,[9d] spheres of smaller diameters and cylindrical micelles were derived from the wedge-shaped molecules, which are not suitable for formation of bilayer structures. In the case of **3-m**, a mixture of spherical and cylindrical micelles is obtained, suggesting that the position of the aliphatic chain exerts strong influence on the morphology of the nanometre-scale assembly. During the preparation and measurements, **3-p** was found to construct more stable organized structures than **3-o** and **3-m**. This observation is consistent with the results presented above. The effects of the hydrophilic chains can be seen in **6-p** and **6-pp** which gave spherical micelles with a diameter of *ca*. 10 nm (Fig. 4d). These observations can be explained in terms of the fact that the larger HEG chains prevent the formation of cylindrical structures. Furthermore, **3-h** and **6-h** provided no ordered morphologies, suggesting that aliphatic chains are required for constructing stable organized nanometre-scale assemblies. The results of the TEM measurements revealed that the delicate balance of the hydrophobic and hydrophilic moieties in amphiphiles is crucial in the formation of rigid organized structures in aqueous solutions (Fig. 5). The sizes of the organized structures are correlated with the AM1-optimized scales of the building blocks: *ca*. 3 nm for **3-o**, 4 nm for **3-p**, 5 nm for **3-pp** and 5 nm for **6-p**.[13] A longer alkyl chain does not always provide larger assemblies as a result of stronger van der Waals interactions, which result in more tightly assembled structures. In contrast to aliphatic chains, hydrophilic chains are known to be folded at the outside of the organized structures in aqueous solutions.

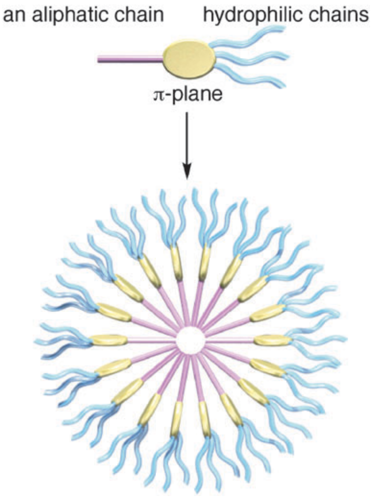

**Fig. 5** Formation a micelle from a wedge-shaped amphiphilic molecule.

## Conclusions

Highly ordered organized structures such as spherical and cylinder micelles were fabricated from water-supported H-aggregates of pyrrole-based wedge-shaped amphiphiles fabricated in aqueous solutions. The morphologies significantly depend on the number, length and positions of aliphatic and hydrophilic substituents and are correlated with the

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electronic and optical properties in aqueous solutions. In particular, *para*-substitution of an aliphatic chain is effective for fabrication of stable organized structures. Anion-responsive behaviour, which was observed for the amphiphiles in $\mathrm{CH_2Cl_2}$, in aqueous and related solvents will be examined in the near future.

## Experimental section

### General procedures

Starting materials were purchased from Wako Pure Chemical Industries Ltd., Nacalai Tesque Inc. and Sigma-Aldrich Co. and used without further purification unless otherwise stated. UV-visible spectra of the solutions were recorded on a Hitachi U-3500 spectrometer and a System Instruments surface and interface spectrometer SIS-50 was used for the solid-state measurements. Fluorescence spectra of the solutions were recorded on a Hitachi F-4500 fluorescence spectrometer and a Hamamatsu Quantum Yields Measurements System for Organic LED Materials C9920-02 was used for estimation of the quantum yields. NMR spectra used in the characterization of the products were recorded on a JEOL ECA-600 600 MHz spectrometer. All NMR spectra were referenced to solvent. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was recorded on a Shimadzu Axima-CFRplus in the negative mode. TLC analyses were carried out on aluminium sheets coated with silica gel 60 (Merck 5554). Column chromatography was performed on Sumitomo alumina KCG-1525, Wakogel C-200, C-300 and Merck silica gel 60 and 60H. The details of precursory diketones and pyrroles are described in the ESI.†

### $\mathrm{BF_2}$ complex of 3-(5-phenylpyrrol-2-yl)-1-(5-(3,4,5-tris-TEG-phenyl)pyrrol-2-yl)-1,3-propanedione, 3-h

To a $\mathrm{CH_2ClCH_2Cl}$ solution (36 mL) of 3-(5-phenylpyrrol-2-yl)-1-(5-(3,4,5-tris-TEG-phenyl)pyrrol-2-yl)-1,3-propanedione **3-h′** (94.8 mg, 0.113 mmol), $\mathrm{BF_3{\cdot}OEt_2}$ (24.1 mg, 0.170 mmol) was added and stirred for 15 min at reflux temperature. The reaction mixture was initially separated using a silica gel short column (Wakogel C-300, eluent: 3% $\mathrm{MeOH/CH_2Cl_2}$) to eliminate acidic entities, followed by purification by silica gel flash column chromatography (eluent: 2.8% $\mathrm{MeOH/CH_2Cl_2}$), which afforded **3-h** (83.5 mg, 83%) as a red oil. $R_\mathrm{f}$ = 0.52 (10% $\mathrm{MeOH/CH_2Cl_2}$). $^1$H NMR (600 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta$ (ppm) 10.48 (br, 1H, pyrrole-NH), 9.63 (br, 1H, pyrrole-NH), 7.64 (d, $J$ = 7.2 Hz, 2H, Ar-H), 7.47 (t, $J$ = 7.8 Hz, 2H, Ar-H), 7.38 (t, $J$ = 7.2 Hz, 1H, Ar-H), 7.22–7.21 (m, 1H, pyrrole-H), 7.20–7.19 (m, 1H, pyrrole-H), 7.02 (s, 2H, Ar-H), 6.73–6.72 (m, 1H, pyrrole-H), 6.65–6.64 (m, 1H, pyrrole-H), 6.55 (br, 1H, CH), 4.27 (t, $J$ = 4.8 Hz, 4H, $\mathrm{OCH_2}$), 4.21 (t, $J$ = 4.8 Hz, 2H, $\mathrm{OCH_2}$), 3.88 (t, $J$ = 4.8 Hz, 4H, $\mathrm{OCH_2}$), 3.80 (t, $J$ = 4.8 Hz, 2H, $\mathrm{OCH_2}$), 3.76–3.75 (m, 4H, $\mathrm{OCH_2}$), 3.72–3.68 (m, 10H, $\mathrm{OCH_2}$), 3.64–3.62 (m, 4H, $\mathrm{OCH_2}$), 3.59–3.55 (m, 6H, $\mathrm{OCH_2}$), 3.40 (s, 3H, $\mathrm{OCH_3}$), 3.34 (s, 6H, $\mathrm{OCH_3}$). UV/vis ($\mathrm{CH_2Cl_2}$, $\lambda_\mathrm{max}$[nm] ($\varepsilon$, $10^5$ $\mathrm{M^{-1}}$ $\mathrm{cm^{-1}}$)): 508.5 (1.14). MALDI-TOF-MS: $m/z$ (% intensity): 887.4 (100), 888.4 (50). Calcd for $\mathrm{C_{44}H_{58}BF_2N_2O_{14}}$ ($[\mathrm{M-H}]^-$): 887.39.

### $\mathrm{BF_2}$ complex of 3-(5-(2-octyloxyphenyl)pyrrol-2-yl)-1-(5-(3,4,5-tris-TEG-phenyl)pyrrol-2-yl)-1,3-propanedione, 3-o

To a $\mathrm{CH_2Cl_2}$ solution (20 mL) of 3-(5-(2-octyloxyphenyl)-pyrrol-2-yl)-1-(5-(3,4,5-tris-TEG-phenyl)pyrrol-2-yl)-1,3-propanedione **3-o′** (145.1 mg, 0.150 mmol), $\mathrm{BF_3{\cdot}OEt_2}$ (66.3 mg, 0.467 mmol) was added and stirred for 15 min at room temperature. The reaction mixture was initially separated using a silica gel short column (Wakogel C-300, eluent: 3% $\mathrm{MeOH/CH_2Cl_2}$) to eliminate acidic entities, followed by purification using silica gel flash column chromatography (eluent: 2% $\mathrm{MeOH/CH_2Cl_2}$), which afforded **3-o** (17.4 mg, 29%) as a red oil. $R_\mathrm{f}$ = 0.56 (10% $\mathrm{MeOH/CH_2Cl_2}$). $^1$H NMR (600 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta$ (ppm) 11.14 (br, 1H, pyrrole-NH), 10.40 (br, 1H, pyrrole-NH), 7.73 (dd, $J$ = 8.4, 1.8 Hz, 1H, Ar-H), 7.31 (td, $J$ = 7.8, 1.8 Hz, 1H, Ar-H), 7.19–7.18 (m, 1H, pyrrole-H), 7.18–7.16 (m, 1H, pyrrole-H), 7.04 (t, $J$ = 7.2 Hz, 1H, Ar-H), 7.04 (d, $J$ = 7.8 Hz, 1H, Ar-H), 6.99 (s, 2H, Ar-H), 6.82–6.81 (m, 1H, pyrrole-H), 6.63–6.62 (m, 1H, pyrrole-H), 6.52 (br, 1H, CH), 4.27 (t, $J$ = 4.8 Hz, 4H, $\mathrm{OCH_2}$), 4.21 (t, $J$ = 4.8 Hz, 2H, $\mathrm{OCH_2}$), 4.19 (t, $J$ = 6.6 Hz, 2H, $\mathrm{O}\mathit{CH_2}$), 3.89 (t, $J$ = 4.8 Hz, 4H, $\mathrm{OCH_2}$), 3.81 (t, $J$ = 4.8 Hz, 2H, $\mathrm{OCH_2}$), 3.76–3.75 (m, 4H, $\mathrm{OCH_2}$), 3.73–3.70 (m, 10H, $\mathrm{OCH_2}$), 3.65–3.62 (m, 4H, $\mathrm{OCH_2}$), 3.58–3.55 (m, 6H, $\mathrm{OCH_2}$), 3.39 (s, 3H, $\mathrm{OCH_3}$), 3.35 (s, 6H, $\mathrm{OCH_3}$), 2.09–2.04 (m, 2H, $\mathrm{OCH_2}\mathit{CH_2}$), 1.48–1.43 (m, 2H, $\mathrm{OC_2H_4}\mathit{CH;_2}$), 1.37–1.25 (m, 8H, $\mathrm{OC_3H_6}\mathit{C_4H_8}$), 0.87 (t, $J$ = 7.2 Hz, 3H, $\mathrm{OC_7H_{14}}\mathit{CH_3}$). UV/vis ($\mathrm{CH_2Cl_2}$, $\lambda_\mathrm{max}$[nm] ($\varepsilon$, $10^5$ $\mathrm{M^{-1}}$ $\mathrm{cm^{-1}}$)): 515.5 (1.22). MALDI-TOF-MS: $m/z$ (% intensity): 1015.5 (100), 1016.5 (80). Calcd for $\mathrm{C_{52}H_{74}BF_2N_2O_{15}}$ ($[\mathrm{M-H}]^-$): 1015.51.

### $\mathrm{BF_2}$ complex of 3-(5-(3-octyloxyphenyl)pyrrol-2-yl)-1-(5-(3,4,5-tris-TEG-phenyl)pyrrol-2-yl)-1,3-propanedione, 3-m

To a $\mathrm{CH_2Cl_2}$ solution (50 mL) of 3-(5-(3-octyloxyphenyl)-pyrrol-2-yl)-1-(5-(3,4,5-tris-TEG-phenyl)pyrrol-2-yl)-1,3-propanedione **3-m′** (61.6 mg, 0.0636 mmol), $\mathrm{BF_3{\cdot}OEt_2}$ (26.5 mg, 0.187 mmol) was added and stirred for 15 min at room temperature. The reaction mixture was initially separated by a silica gel short column (Wakogel C-300, eluent: 3% $\mathrm{MeOH/CH_2Cl_2}$) to eliminate acidic entities. Subsequent purification using silica gel flash column chromatography (eluent: 1.5% $\mathrm{MeOH/CH_2Cl_2}$) and a short alumina column (eluent: 1% $\mathrm{MeOH/CH_2Cl_2}$) afforded **3-m** (16.8 mg, 26%) as a red oil. $R_\mathrm{f}$ = 0.60 (10% $\mathrm{MeOH/CH_2Cl_2}$). $^1$H NMR (600 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta$ (ppm) 10.50 (br, 1H, pyrrole-NH), 9.61 (br, 1H, pyrrole-NH), 7.36 (t, $J$ = 7.8 Hz, 1H, Ar-H) 7.22–7.21 (m, 1H, pyrrole-H), 7.21 (d, $J$ = 7.2 Hz, 1H, Ar-H), 7.19–7.18 (m, 1H, pyrrole-H), 7.13 (m, 1H, Ar-H), 7.02 (s, 2H, Ar-H), 6.91 (dd, $J$ = 8.4, 2.4 Hz, 1H, Ar-H), 6.71–6.70 (m, 1H, pyrrole-H), 6.65–6.64 (m, 1H, pyrrole-H), 6.55 (br, 1H, CH), 4.27 (t, $J$ = 4.8 Hz, 4H, $\mathrm{OCH_2}$), 4.21 (t, $J$ = 4.8 Hz, 2H, $\mathrm{OCH_2}$), 4.04 (t, $J$ = 6.6 Hz, 2H, $\mathrm{OCH_2}$), 3.88 (t, $J$ = 4.8 Hz, 4H, $\mathrm{OCH_2}$), 3.80 (t, $J$ = 4.8 Hz, 2H, $\mathrm{OCH_2}$), 3.76–3.75 (m, 4H, $\mathrm{OCH_2}$), 3.72–3.68 (m, 10H, $\mathrm{OCH_2}$), 3.64–3.62 (m, 4H, $\mathrm{OCH_2}$), 3.59–3.55 (m, 6H, $\mathrm{OCH_2}$), 3.40 (s, 3H, $\mathrm{OCH_3}$), 3.34 (s, 6H, $\mathrm{OCH_3}$), 1.85–1.80 (m, 2H, $\mathrm{OCH_2}\mathit{CH_2}$), 1.52–1.47 (m, 2H, $\mathrm{OC_2H_4}\mathit{CH_2}$), 1.40–1.25 (m, 8H, $\mathrm{OC_3H_6}\mathit{C_4H_8}$), 0.89 (t, $J$ = 6.6 Hz, 3H, $\mathrm{OC_7H_{14}}\mathit{CH_3}$). UV/vis ($\mathrm{CH_2Cl_2}$, $\lambda_\mathrm{max}$[nm] ($\varepsilon$, $10^5$ $\mathrm{M^{-1}}$ $\mathrm{cm^{-1}}$)): 510.0 (1.07).

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MALDI-TOF-MS: *m*/*z* (% intensity): 1015.5 (100), 1016.5 (91). Calcd for $C_{52}H_{74}BF_2N_2O_{15}$ ([M − H]$^-$): 1015.51.

### $BF_2$ complex of 3-(5-(4-octyloxyphenyl)pyrrol-2-yl)-1-(5-(3,4,5-tris-TEG-phenyl)pyrrol-2-yl)-1,3-propanedione, 3-p

To a $CH_2Cl_2$ solution (20 mL) of 3-(5-(4-octyloxyphenyl)-pyrrol-2-yl)-1-(5-(3,4,5-tris-TEG-phenyl)pyrrol-2-yl)-1,3-propanedione **3-p′** (57.9 mg, 0.0597 mmol), $BF_3{\cdot}OEt_2$ (13.3 mg, 0.0934 mmol) was added and stirred for 15 min at room temperature. The reaction mixture was initially separated by a silica gel short column (Wakogel C-300, eluent: 7% $MeOH/CH_2Cl_2$) to eliminate acidic entities, followed by purification using silica gel flash column chromatography (eluent: 2% $MeOH/CH_2Cl_2$) and a short alumina column (eluent: 1% $MeOH/CH_2Cl_2$), which afforded **3-p** (17.4 mg, 29%) as a red oil. $R_f$ = 0.28 (5% $MeOH/CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 10.46 (br, 1H, pyrrole-NH), 9.55 (br, 1H, pyrrole-NH), 7.56 (t, *J* = 9.0 Hz, 2H, Ar-H), 7.20–7.19 (m, 1H, pyrrole-H), 7.19–7.18 (m, 1H, pyrrole-H), 7.00 (s, 2H, Ar-H), 6.98 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.64–6.63 (m, 2H, pyrrole-H), 6.52 (br, 1H, CH), 4.27 (t, *J* = 4.8 Hz, 4H, $OCH_2$), 4.21 (t, *J* = 4.8 Hz, 2H, $OCH_2$), 4.01 (t, *J* = 6.6 Hz, 2H, $OCH_2$), 3.88 (t, *J* = 4.8 Hz, 4H, $OCH_2$), 3.80 (t, *J* = 4.8 Hz, 2H, $OCH_2$), 3.76–3.75 (m, 4H, $OCH_2$), 3.72–3.67 (m, 10H, $OCH_2$), 3.64–3.62 (m, 4H, $OCH_2$), 3.58–3.55 (m, 6H, $OCH_2$), 3.39 (s, 3H, $OCH_3$), 3.34 (s, 6H, $OCH_3$), 1.83–1.78 (m, 2H, $OCH_2\mathit{CH_2}$), 1.50–1.45 (m, 2H, $OC_2H_4\mathit{CH_2}$), 1.39–1.25 (m, 8H, $OC_3H_6\mathit{C_4H_8}$), 0.89 (t, *J* = 7.2 Hz, 3H, $OC_7H_{14}\mathit{CH_3}$). UV/vis ($CH_2Cl_2$, $\lambda_{max}$[nm] (ε, $10^5$ $M^{-1}$ $cm^{-1}$)): 519.0 (1.12). MALDI-TOF-MS: *m*/*z* (% intensity): 1015.5 (100), 1016.5 (71). Calcd for $C_{52}H_{74}BF_2N_2O_{15}$ ([M − H]$^-$): 1015.51.

### $BF_2$ complex of 3-(5-(4-hexadecyloxyphenyl)pyrrol-2-yl)-1-(5-(3,4,5-tris-TEG-phenyl)pyrrol-2-yl)-1,3-propanedione, 3-pp

To a $CH_2Cl_2$ solution (50 mL) of 3-(5-(4-hexadecyloxyphenyl)-pyrrol-2-yl)-1-(5-(3,4,5-tris-TEG-phenyl)pyrrol-2-yl)-1,3-propanedione **3-pp′** (234.7 mg, 0.217 mmol), $BF_3{\cdot}OEt_2$ (46.37 mg, 0.326 mmol) was added and stirred for 40 min at room temperature. The reaction mixture was initially separated by a silica gel short column (Wakogel C-300, eluent: 4% $MeOH/CH_2Cl_2$) to eliminate acidic entities, followed by purification using silica gel flash column chromatography (eluent: $MeOH/CHCl_3/EtOAc$ = 2/49/49) and a short alumina column (eluent: 1% $MeOH/CH_2Cl_2$), which afforded **3-pp** (150.8 mg, 62%) as a red oil. $R_f$ = 0.62 (5% $MeOH/CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 10.38 (br, 1H, pyrrole-NH), 9.52 (br, 1H, pyrrole-NH), 7.56 (t, *J* = 9.0 Hz, 2H, Ar-H), 7.20–7.19 (m, 1H, pyrrole-H), 7.19–7.18 (m, 1H, pyrrole-H), 7.00 (s, 2H, Ar-H), 6.98 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.64–6.63 (m, 2H, pyrrole-H), 6.52 (br, 1H, CH), 4.27 (t, *J* = 4.8 Hz, 4H, $OCH_2$), 4.21 (t, *J* = 4.8 Hz, 2H, $OCH_2$), 4.01 (t, *J* = 6.6 Hz, 2H, $OCH_2$), 3.88 (t, *J* = 4.8 Hz, 4H, $OCH_2$), 3.80 (t, *J* = 4.8 Hz, 2H, $OCH_2$), 3.76–3.75 (m, 4H, $OCH_2$), 3.72–3.68 (m, 10H, $OCH_2$), 3.64–3.62 (m, 4H, $OCH_2$), 3.58–3.55 (m, 6H, $OCH_2$), 3.39 (s, 3H, $OCH_3$), 3.34 (s, 6H, $OCH_3$), 1.83–1.78 (m, 2H, $OCH_2\mathit{CH_2}$), 1.49–1.45 (m, 2H, $OC_2H_4\mathit{CH_2}$), 1.39–1.26 (m, 24H, $OC_3H_6\mathit{C_{12}H_{24}}$), 0.88 (t, *J* = 6.6 Hz, 3H, $OC_{15}H_{30}\mathit{CH_3}$). UV/vis ($CH_2Cl_2$, $\lambda_{max}$[nm] (ε, $10^5$ $M^{-1}$ $cm^{-1}$)): 519.5 (1.24). MALDI-TOF-MS: *m*/*z* (% intensity): 1127.6 (100), 1128.7 (80). Calcd for $C_{60}H_{90}BF_2N_2O_{15}$ ([M − H]$^-$): 1127.64.

### $BF_2$ complex of 1-(5-(3,4,5-tris-HEG-phenyl)pyrrol-2-yl)-3-(5-phenylpyrrol-2-yl)-1,3-propanedione, 6-h

To a $CH_2Cl_2$ solution (50 mL) of 1-(5-(3,4,5-tris-HEG-phenyl)-pyrrol-2-yl)-3-(5-phenylpyrrol-2-yl)-1,3-propanedione **6-h′** (228.0 mg, 0.184 mmol), $BF_3{\cdot}OEt_2$ (79.5 mg, 0.560 mmol) was added and stirred for 15 min at room temperature. The reaction mixture was initially separated by a silica gel short column (Wakogel C-300, eluent: 6% $MeOH/CH_2Cl_2$) to eliminate acidic entities, followed by purification using silica gel flash column chromatography (eluent: 4.5% $MeOH/CH_2Cl_2$) and a short alumina column (eluent: 1% $MeOH/CH_2Cl_2$), which afforded **6-h** (115.8 mg, 49%) as a red oil. $R_f$ = 0.42 (5% $MeOH/CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 10.86 (br, 1H, pyrrole-NH), 9.68 (br, 1H, pyrrole-NH), 7.64 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.47 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.38 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.25–7.24 (m, 1H, pyrrole-H), 7.21–7.20 (m, 1H, pyrrole-H), 7.12 (s, 2H, Ar-H), 6.73–6.72 (m, 1H, pyrrole-H), 6.66–6.65 (m, 1H, pyrrole-H), 6.60 (br, 1H, CH), 4.30 (t, *J* = 4.8 Hz, 4H, $OCH_2$), 4.23 (t, *J* = 4.8 Hz, 2H, $OCH_2$), 3.88 (t, *J* = 4.8 Hz, 4H, $OCH_2$), 3.80 (t, *J* = 4.8 Hz, 2H, $OCH_2$), 3.74–3.73 (m, 4H, $OCH_2$), 3.69–3.50 (m, 56H, $OCH_2$), 3.38 (s, 3H, $OCH_3$), 3.34 (s, 6H, $OCH_3$). UV/vis ($CH_2Cl_2$, $\lambda_{max}$[nm] (ε, $10^5$ $M^{-1}$ $cm^{-1}$)): 509.5 (1.07). MALDI-TOF-MS: *m*/*z* (% intensity): 1283.6 (100), 1284.7 (77). Calcd for $C_{62}H_{94}BF_2N_2O_{23}$ ([M − H]$^-$): 1283.63.

### $BF_2$ complex of 1-(5-(3,4,5-tris-HEG-phenyl)pyrrol-2-yl)-3-(5-(4-octyloxyphenyl)pyrrol-2-yl)-1,3-propanedione, 6-p

To a $CH_2Cl_2$ solution (50 mL) of 1-(5-(3,4,5-tris-HEG-phenyl)-pyrrol-2-yl)-3-(5-(4-octyloxyphenyl)pyrrol-2-yl)-1,3-propanedione **6-p′** (171.8 mg, 0.125 mmol), $BF_3{\cdot}OEt_2$ (53.0 mg, 0.373 mmol) was added and stirred for 15 min at room temperature. The reaction mixture was initially separated by a silica gel short column (Wakogel C-300, eluent: 6% $MeOH/CH_2Cl_2$) to eliminate acidic entities, followed by purification using silica gel flash column chromatography (eluent: 4.5% $MeOH/CH_2Cl_2$) and a short alumina column (eluent: 1% $MeOH/CH_2Cl_2$), which afforded **6-p** (111.2 mg, 63%) as a red oil. $R_f$ = 0.54 (10% $MeOH/CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 10.78 (br, 1H, pyrrole-NH), 9.57 (br, 1H, pyrrole-NH), 7.57 (t, *J* = 8.4 Hz, 2H, Ar-H), 7.22–7.20 (m, 1H, pyrrole-H), 7.20–7.19 (m, 1H, pyrrole-H), 7.10 (s, 2H, Ar-H), 6.98 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.64–6.63 (m, 1H, pyrrole-H), 6.63–6.62 (m, 1H, pyrrole-H), 6.57 (br, 1H, CH), 4.29 (t, *J* = 4.8 Hz, 4H, $OCH_2$), 4.22 (t, *J* = 4.8 Hz, 2H, $OCH_2$), 4.01 (t, *J* = 6.6 Hz, 4H, $OCH_2$), 3.88 (t, *J* = 4.8 Hz, 4H, $OCH_2$), 3.80 (t, *J* = 4.8 Hz, 2H, $OCH_2$), 3.74–3.73 (m, 4H, $OCH_2$), 3.69–3.51 (m, 56H, $OCH_2$), 3.38 (s, 3H, $OCH_3$), 3.34 (s, 6H, $OCH_3$), 1.83–1.79 (m, 2H, $OCH_2\mathit{CH_2}$), 1.50–1.45 (m, 2H, $OC_2H_4\mathit{CH_2}$), 1.38–1.25 (m, 8H, $OC_3H_6\mathit{C_4H_8}$), 0.89 (t, *J* = 6.6 Hz, 3H, $OC_7H_{14}\mathit{CH_3}$). UV/vis ($CH_2Cl_2$, $\lambda_{max}$ [nm] (ε, $10^5$ $M^{-1}$ $cm^{-1}$)): 518.5 (0.98).

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MALDI-TOF-MS: *m*/*z* (% intensity): 1411.7 (100), 1412.8 (78). Calcd for $C_{70}H_{110}BF_2N_2O_{24}$ ([M − H]$^-$): 1411.75.

### BF$_2$ complex of 3-(5-(4-hexadecyloxyphenyl)pyrrol-2-yl)-1-(5-(3,4,5-tris-HEG-phenyl)pyrrol-2-yl)-1,3-propanedione, 6-pp

To a $CH_2Cl_2$ solution (80 mL) of 3-(5-(4-hexadecyloxyphenyl)-pyrrol-2-yl)-1-(5-(3,4,5-tris-HEG-phenyl)pyrrol-2-yl)-1,3-propanedione **6-pp′** (237.7 mg, 0.161 mmol), $BF_3{\cdot}OEt_2$ (68.5 mg, 0.482 mmol) was added and stirred for 15 min at reflux temperature. The reaction mixture was initially separated by a silica gel short column (Wakogel C-300, eluent: 4.5% MeOH/$CH_2Cl_2$) to eliminate acidic entities, followed by purification using silica gel flash column chromatography (eluent: 3% MeOH/$CH_2Cl_2$) and a short alumina column (eluent: 1% MeOH/$CH_2Cl_2$), which afforded **6-pp** (17.4 mg, 29%) as a red oil. $R_f$ = 0.28 (5% MeOH/$CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$, 20 °C): $\delta$ (ppm) 10.78 (br, 1H, pyrrole-NH), 9.57 (br, 1H, pyrrole-NH), 7.56 (t, *J* = 9.0 Hz, 2H, Ar-H), 7.22–7.20 (m, 1H, pyrrole-H), 7.20–7.19 (m, 1H, pyrrole-H), 7.11 (s, 2H, Ar-H), 6.97 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.64–6.63 (m, 1H, pyrrole-H), 6.63–6.62 (m, 1H, pyrrole-H), 6.57 (br, 1H, CH), 4.29 (t, *J* = 4.8 Hz, 4H, $OCH_2$), 4.22 (t, *J* = 4.8 Hz, 2H, $OCH_2$), 4.01 (t, *J* = 6.6 Hz, 2H, $OCH_2$), 3.88 (t, *J* = 4.8 Hz, 4H, $OCH_2$), 3.80 (t, *J* = 4.8 Hz, 2H, $OCH_2$), 3.74–3.73 (m, 4H, $OCH_2$), 3.69–3.51 (m, 56H, $OCH_2$), 3.38 (s, 3H, $OCH_3$), 3.34 (s, 6H, $OCH_3$), 1.83–1.78 (m, 2H, $\mathrm{OCH_2}\mathit{CH_2}$), 1.49–1.44 (m, 2H, $\mathrm{OC_2H_4}\mathit{CH_2}$), 1.39–1.26 (m, 24H, $\mathrm{OC_3H_6}\mathit{C_{12}H_{24}}$), 0.88 (t, *J* = 7.2 Hz, 3H, $\mathrm{OC_{15}H_{30}}\mathit{CH_3}$). UV/vis ($CH_2Cl_2$, $\lambda_{max}$[nm] ($\varepsilon$, $10^5$ M$^{-1}$ cm$^{-1}$)): 518.5 (1.33). MALDI-TOF-MS: *m*/*z* (% intensity): 1523.9 (100), 1524.9 (81). Calcd for $C_{78}H_{126}BF_2N_2O_{24}$ ([M − H]$^-$): 1523.87.

### Methods for DLS

DLS measurements were obtained with a Malvern Zetasizer Nano-ZS differential light scattering.

### TEM measurements

For the study of self-assembled structures in aqueous solution, a drop of solution of amphiphilic molecules was placed on a carbon-coated grid and the solution was allowed to evaporate under ambient conditions. The samples were stained by depositing uranyl acetate onto the surface of the sample-loaded grid. The dried specimen was observed by using a JEOL-JEM 2010 instrument operating at 120 kV.

### AM1 calculation

Semi-empirical calculations were carried out by using the Gaussian 03 program[13] and an HP Compaq dc5100 SFF computer. The structures were optimized, and the total electronic energies were calculated at the AM1 level.

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