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Self-Assembly of Oligothiophene Chromophores by *m*-Calix[3]amide Scaffold

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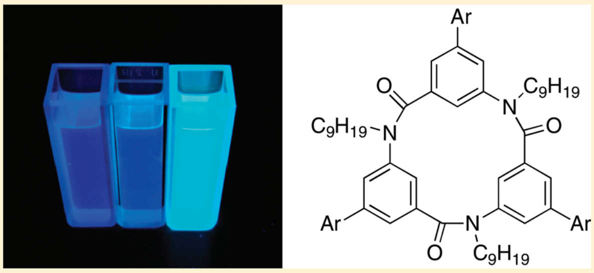
S *Supporting Information*



ABSTRACT: *m*-Calix[3]amides carrying the bithiophene chromophore (**BTC3A**) and terthiophene chromophore (**TTC3A**) were synthesized by the cyclic trimerization of *m*-aminobenzoic acid esters for the purpose of the control and understanding of the self-assembly of oligothiophene chromophores. Polymers and model compounds were also prepared for comparison. From the ^{1}H NMR experiments, cyclic trimer **BTC3A** showed the *syn*/*anti* equilibrium in solution, and the *syn*/*anti* conformer ratio (76/24 in $CDCl_3$) was influenced by the solvent character. Namely, the population of the *syn* conformer was lowest (70%) in THF-d_8 and was highest (86%) in $CDCl_3$/CD_3OD (1/1 in volume). On the other hand, the population of the *syn* conformer of cyclic trimer **TTC3A** was high (84%) even in $CDCl_3$. In a $CHCl_3$ solution of cyclic trimer **BTC3A**, the absorption maximum (342 nm) blue-shifted and the emission maximum (448 nm) red-shifted compared with those of polymer **BTPA** and model compound **BTM**. The solvent character also had an impact on the optical properties of cyclic trimer **BTC3A**. The red-shifted emission maximum (481 nm) of cyclic trimer **BTC3A** in CH_3OH indicated the interaction between three bithiophene chromophores. The emission maxima of cyclic trimer **TTC3A** (486 nm) demonstrated a small red-shift from model compound **TTM** (477 nm), and no solvent dependency was observed, unlike cyclic trimer **BTC3A**.

INTRODUCTION

Cyclic molecules are useful building blocks in the supramolecular chemistry and have attracted increasing attention as one of the leading player in molecular recognition events.[1] Among them, cyclic oligoamides[2] and oligopeptides[3] are of interest from the material and biological viewpoints as represented by self-assembling peptide nanotubes. In these classes of molecules, the intermolecular hydrogen bonding between N—H and C═O has a crucial role to permit the supramolecular association. Meanwhile, cyclic aromatic triamides made of three *N*-alkyl benzanilide units, abbreviated hereafter as calix[3]amides, have also constituted a new class of cyclic oligomers.[4] In contrast to the secondary amide counterpart, *N*-alkyl benzanilide preferentially adopts the *cis*-amide structure[5] that enables the cyclic trimerization through the self-condensation of *N*-alkylaminobenzoic acids.[6] Thus, calix[3]amides were obtained in good yields by using tetrachlorosilane or dichlorotriphenylphosphorane as the condensation reagents. Especially, the single crystal X-ray structure analysis and the relationship between the solvent character and the conformation of *m*-calix[3]amides whose amide nitrogen and carbonyl group are located at the *meta*-position are well-decumented.[4c] In view of the supramolecular chemistry, however, the inner cavities provided by *m*-calix[3]amide hosts might be too small to encapsulate guest molecules. Yokozawa and co-workers reported the synthesis of *para*-linked cyclic aromatic triamide with the large triangular cavity by inserting a phenylene-ethynylene unit as the additional linker between the amide and phenylene groups.[7] On the other hand, bowl-shaped *m*-calix[3]amides would be expected as a reliable template for functional groups to be located in close proximity and to enjoy intimate interactions with each other. To the best of our knowledge, however, there are few examples installing a functional group into the *m*-calix[3]amide skeleton.[8]

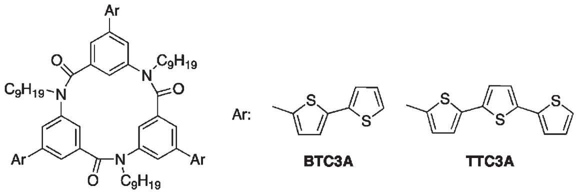


Figure 1. Chemical structure of *m*-calix[3]amides bearing bithiophene and terthiophene chromophore.

π-Conjugated oligomers with the tailored molecular length and the minimum structural defect play a central role in molecular devices including light-emitting diodes[9] and field-effect transistors[10] because of the feasible tuning of optoelectronic properties. A precision assembly of conjugated oligomers is of much importance for understanding the nanostructure of these molecules and ensuring the best performances in the solid state. Along this line, substantial efforts have been paid to obtain new (macro)molecules

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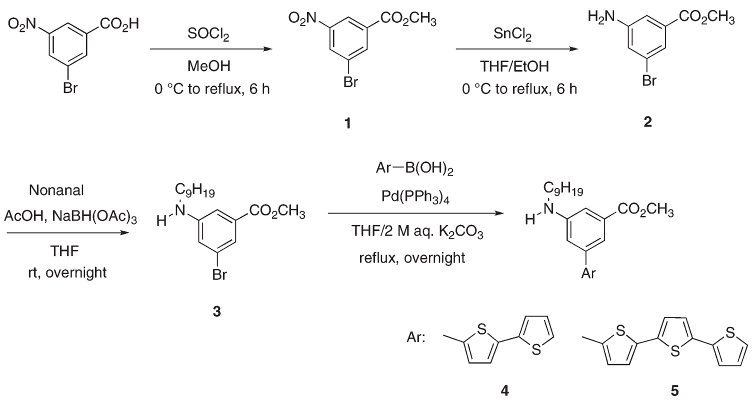
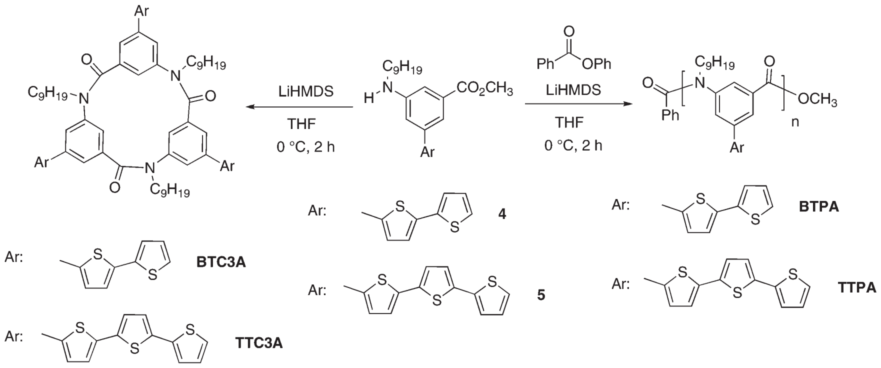
Scheme 1. Synthetic Route of Monomers 4 and 5



Scheme 2. Synthetic Route of Cyclic Trimers and Polymers from Monomers 4 and 5



that attain the programmed arrangement of multichromophores at the defined positions.[11] Oligothiophenes and polythiophenes are important classes of π-conjugated organic molecules that have been extensively investigated and explored as the active material for optoelectronic devices.[12] Thus, we became interested in investigating the alignment of oligothiophene chromophores in a controlled fashion by utilizing the *m*-calix[3]amide scaffold. In this context, we have prepared *m*-calix[3]amides carrying bithiophene and terthiophene chromophore in a confined space (Figure 1) and studied their conformation in solution. Polymers and model compounds were also prepared for comparison. The absorption/emission properties of these materials were carefully investigated to disclose a potential utility of the *m*-calix[3]amide framework. Especially, the polymers carrying multiple chromophores were examined in order to highlight the character of *m*-calix[3]amides although there is a room for discussion about the conformation of *N*-substituted poly-*m*-benzamides.

■ RESULTS AND DISCUSSION

1. Synthesis and Characterization of Materials. Methyl 3-(nonylamino)benzoate carrying the bithiophene chromophore at the 5-position (**4**) was synthesized from 3-bromo-5-nitrobenzoic acid in four steps (Scheme 1). The dropwise addition of lithium bis(trimethylsilyl)amide (LiHMDS) into a dilute THF solution of monomer **4** gave a crude mixture of oligomeric products (Scheme 2, left arrow).[7] Although the peak intensity corresponding to the cyclic trimer was high in the MALDI-TOF-MS spectrum, uncharacterizable peaks and higher molecular weight cyclic oligomers were also detected (Figure S10). Thus, the isolated yield of a target *m*-calix[3]amide (**BTC3A**) was low (15%), which was performed by SiO_2 chromatography and subsequent preparative GPC. The narrow melting temperature range, the ^{1}H NMR spectrum, and the MALDI-TOF-MS spectrum (Figure 2) indicated the isolation of the cyclic trimer. Likewise, cyclic trimer **TTC3A** carrying the terthiophene chromophore was synthesized from monomer **5** (Figures S14−S16).

For more detailed investigation into the characteristics of the *m*-calix[3]amide scaffold, polymers were also prepared for comparison. Following the conditions of the chain-growth polycondensation reported by Yokozawa et al.,[13] monomer **4** dissolved in THF was slowly added to a THF solution of LiHMDS and phenyl benzoate (Scheme 2, right arrow). The obtained product was purified by preparative GPC to isolate polymer **BTPA** having the number-averaged molecular weight of 5300. The molecular weight distribution ($M_w/M_n = 1.59$) was larger than that of *N*-substituted poly(*m*-benzamide)s without the bithiophene chromophore ($M_w/M_n < 1.19$). The MALDI-TOF-MS spectrum of the lower molecular weight part recovered from preparative GPC indicated the formation of cyclic trimer **BTC3A**. These results indicate that the initiator (phenyl benzoate) does not fulfill an ideal role and the self-condensation of monomer **4** may take place. Since the measurement of the MALDI-TOF-MS spectrum was not available, the chemical structure of the polymer termini could not be determined. Since the narrow molecular weight distribution is not a prerequisite factor in the present research, the optimization of the ester groups in monomer **4** and the initiator was not attempted. In the ^{1}H NMR spectrum of polymer **BTPA**, the signal of methyl ester at the propagating end was detected at 3.91 ppm. Interestingly, there was noticeable difference on the chemical shift for methylene protons adjacent to the amide nitrogen between cyclic trimer **BTC3A** and polymer **BTPA**. Cyclic trimer **BTC3A** showed the bimodal signal at around 3.59−4.11 ppm (Figure S11), while polymer **BTPA** showed the single broad signal at the relatively higher magnetic field region (3.57 ppm) (Figure S13). The different peak position might have arisen from the conformation of the materials and the magnetic environment of the methylene protons that will be clarified in the future. A model compound bearing the bithiophene chromophore (**BTM**) was also synthesized as shown in Scheme 3. Polymer **TTPA** ($M_n = 7000$, $M_w/M_n = 1.45$) and model compound **TTM** carrying the terthiophene chromophore were likewise prepared.

The original *m*-calix[3]amide without any chromophore on the benzene ring is known to have two conformers in solution.[4c] Namely, the *syn* conformer has three benzene rings in the same orientation relative to the amide bond, and the *anti* conformer has one benzene ring turning in other direction. To determine the *syn*/*anti* conformer ratio at various temperatures, cyclic trimer **BTC3A** was subjected to the variable temperature (VT) NMR measurement in a $CDCl_3$ solution (Figure S23). The minor signal assignable to a benzene proton of the *anti* conformer was observed at 6.39 ppm at 293 K,[14] and the signal intensity was increased at low temperature (263 K) (Figure 3). The corresponding proton signal of the *syn* conformer was buried in other aromatic proton signals, which made the calculation of the activation energy from one conformer to another difficult. The *syn*/*anti* conformer ratio was 76/24 at 293 K, calculated from the integral ratio of this minor proton signal, and the population of the *syn* conformer was decreased to reach 66% at 233 K. The population of the *syn* conformer was increased to reach 86% at 293 K in a $CDCl_3$/CD_3OD solution (1/1 in volume) in good agreement with the trend of *m*-calix[3]amide without the bithiophene chromophore, and on the other hand, the value was decreased to 70% at 293 K in a THF-d_8 solution (Figure S24). This phenomenon seems to be related to the acceptor number of solvents[15] (8.0 for THF, 23 for $CHCl_3$, and 41 for CH_3OH) rather than the dielectric constant of solvents (7.5 for THF, 4.8 for $CHCl_3$, and 33 for CH_3OH). The carbonyl stretching vibration signal of cyclic trimer **BTC3A** actually shifted from 1659 cm^{-1} in THF to 1648 cm^{-1} in $CHCl_3$, from which the solvent interaction with the amide carbonyl group was suggested. Although the *cis* or *trans* structure of the amide moiety is unknown for the *anti* conformer of *m*-calix[3]amide, the solvent character would influence the dihedral angle between the amide plane and the benzene ring through the interaction with the carbonyl group to eventually impact the *syn*/*anti* conformer ratio of the material. The *syn*/*anti* conformer ratio for cyclic trimer **TTC3A** was 84/26 at 293 K in a $CDCl_3$ solution. Since the bowl-shaped *m*-calix[3]amide in the *syn* conformation has a truncated cone structure (pseudo-C_3 symmetry),[4c] three oligothiophene units would adopt a nonparallel arrangement even in the self-assembled state and the π-stacking of chromophores could not be confirmed by the peak shift in the NMR measurement.

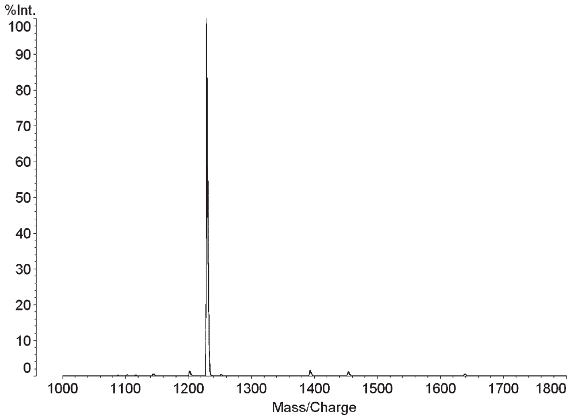
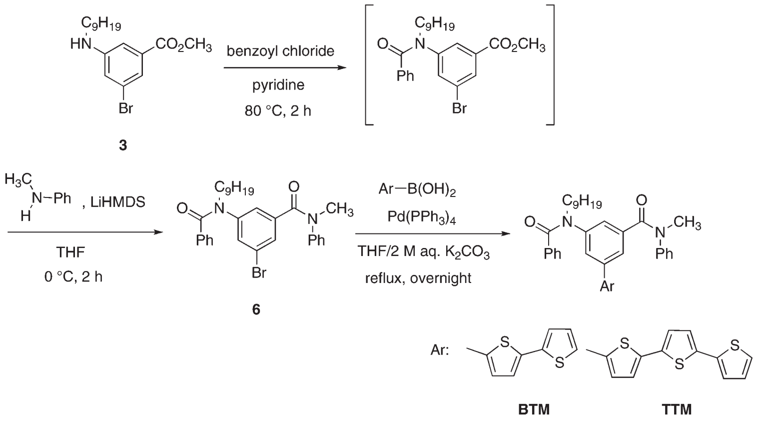


Figure 2. MALDI-TOF-MS spectrum of cyclic trimer **BTC3A**.

2. Optical Properties of Materials. The UV spectra of bithiophene-carrying materials (cyclic trimer **BTC3A**, polymer **BTPA**, and model compound **BTM**) were collected in a $CHCl_3$ solution. The absorption maximum of cyclic trimer **BTC3A** (342 nm) shifted to the shorter wavelength region compared with those of polymer **BTPA** (348 nm) and model compound **BTM** (351 nm) (Figure 4A). On the other hand, the PL spectra demonstrated a marked difference among three materials (see also Figure S25). The emission maximum red-shifted in the order of model compound **BTM** (422 nm), polymer **BTPA** (431 nm), and cyclic trimer **BTC3A** (448 nm) (Figure 4B).[16] These peak shifts do not have a simple correlation with the number of

Scheme 3. Synthetic Route of Model Compounds



the bithiophene chromophore (3mer for cyclic trimer **BTC3A**, 13mer for polymer **BTPA**,[17] and 1mer for model compound **BTM**). The full-width at half-maximum (fwhm) of the PL spectrum of cyclic trimer **BTC3A** (113 nm) was quite larger than that of model compound **BTM** (64 nm). One plausible reason is that the *syn* and *anti* conformers of cyclic trimer **BTC3A** have the different electronic structure at the excited state, and they emit fluorescence with the different wavelength (*vide infra*).

Since Shudo et al. reported the twisted intramolecular charge transfer (TICT) fluorescence at the longer wavelength region (518 nm) for acyclic *N*-methylbenzanilide especially in nonpolar solvents,[18] the emission properties of cyclic trimer **BTC3A** are of much interest. In order to gain deeper insight into the large wavelength shift of the emission maximum of cyclic trimer **BTC3A**, the UV and PL spectra of cyclic trimer **BTC3A** and model compound **BTM** were collected in various solvents. As a result, the UV and PL spectra of model compound **BTM** showed a small shift on going from a $CHCl_3$ solution to a CH_3OH solution probably because the hydrogen bonding interaction of CH_3OH with the amide carbonyl group has an influence upon the electronic structure of the bithiophene chromophore (Figure S26). In contrast, cyclic trimer **BTC3A** showed the noticeable solvato(fluoro)chromic behavior. The absorption maxima blue-shifted from 342 nm in $CHCl_3$ to 336 nm in CH_3OH, while the emission maxima showed the pronounced and opposite shift from 448 nm in $CHCl_3$ to 481 nm in CH_3OH (Figure 5). The emission maxima demonstrated hypsochromic shifts when the spectra were collected in THF (430 nm) and in methylcyclohexane (MCH) (420 nm). These emission wavelength shifts seem to have a good correlation with the population of the *syn* conformer in solution although the value in MCH is not available. Taking the fact that cyclic trimer **BTC3A** preferably adopts the *syn* conformation in a $CDCl_3/CD_3OD$ solution (*vide supra*) into account, the self-assembly of the bithiophene segments enables the chromophore interaction in a CH_3OH solution. Three bithiophene chromophores included in the *syn* conformer, however, take the nonparallel arrangement, and they cannot enjoy the greatest benefit of the π-electron cloud overlap. Nonetheless, the obvious red-shift of the PL spectra indicates that an intramolecular interaction between three bithiophene chromophores gives an emission at the longer wavelength in CH_3OH. Neckers et al. reported the preparation and optical properties of bithiophene-functionalized metal nanoparticles (NPs), where 5-mercapto-2,2′-bithiophene (BTSH) and 5-(5-mercaptopentyl)-2,2′-bithiophene (BTC_5SH) were assembled on the NP surface.[19] The NP decorated with BTSH showed a blue-shift in the UV spectra and red-shift in the PL spectra as compared with the NP bearing BTC_5SH with a flexible methylene chain. They suggest that *trans*-BTSHs on the NP surface interact through intermolecular van der Waals forces to restrict isomerization giving enhanced blue emission. The type of self-assembled structure is different; however, a similar intramolecular interaction between three bithiophene chromophores likely exists in cyclic trimer **BTC3A**. The PL spectrum collected in a MCH solution showed a smooth shoulder at ca. 480 nm, probably ascribed to the emission from the *syn* conformer, that became the maximum peak when the spectrum was measured in a CH_3OH solution. The emission maximum wavelength of cyclic trimer **BTC3A** in a spin-coated thin film (494 nm) showed a further red-shift from that in a CH_3OH solution due to the intermolecular chromophore interaction besides the intramolecular one.

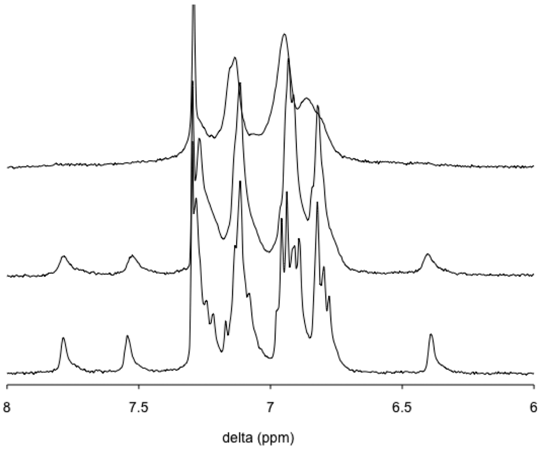


Figure 3. VT NMR spectra of cyclic trimer **BTC3A** in $CDCl_3$ (top, 323 K; middle, 293 K; and bottom, 263 K).

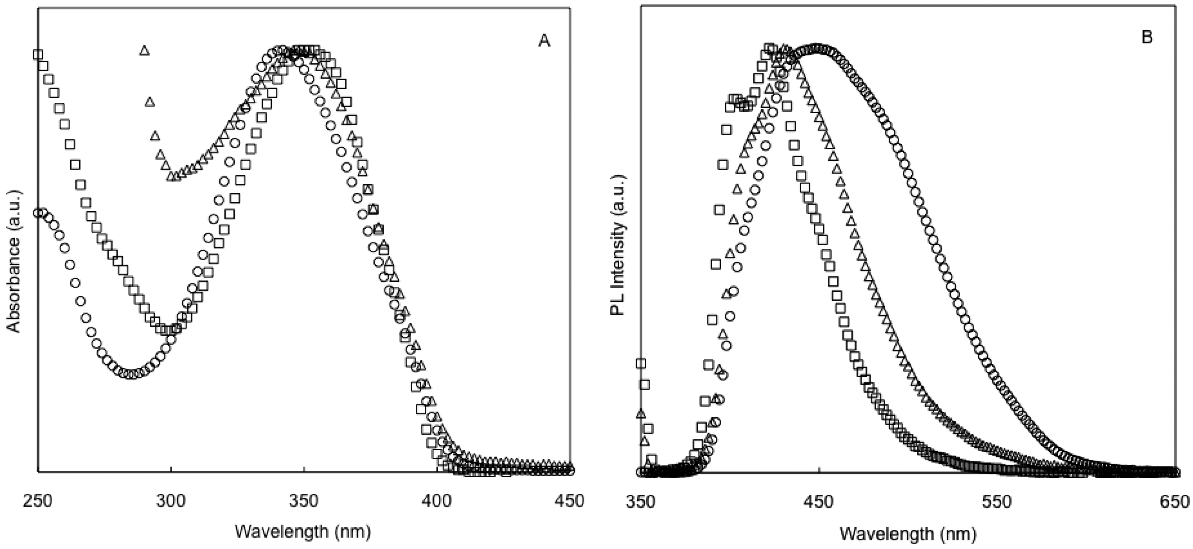


Figure 4. UV (A) and PL (B) spectra of cyclic trimer **BTC3A** (○), polymer **BTPA** (△), and model compound **BTM** (☐) in $CHCl_3$ at 298 K (10^{-5} M). The excitation wavelengths were those of absorption maxima.

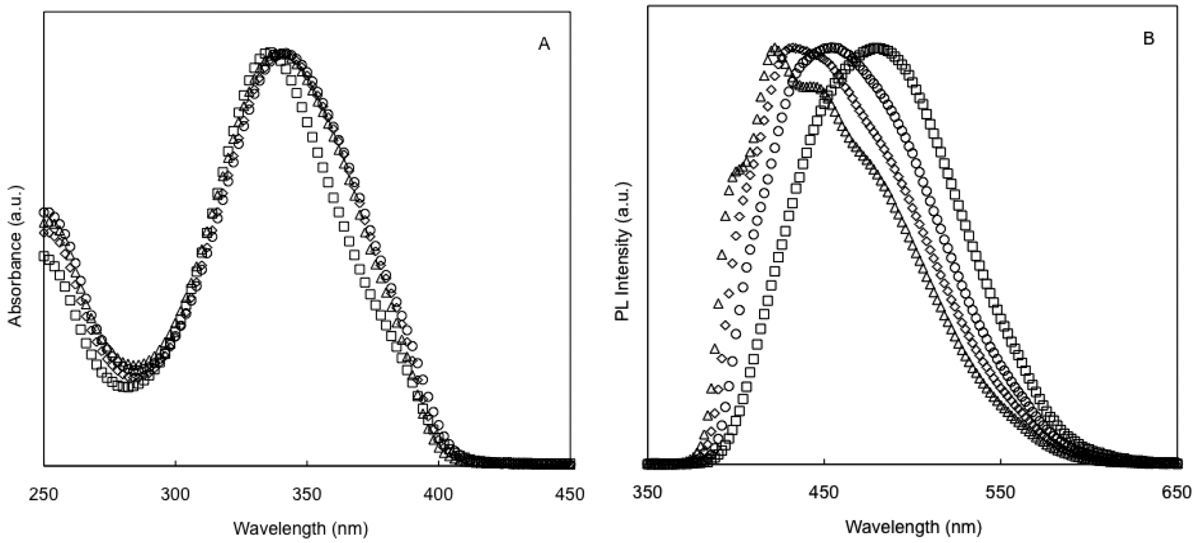


Figure 5. UV (A) and PL (B) spectra of cyclic trimer **BTC3A** in MCH (△), THF (◇), $CHCl_3$ (○), and CH_3OH (□) at 298 K (10^{-5} M). The excitation wavelengths were those of absorption maxima.

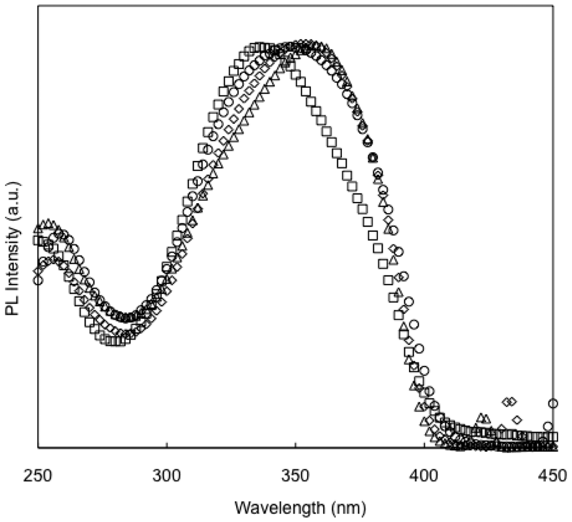


Figure 6. Excitation spectra of cyclic trimer **BTC3A** in MCH (△), THF (◇), $CHCl_3$ (○), and CH_3OH (□) at 298 K (10^{-5} M).

The excitation spectra of cyclic trimer **BTC3A** were also measured in the same series of solvents, and the maximum wavelengths were observed at 357 nm (MCH and THF), 349 nm ($CHCl_3$), and 338 nm (CH_3OH) (Figure 6). There was a small wavelength shift between the absorption maximum (336 nm) and the excitation maximum (338 nm) in the case of a CH_3OH solution. In a MCH solution, on the other hand, the excitation maximum was observed at 357 nm that was red-shifted compared with that of absorption maximum (342 nm). Otsubo et al. described the preparation and properties of a family of [*n.n*]quinquethiophenophanes as a useful π-dimer model.[11b] They pointed out that the blue-shifted absorption maximum as compared with that of monomeric quinquethiophene could stem from the nonbonded interaction between face-to-face chromophores. With this report in mind, the population of the *syn* conformer with three bithiophene chromophores in close proximity might be low in the excited state rather than the ground state. We now speculate that the photoexcitation of cyclic trimer **BTC3A** induces the flip of the bithiophene chromophore enabling the conversion from the *syn* conformer to the *anti* one especially in a MCH solution.

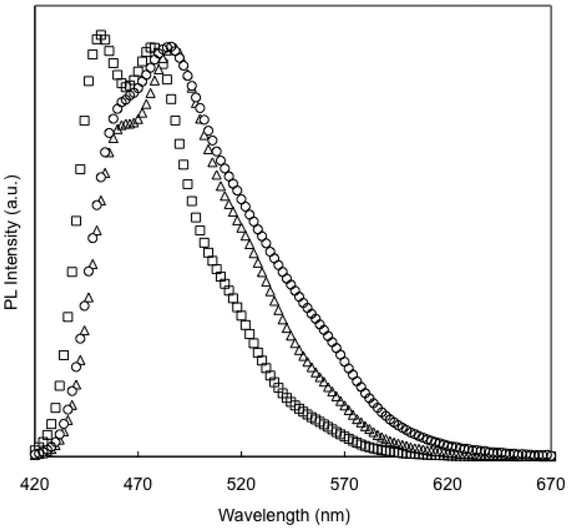


Figure 7. PL spectra of cyclic trimer **TTC3A** (○), polymer **TTPA** (△), and model compound **TTM** (□) in $CHCl_3$ at 298 K (10^{-5} M). The excitation wavelengths were those of absorption maxima.

Finally, the optical properties of terthiophene-carrying materials (cyclic trimer **TTC3A**, polymer **TTPA**, and model compound **TTM**) were investigated in a $CHCl_3$ solution. As expected, the absorption maxima of these materials are red-shifted compared with those of bithiophene-carrying analogues. The absorption maximum of cyclic trimer **TTC3A** (379 nm) was observed at the shorter wavelength region compared to those of polymer **TTPA** (386 nm) and model compound **TTM** (390 nm), which is similar to the trend of cyclic trimer **BTC3A**. However, the emission maximum of cyclic trimer **TTC3A** was detected at 486 nm (Figure 7), and the shift width from that of model compound **TTM** was smaller (9 nm) than that of cyclic trimer **BTC3A** (24 nm) in spite of the higher population of the *syn* conformer (*vide supra*). Since the *m*-calix[3]amide framework has a truncated cone structure,[4c] the edge-to-edge distance between neighboring terthiophene chromophores in cyclic trimer **TTC3A** would be longer than that of bithiophene-carrying cyclic trimer **BTC3A**. It is thus considered that the intramolecular interaction between the self-assembled chromophores does not effectively work in cyclic trimer **TTC3A**. The emission maximum was likewise observed at 486 nm when the PL spectrum was measured in a CH_3OH solution.

In conclusion, we herein prepared two *m*-calix[3]amides bearing the oligothiophene unit to accomplish the self-assembly of chromophores. The conformational study was carried out using ^1H NMR spectra. The *syn*/*anti* conformer ratio of *m*-calix[3]amide carrying the bithiophene chromophore was influenced by the solvent character. The UV and PL spectra were measured to know a relationship between the conformation and the optical properties of materials. The absorption and emission maxima of *m*-calix[3]amide carrying the bithiophene chromophore shifted from those of polymer and model compound. The emission maximum wavelengths were dramatically influenced by the solvent character. On the other hand, *m*-calix[3]amide carrying the terthiophene chromophore showed a relatively small shift of the emission maxima compared with the model compound, and the maximum wavelength was independent upon the solvent character. These results indicate that the *m*-calix[3]amide framework would be the intriguing scaffold for the self-assembly of π-conjugated chromophores.

EXPERIMENTAL SECTION

1. Monomer Synthesis. For methyl 3-bromo-5-nitrobenzoate (**1**),[20] to a MeOH (15 mL) solution of 3-bromo-5-nitrobenzoic acid (0.25 g, 1.0 mmol)[21] was added $SOCl_2$ (0.11 mL, 1.5 mmol) at 0 °C. After the mixture was heated to reflux for 6 h, MeOH was evaporated. Then, saturated aq $NaHCO_3$ was added, and the system was extracted with ethyl acetate. The organic phase was dried over $MgSO_4$, and solvents were removed by a rotary evaporator. The crude product was recrystallized from EtOH to obtain colorless crystals in 0.33 g (63% yield). Mp 71−72 °C. ^1H NMR (δ, 200 MHz, $CDCl_3$) 8.79 (d, J = 1.6 Hz, 1H), 8.55 (d, J = 1.9 Hz, 1H), 8.49 (t, J = 1.5 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 163.6, 148.6, 138.1, 133.1, 130.3, 123.0, 122.9, 53.0. IR (cm^{-1}) 3089, 1727, 1531, 1452, 1345, 1276, 1197, 1153, 983, 735.

For methyl 3-amino-5-bromobenzoate (**2**),[22] to an EtOH (30 mL) solution of $SnCl_2$ (52 g, 0.23 mol) was added dropwise **1** (12 g, 46 mmol) dissolved in THF/EtOH (30 mL/30 mL) under cooling in a water bath. After the addition was completed, the mixture was heated to reflux for 6 h. Then, saturated aq $NaHCO_3$ was added, and a precipitate was filtered off. The filtrate was washed with water, and the aqueous phase was extracted with ethyl acetate. A combined organic phase was dried over $MgSO_4$, and solvents were removed by a rotary evaporator. The crude product was recrystallized from hexane to obtain colorless crystals in 8.7 g (82% yield). Mp 92−93 °C. ^1H NMR (δ, 200 MHz, $CDCl_3$) 7.52 (d, J = 1.3 Hz, 1H), 7.26 (s, 1H), 6.99 (t, J = 1.8 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 166.0, 147.7, 132.4, 122.8, 122.0, 121.5, 114.5, 52.3. IR (cm^{-1}) 3409, 1708, 1569, 1430, 1307, 1241, 1114, 1003, 852, 766.

For methyl 3-(nonylamino)-5-bromobenzoate (**3**),[23] to a THF (3.2 mL) solution of **2** (0.23 g, 1.0 mmol), nonanal (0.18 mL, 1.0 mmol), and AcOH (32 μL, 0.55 mmol) was added $NaBH(OAc)_3$ (0.26 g, 1.2 mmol) at room temperature. The system was stirred overnight. After saturated aq $NaHCO_3$ was added, the aqueous phase was extracted with ethyl acetate. A combined organic phase was dried over $MgSO_4$, and solvents were removed by a rotary evaporator. The crude product was purified by SiO_2 chromatography (CH_2Cl_2, R_f = 0.7) to obtain a colorless solid in 0.20 g (56% yield). Mp 65−66 °C. ^1H NMR (δ, 200 MHz, $CDCl_3$) 7.44 (s, 1H), 7.15 (t, J = 1.5 Hz, 1H), 6.87 (t, J = 1.8 Hz, 1H), 3.89 (s, 3H), 3.82 (br s, 1H), 3.10 (t, J = 7.0 Hz, 2H), 1.62 (m, 2H), 1.46−1.18 (12H), 0.89 (t, J = 6.0 Hz, 3H). IR (cm^{-1}) 3395, 2924, 2847, 2360, 1710, 1512, 1323, 1246, 765.

For methyl 3-(nonylamino)-5-(2′-(5′,2′′-bithienyl))benzoate (**4**), to a THF (30 mL) solution of **3** (1.1 g, 3.0 mmol) and 2-(5,2′-bithienyl)boronic acid[24] (0.63 g, 3.0 mmol) were added 2 M aq K_2CO_3 (12 mL) and $Pd(PPh_3)_4$ (35 mg, 30 μmol), and the system was heated to reflux overnight. After the aqueous phase was extracted with CH_2Cl_2, a combined organic phase was dried over $MgSO_4$. Solvents were removed by a rotary evaporator. The crude product was purified by SiO_2 chromatography (CH_2Cl_2, R_f = 0.6) followed by recrystallization from hexane to obtain pale green crystals in 0.54 g (41% yield). Mp 74−75 °C. ^1H NMR (δ, 200 MHz, $CDCl_3$) 7.59 (s, 1H), 7.24−7.08 (5H), 7.02 (dd, J = 3.5 Hz, 5.0 Hz, 1H), 6.95 (t, J = 1.9 Hz, 1H), 3.92 (s, 3H), 3.82 (br s, 1H), 3.18 (t, J = 6.9 Hz, 2H), 1.64 (m, 2H), 1.48−1.16 (12H), 0.87 (t, J = 6.7 Hz, 3H). ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 167.2, 148.9, 142.6, 137.3, 136.7, 134.9, 131.6, 127.8, 124.4, 124.3, 124.0, 123.6, 115.5, 113.5, 112.4, 52.1, 43.8, 31.8, 29.5, 29.4, 29.2, 27.1, 22.6, 14.1. IR (cm^{-1}) 3403, 2924, 1703, 1600, 1251, 802, 688. Anal. Found: C, 67.64; H, 6.86; N, 3.06%. Calcd for $C_{25}H_{31}NO_2S_2$: C, 67.99; H, 7.07; N, 3.17%. HRMS (EI) Calcd for $C_{25}H_{31}NO_2S_2$: 441.1796. Found: 441.1792.

For methyl 3-(nonylamino)-5-(2′-(5′,2′′,5′′,2′′′-terthienyl))benzoate (**5**), the material was similarly prepared from **3** and 2-(5,2′,5′,2′′-terthienyl)boronic acid[24] in 31% yield. Mp 88−89 °C. ^1H NMR (δ, 200 MHz, $CDCl_3$) 7.59 (s, 1H), 7.24−7.08 (7H), 7.02 (dd, J = 3.6 Hz, 5.0 Hz, 1H), 6.95 (t, J = 1.9 Hz, 1H), 3.92 (s, 3H), 3.89−3.70 (br s, 1H), 3.18 (t, J = 7.0 Hz, 2H), 1.64 (m, 2H), 1.48−1.18 (12H), 0.89 (t, J = 6.7 Hz, 3H). ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 167.1, 148.8, 142.7, 137.0, 136.4, 136.1, 136.0, 134.8, 131.6, 127.8, 124.4, 124.3, 124.1, 123.6, 115.4, 113.5, 112.5, 52.1, 43.8, 31.8, 29.5, 29.4, 29.2, 27.1, 22.6, 14.1. IR (cm^{-1}) 3385, 2921, 2850, 1719, 1598, 1451, 1254, 789, 765. HRMS (EI) Calcd for $C_{29}H_{33}NO_2S_3$: 523.1673. Found: 523.1681.

2. Synthesis of Cyclic Trimers and Polymers. For the cyclic trimer of **4** (**BTC3A**),[7] to a THF (2 mL) solution of monomer **4** (0.17 g, 0.40 mmol) was added dropwise LiHMDS (1.0 M in THF, 0.64 mL, 0.64 mmol) at 0 °C, and the system was stirred for 2 h. After saturated aq NH_4Cl was added, the aqueous phase was extracted with $CHCl_3$. A combined organic phase was dried over $MgSO_4$, and solvents were removed by a rotary evaporator. The crude product was purified by SiO_2 chromatography (CH_2Cl_2/acetone = 3/1 in volume, R_f = 0.7), followed by preparative GPC ($CHCl^3$ as an eluent) to obtain yellow solid in 0.02 g (15% yield). Mp 51−53 °C. ^1H NMR (δ, 200 MHz, $CDCl_3$) 7.95−6.32 (24H), 4.11−3.59 (br m, 6H), 1.82−1.51 (br s, 6H), 1.49−1.10 (36H), 1.05−0.76 (br, 9H). ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 169.7, 142.9, 139.8, 139.4, 138.2, 136.6, 135.3, 127.7, 127.6, 125.0, 124.6, 124.5, 124.3, 124.2, 123.8, 49.6, 31.8, 29.5, 29.2, 27.6, 26.8, 22.6, 14.1. IR (cm^{-1}) 2923, 2852, 2360, 1650, 1585, 1387, 688. MALDI-TOF-MS Calcd for $C_{72}H_{82}N_3O_3S_6$ $[M + H]^+$: 1229.82. Found: 1229.65.

For the polymer of **4** (**BTPA**),[13] to a THF (0.4 mL) solution of phenyl benzoate (1.6 mg, 8.0 μmol) mixed with LiHMDS (1.0 M in THF, 0.44 mL, 0.44 mmol) was added dropwise a THF (0.4 mL) solution of monomer **4** (0.18 g, 0. 40 mmol) at 0 °C. After a few hours, saturated aq NH_4Cl was added, and the aqueous phase was extracted with $CHCl_3$. A combined organic phase was dried over $MgSO_4$, and solvents were removed by a rotary evaporator. In order to remove low molecular weight oligomers, the crude product was purified by preparative GPC ($CHCl_3$ as an eluent) to obtain brown solid in 93 mg (56% yield). ^1H NMR (δ, 200 MHz, $CDCl_3$) 8.05−6.60 (8H), 3.91 (br, small), 3.80−3.35 (br, 2H), 1.80−1.42 (br, 2H), 1.40−0.96 (12H), 0.92−0.72 (br, 3H). IR (cm^{-1}) 2924, 2360, 1648, 1581, 1258, 687. GPC (THF, PSt standard) M_n = 5300, M_w/M_n = 1.59.

For the cyclic trimer of **5** (**TTC3A**),[7] the material was similarly prepared from monomer **5** in 13% yield. Mp 183−185 °C. ^1H NMR (δ, 200 MHz, $CDCl_3$) 8.00−6.35 (30H), 4.02−3.52 (br m, 6H), 1.85−1.52 (br s, 6H), 1.50−1.05 (36H), 1.00−0.72 (br, 9H). ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 169.8, 143.0, 139.9, 139.4, 138.2, 137.0, 136.6, 135.2, 128.0, 127.9, 125.0, 124.8, 124.7, 124.6, 124.5, 124.4, 124.3, 124.2, 123.7, 123.6, 49.6, 31.9, 29.6, 29.3, 27.7, 26.9, 22.7, 14.1. IR (cm^{-1}) 2923.6, 2360.4, 1651.7, 1585.2, 1387.5, 785.9. MALDI-TOF-MS Calcd for $C_{84}H_{87}N_3O_3S_9$ $[M + H]^+$: 1476.19. Found: 1476.66.

For the polymer of **5** (**TTPA**),[13] the material was similarly prepared from monomer **5** in 56% yield. ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 7.95−6.45 (10H), 3.90 (br, small), 3.82−3.25 (br, 2H), 1.81−1.42 (br, 2H), 1.40−0.96 (12H), 0.92−0.72 (br, 3H). IR (cm^{-1}) 2923, 2360, 1647, 1583, 789. GPC (THF, PSt standard) M_n = 7000, M_w/M_n = 1.45.

3. Synthesis of Model Compound. 3-(*N*-Nonyl-*N*-benzoylamino)-5-bromo-*N*′-methylbenzanilide (**6**) A pyridine (4 mL) solution of **3** (0.36 g, 1.0 mmol) and BzCl (1.5 mL, 1.2 mmol) was heated at 80 °C for 2 h.[25] After pouring into iced-water, the aqueous phase was extracted with ethyl acetate. The organic phase was washed with 1 M HCl and subsequently with saturated aq. $NaHCO_3$. From the organic phase dried over $MgSO_4$, solvents were removed by a rotary evaporator to obtain methyl 3-(*N*-nonyl-*N*-benzoylamino)-5-bromobenzoate as pale brown viscous oil which was used without further purification. To a THF (1.6 mL) solution of 3-(*N*-nonyl-*N*-benzoylamino)-5-bromobenzoate (0.36 g, 0.78 mmol) and *N*-methylaniline (86 μL, 0.79 mmol) was added dropwise LiHMDS (1.0 M in THF, 0.78 mL, 0.78 mmol) at 0 °C, and the system was stirred for 2 h. After saturated aq. NH_4Cl was added, the aqueous phase was extracted with ethyl acetate. A combined organic phase was dried over $MgSO_4$ and solvents were removed by a rotary evaporator to obtain pale brown viscous oil in 0.41 g (98% yield). ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 7.40−6.80 (13H), 3.60 (t, J = 8.1 Hz, 2H), 3.44 (s, 3H), 1.50−1.10 (14H), 0.87 (t, J = 6.5 Hz, 3H).

For 3-(*N*-nonyl-*N*-benzoylamino)-5-(2′-(5′,2″-bithienyl))-*N*′-methylbenzanilide (**BTM**), to a THF (5 mL) solution of **6** (0.14 g, 0.25 mmol) and 2-(5, 2′-bithienyl)boronic acid[24] (0.06 g, 0.25 mmol) were added 2 M aq K_2CO_3 (2 mL) and $Pd(PPh_3)_4$ (2.8 mg, 2.0 μmol), and the system was heated to reflux overnight. After the aqueous phase was extracted with CH_2Cl_2, a combined organic phase was dried over $MgSO_4$. Solvents were removed by a rotary evaporator. The crude product was purified by SiO_2 chromatography (CH_2Cl_2/acetone = 5/1 in volume, R_f = 0.7) followed by washed with hexane to obtain brown viscous oil in 45 mg (29% yield). ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 7.40−6.80 (18H), 3.67 (t, J = 7.8 Hz, 2H), 3.49 (s, 3H), 1.43 (m, 2H), 1.33−1.10 (12H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 170.1, 169.0, 144.5, 143.4, 140.6, 137.7, 137.4, 136.9, 135.8, 134.5, 129.6, 129.3, 128.5, 127.8, 126.9, 126.3, 125.7, 124.7, 124.5, 124.4, 123.9, 50.1, 38.3, 31.8, 29.5, 29.3, 29.2, 27.6, 26.8, 22.6, 14.0. IR (cm^{-1}) 3726, 2924, 2360, 1644, 1586, 1494, 1446, 1378, 694. Anal. Found: C, 73.32; H, 6.36; N, 4.42%. Calcd for $C_{38}H_{40}N_2O_2S_2$: C, 73.51; H, 6.49; N, 4.51%. HRMS (EI) Calcd for $C_{38}H_{40}N_2O_2S_2$: 620.2531. Found: 620.2515.

For 3-(*N*-nonyl-*N*-benzoylamino)-5-(2′-(5′,2″,5″,2‴-terthienyl))-*N*′-methylbenzanilide (**TTM**), the material was similarly prepared from **7** in 57% yield. ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 7.40−6.80 (20H), 3.67 (t, J = 7.7 Hz, 2H), 3.49 (s, 3H), 1.43 (m, 2H), 1.33−1.10 (12H), 0.87 (t, J = 6.6 Hz, 3H). ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 170.1, 169.0, 144.5, 143.5, 140.7, 137.5, 137.3, 136.8, 136.6, 135.8, 135.5, 134.4, 129.6, 129.4, 128.5, 127.8, 126.9, 126.3, 125.8, 124.6, 124.5, 124.4, 124.3, 123.8, 50.1, 38.3, 31.8, 29.5, 29.3, 29.2, 27.6, 26.8, 22.6, 14.1. IR (cm^{-1}) 2924.5, 1645.0, 1583.3, 1374.0, 787.8, 695.2. HRMS (EI) Calcd for $C_{42}H_{42}N_2O_2S_3$: 702.2408. Found: 702.2389.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Spectroscopic data (NMR and MALDI-TOF-MS) of materials. Conformational study of cyclic trimer **BTC3A** using VT NMR spectra. Optical properties of materials bearing bithiophene chromophore in various solvents. This material is available free of charge via the Internet at http://pubs.acs.org.

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