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Synthesis, Crystal Structures, and Supramolecular Assemblies of Pyrrole-Based Anion Receptors Bearing Modified Pyrrole β-Substituents

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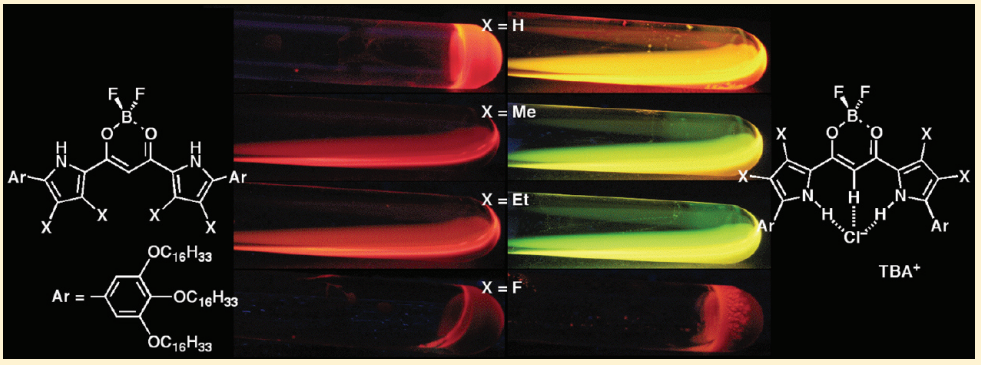
Supporting Information

ABSTRACT:



Dipyrrolyldiketone BF_2 complexes acting as acyclic anion receptors form supramolecular assemblies with structures and properties that are dependent on the pyrrole β-substituents. In particular, although β-alkyl substituents interfered with the formation of stable gel states, the introduction of fluorine moieties induced a stable supramolecular gel when compared to that of β-unsubstituted receptor.

INTRODUCTION

One of the strategies to form functional supramolecular assemblies on the basis of noncovalent interactions is the introduction of appropriate substituents to the core π-conjugated platforms. In particular, molecules possessing guest-binding ability are essential building blocks of stimuli-responsive soft materials. For example, appropriately programmed molecules afford soft materials such as supramolecular gels, which comprise solvent molecules and dimensionally controlled fibrous or sheetlike assemblies[1] that can exhibit dramatic changes in their states in response to various external stimuli. Recently, supramolecular gels that are responsive to anions[2] have attracted considerable attentions because they are soft materials that can be tuned by the incorporation of various ionic components including both bound anions and their counter cations.[3] Such charge-based soft materials would exhibit stimuli-responsive ferroelectric properties based on polarized ion pairs and may show charge-carrier behaviors if the charged components are appropriately arranged. However, further detailed investigations of such soft materials comprising charged species require the preparation and examination of suitable π-conjugated molecules that efficiently bind anions. As potential candidates, boron complexes of 1,3-dipyrrolyl-1,3-propanediones (e.g., **1a**,**b**, Figure 1a)[4,5] form anion-responsive supramolecular gels via the introduction of aliphatic chains to α-aryl moieties such as **1c**.[5d] On the other hand, pyrrole β-substituents such as those bearing methyl (**2a**),[5g] ethyl (**3a**),[5c] and fluorine (**4a**)[5b] moieties are also essential factors for controlling the anion-binding and assembling properties of the anion receptors. In contrast to the cases of **1a**, **2a**, and **4a**, the β-ethyl groups in **3a** interfere with the construction of efficient stacking structures, as suggested by the solid-state assembly.[5a,b,g] However, π-extension at pyrrole α-positions provides solid-state stacking dimers, such as those found in α-phenyl **3b** and related derivatives.[4,5f]

Focusing on the substituents, introduction of electron-withdrawing fluorine moieties at pyrrole β-positions changes the properties of the corresponding oligopyrrole molecules compared to those of alkyl moieties.[6] For example, Sessler et al. reported the β-fluorinated derivatives of calix[4]pyrrole and dipyrrolylquinoxaline, exhibiting enhanced binding constants for anions.[6a,b] As for π-conjugated macrocycles, Osuka and Furuta et al. reported perfluorinated *meso*-aryl-substituted expanded porphyrins, which exhibited extremely red-shifted absorption, for example, >1000 nm in the case of [38]octaphyrin.[6c] The fluorine moiety does not significantly affect the geometries of molecules because of its small size but can perturb

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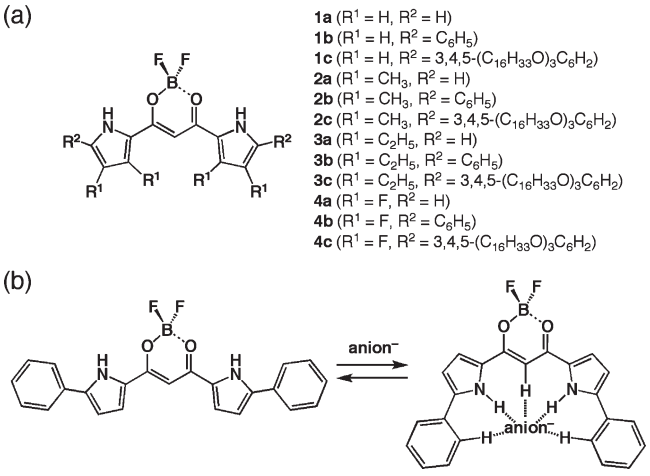

Figure 1. (a) BF_2 complexes of dipyrrolyldiketones (β-unsubstituted **1a**−**c**, β-alkyl-substituted **2a**−**c** and **3a**−**c**, and β-fluorine-substituted **4a**−**c**) and (b) anion-binding mode of **1b**. Synthesis of some derivatives has already been reported in ref 5a for **1a**, ref 5d for **1b**,**c**, ref 5g for **2a**, ref 5c for **3a**, ref 5f for **3b**, and ref 5b for **4a**.

the states of π-conjugated systems, resulting in the stabilization of molecules as well as the modulation of electronic properties and assembled structures. In this paper, on the basis of the initial findings by our group,[4,5] we show the modifications of the α-positions of the β-substituted receptors to form functional assembled structures, especially, anion-responsive supramolecular gels. In particular, introduction of fluorine moieties at the pyrrole β-positions was found to enable the formation of supramolecular gel at rt even in the presence of Cl^- as a tetraalkylammonium salt, suggesting that more stable and useful soft materials consisting of charged species would be prepared using β-fluorinated receptors if anions as salts of appropriate countercation are incorporated.

RESULTS AND DISCUSSION

Synthesis and Initial Characterization. Following the protocol reported for the preparation of **3b** from **3a**,[5f] α-phenyl-substituted **2b** and **4b** were obtained in 46% and 20% yields, respectively, by α-iodination using *N*-iodosuccinimide (NIS) and subsequent Suzuki cross-coupling with phenylboronic acid for **2a** and **4a**. Similar to the cases for **2b**, **3b**, and **4b**, reactions with 3,4,5-trihexadecyloxyphenyl-substituted boronic acid pinacol ester afforded **2c**, **3c**, and **4c** from the corresponding α-unsubstituted derivatives (**2a**, **3a**, and **4a**) in 41%, 48%, and 20% yields, respectively. Relatively low yields of β-fluorinated **4b**,**c** were due to the partial removal of BF_2 units to provide the corresponding α-aryl-substituted dipyrrolyldiketones, which were also converted to **4b**,**c** by treatment with $BF_3 \cdot OEt_2$. The chemical identifications of **2b**,**c**, **3c**, and **4b**,**c** were performed by ^{1}H NMR and MALDI-TOF-MS and ESI-TOF-MS. Electronic properties of α-phenyl-substituted derivatives were also modulated by β-substituents with the absorption maxima (λ_{max}) and fluorescence emission maxima (λ_{em}) of **2b**, **3b**, and **4b** excited at each λ_{max} in CH_2Cl_2 at 499, 499, and 492 nm (λ_{max}) and 534, 535, and 521 nm (λ_{em}), respectively. These values are comparable to those obtained from the analysis of **1b** (500 and 529 nm). The slight blue shifts of **4b** were presumably due to the electron-withdrawing β-fluorine moieties. Further, the corresponding emission quantum yields of **2b**, **3b**, and **4b** were 0.89, 0.94, and 0.89, respectively, suggesting that these molecules have highly emissive properties in the solution state.

The single-crystal X-ray structure of the anion receptor affords essential insights into the supramolecular stacking structures (Figure 2). Similar to other derivatives **1b** and **3b**,[5d,f] the receptor **2b** exhibits a fairly planar structure with terminal phenyl rings tilted to the core plane consisting of 16 atoms at 22.7° and 29.3°, which are intermediate values in average between **1b** (20.0° and 28.6°)[5d] and **3b** (24.3° and 31.9°).[5f] On the other hand, receptor **4b** shows highly planar structure with a small tilted angle of 0.58° between phenyl ring and core plane consisting of 16 atoms due to the weak interaction between pyrrole β-fluorine moiety and terminal phenyl *o*-CH. Further, β-methyl **2b** and β-fluorinated **4b** form infinite $\pi-\pi$ stacking structures similar to **1b**, in sharp contrast to the weakly stacked structures by β-ethyl **3b**. In fact, the distances between the stacking core planes, defined as the average distance between the plane consisting of 16 core atoms and each atom in the neighboring plane, in **3b** were longer (3.73 and 4.19 Å) than those of **1b** (3.19 Å), **2b** (3.46 and 3.55 Å), and **4b** (3.41 Å). This difference may have been due to interference by β-ethyl substituents.

Anion-Binding Properties. The anion-binding behavior of the β-substituted receptors was elucidated by ^{1}H NMR upon the addition of Cl^- as a tetrabutylammonium (TBA) salt at −50 °C. For example, the signals of pyrrole NH, bridging CH, and phenyl *o*-CH of β-methyl **2b** at 9.48, 7.55, and 6.45 ppm in CD_2Cl_2 disappeared, and new signals arose in the downfield region at 11.98 ppm (+ 2.50 ppm), 7.82 ppm (+ 0.27 ppm), and 8.53 ppm (+ 2.08 ppm), respectively. Similar NMR spectral changes were also observed for β-ethyl **3b**[5f] and β-fluorinated **4b**. These observations suggest the formation of pentacoordinated [1 + 1]-type receptor-anion complexes, which is supported by density functional theory (DFT) calculations.[7] In addition, similar to **1b**$\cdot Cl^-$,[5d] single-crystal X-ray analysis revealed the [1 + 1]-type anion complexes, **2b**$\cdot Cl^-$ and **4b**$\cdot Cl^-$, as tetrapropylammonium (TPA) and TBA salts, respectively (Figure 3). The binding mode of **4b**$\cdot Cl^-$ was in sharp contrast to that of **4a**$\cdot Cl^-$, with completely uninverted pyrrole rings to form a 1-D chain structure.[5b] In **2b**$\cdot Cl^-$, peripheral phenyl units are tilted in the angle range of 30.99−47.68° due to the interference with β-methyl units, whereas those of **4b**$\cdot Cl^-$ are fairly coplanar with the core unit with dihedral angles of 4.65° and 24.67°. Further, both anion complexes **2b**$\cdot Cl^-$ and **4b**$\cdot Cl^-$ formed charge-by-charge assemblies,[5h] consisting of negatively charged receptor−anion complexes and counter tetraalkylammonium cations, in different stacking modes. In contrast to **2b**$\cdot Cl^-$, which is a TPA salt showing alternate stacking of anionic and cationic components, **4b**$\cdot Cl^-$ is a TBA salt with columnar assemblies comprising a pair of complexes and that of cations in a row. Neighboring Cl^- were closely located with a distance of 4.287 Å, whereas the shortest distance between Cl^- and TBA-N was 4.286 Å. Based on the 1:1 binding stoichiometry determined by the Job plot, anion-binding affinities of **2b** and **4b** were also estimated by UV/vis absorption spectral changes in CH_2Cl_2 upon the addition of TBA salts of anions (Table 1). In contrast to the β-unsubstituted receptors, which showed enhanced K_a values for halide anions via introduction of phenyl moieties at α-positions, α-phenyl substitutions of β-alkyl-substituted receptors were found to interfere with efficient anion binding. This may have occurred due to there being less planar coordination by β-substituents. Conversely, phenyl substitution of β-fluorinated **4a** to **4b** provided comparable K_a values for halide anions in both

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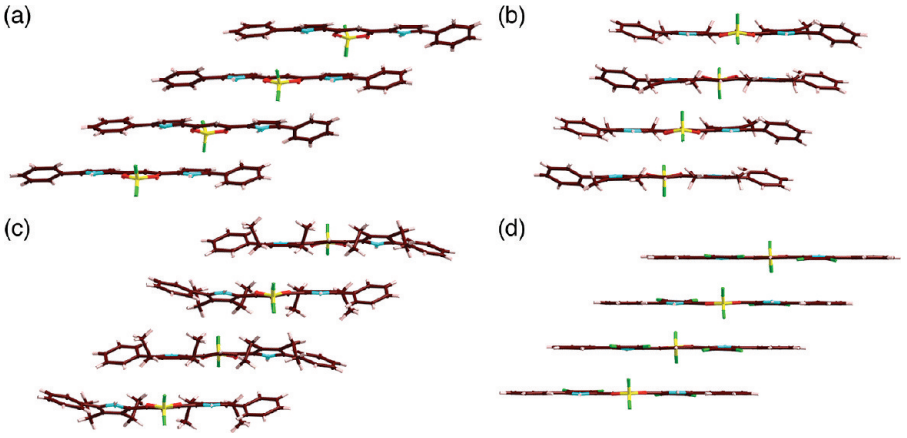

Figure 2. Single-crystal X-ray structures (side view showing stacking structures) of (a) **1b**,[5d] (b) **2b**, (c) **3b**,[5f] and (d) **4b**. Solvent molecules are omitted for clarity in (b) and (d). Atom color code: brown, pink, yellow, green, blue, and red refer to carbon, hydrogen, boron, fluorine, nitrogen, and oxygen, respectively.

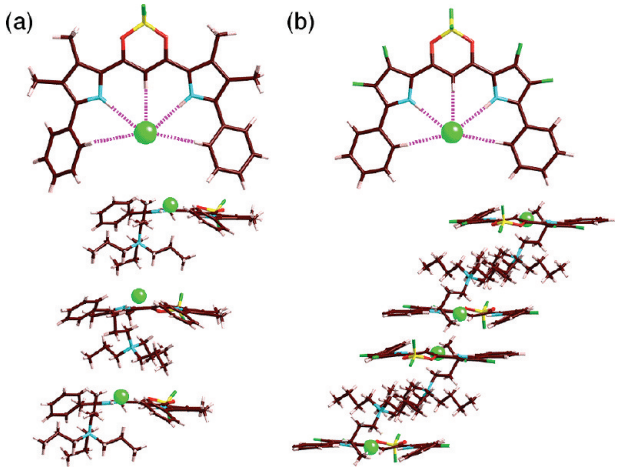

Figure 3. Single-crystal X-ray structures (top view showing single molecules and side view showing charge-by-charge stacking structures) of (a) **2b**·TPACl (one of the four independent complexes is represented) and (b) **4b**·TBACl. Atom color code: yellow green represents chlorine.

Table 1. Binding Constants (K_a, M^{-1}) of 1b,[b] 2b, 3b,[c] and 4b with Various Anions as TBA Salts in CH_2Cl_2 at 20 °C[a]

	1b (1a)	2b (2a)	3b (3a)	4b (4a)
Cl^-	30,000 (15,000)	2,500 (4,900)	2,700 (6,800)	30,000 (26,000)
Br^-	2,800 (2,100)	320 (680)	300 (1,200)	1,600 (1,700)
$CH_3CO_2^-$	210,000 (930,000)	35,000 (61,000)	27,000 (210,000)	n.d.[h] (960,000)
$H_2PO_4^-$	72,000 (270,000)	2,700 (87,000)	2,200 (91,000)	n.d.[h] (190,000)

[a] The values shown in parentheses are the K_a values of the corresponding β-unsubstituted derivatives **1a**,[d] **2a**,[e] **3a**,[f] and **4a**[g]. The errors in K_a for anions are within 10% as described in the Supporting Information. [b] Ref 5d. [c] Ref 5f. [d] Ref 5e. [e] Ref 5g. [f] Ref 5c. [g] Ref 5b. [h] Not determined.

receptors due to the presence of less sterical hindrance of β-fluorine moieties. Further, by addition of oxoanions, α-phenyl and β-fluorinated **4b** showed the complicated spectral changes including deprotonation of pyrrole NH; this behavior is presumably because of the electron-withdrawing effect of β-fluorine moiety and the stabilization by intramolecular C−H···N hydrogen bonding using α-phenyl *o*-CH. Even though β-fluorinated **4a,b** have electron-withdrawing substituents, they were found to have K_a values similar to **1a,b**, which was likely due to the presence of less stable pyrrole-inverted preorganized conformations in **4a,b** than in **1a,b**.

Anion-Responsive Supramolecular Gels. The formation of supramolecular gels of β-substituted receptors bearing aliphatic chains was also examined. In contrast to **1c**, which forms supramolecular gels,[5d] β-alkyl **2c** and **3c** could not form gel states at rt from octane (10 mg/mL). For example, the UV/vis spectrum of **2c** in octane (10 mg/mL) revealed a blue-shifted absorption band with a λ_{max} of 488 nm caused by the formation of H-aggregates, whereas in diluted octane (10^{-5} M) a band was produced at 490 nm, suggesting a dispersed monomer state. Conversely, β-fluorinated **4c** afforded octane gel (Figure 4a (i)) at a sol−gel transition temperature at 38 °C, which is 10 °C higher than that of **1c** (27.5 °C), suggesting that the stability was enhanced by β-fluorine moieties. Similar to the case of **1c**,[5d] the octane gel of **4c** exhibited split broad absorption bands at 463, 523, and 555 nm, and a fluorescence maximum at 646 nm due to the stacking receptor π-planes (Figure 4b (i), solid lines). It is noteworthy that these absorption bands of **4c** in the gel state were in contrast to the sharp band at 518 nm in diluted CH_2Cl_2 derived from the dispersed monomeric state; this electronic property was correlated with the fluorescence maximum of the gel, which was red-shifted compared to that at 577 nm in diluted CH_2Cl_2 (Figure 4b (i), broken lines). An assembled structure such as that observed in the gel was also formed in diluted octane (10^{-5} M).

In sharp contrast to the transition to solution of **1c** that was observed in response to the addition of TBACl (1 equiv),[5d] **4c** formed an another gelated material (Figure 4a) that had promising electronic and electrooptical properties such as a broad absorption band around 565 nm reaching ca. 800 nm at the edge (Figure 4b (ii), solid line)). The fluorescence maximum of the gel of the Cl^- complex was observed at 591 nm, which was blue-shifted compared to the fluorescence maximum of anion-free gel from **4c** at 646 nm. The electronic and electrooptical properties of the gel that contained Cl^- as a TBA salt, which was

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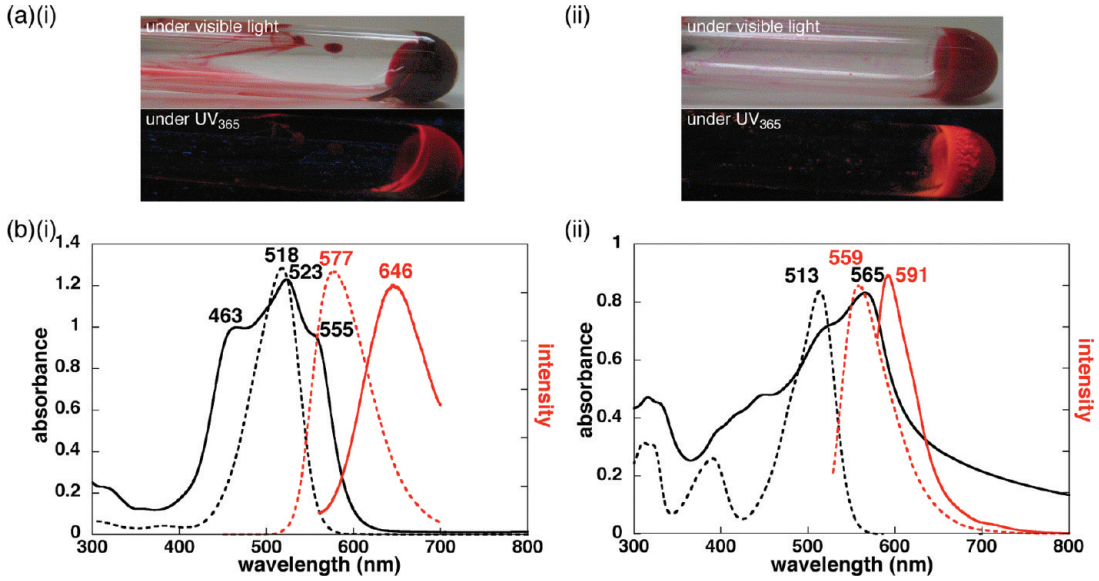

Figure 4. (a) Photographs of supramolecular octane gels of **4c** and (b) UV/vis absorption (black) and fluorescence emission (red) spectra of octane gels (solid lines) and CH_2Cl_2 solution (1×10^{-5} M, broken lines) of **4c** in the (i) absence and (ii) presence of TBACl (1 and 120 equiv for gel and solution, respectively).

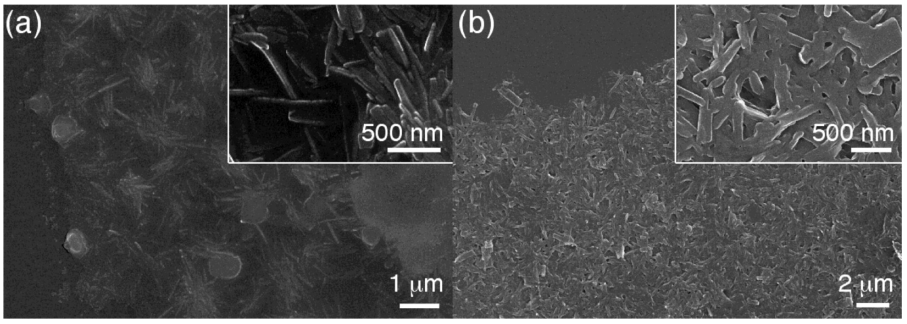

Figure 5. SEM images of xerogels from octane of (a) **4c** and (b) **4c** with TBACl (1 equiv).

completely different from the dispersed states in octane solutions from **1c**, **2c**, and **3c** with TBACl, suggested that the interactions occurred between receptor−anion complexes **4c**·Cl^- in the gel state. The properties of the gel state of **4c** containing TBACl were also distinct from those of **4c**·Cl^- in diluted CH_2Cl_2, which exhibited sharp absorption and fluorescence bands with the maxima at 513 and 559 nm, respectively, owing to the dispersed state of **4c**·Cl^- (Figure 4b (ii), broken lines).

Further information regarding the organized structures of xerogels from **4c** and the Cl^- complex as a TBA salt, which were prepared by freeze-drying procedures, was obtained by scanning electron microscopy (SEM) (Figure 5). The samples were fabricated on a silicon substrate. In the case of anion-free **4c** (Figure 5a), submicrometer-scale flakelike objects with flake thickness of several tens of nanometers were assembled to form more highly organized structures. These findings contrasted the fairly unidentified objects observed in the octane gel of **1c**. Conversely, xerogel of **4c** as a mixture with TBACl (Figure 5b) revealed the assembly of rodlike objects with a length of ca. 1 μm. Preliminary investigation of synchrotron X-ray diffractions of xerogels of **1c** and **4c** suggested that there were similar stacking structures with distances of ca. 4.5 Å along with interactions between alkyl chains (ca. 4.2 Å). Although further investigations are required, introduction of an electron-withdrawing moiety such as fluorine can induce the dipoles of the receptors and anion complexes, resulting in the formation of stable stacking organized structures. In addition, less bulky fluorine moieties do not interfere with the stacking structures of both the anion-free receptor and the Cl^- complex. In contrast to ordinary hydrogen-bonding-based supramolecular gels that show anion-responsive behaviors,[3] the gelation behavior observed in **4c** suggests that, since hydrogen bonding is not a main driving force to construct supramolecular gel in the anion-free form, anion binding of the receptors as gelating molecules can modulate the state of soft materials but does not always interfere the formation of gelated state.

SUMMARY

Modification of pyrrole β-positions was found to be essential for the modulation of the supramolecular assemblies as well as the electronic and electrooptical properties. While β-alkyl substituents interfered with the formation of stable gel states, the introduction of fluorine moieties induced a stable supramolecular gel when compared to that of β-substituted receptor. Moreover, β-fluorine groups enabled the receptor to form uncommon gelated materials, even in the presence of Cl^- as a TBA salt. Modification both at the

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pyrrole periphery on the basis of a sufficient *pyrrole library* and at a boron moiety[8] would provide various useful materials. Further investigation of the formation of charge-by-charge assemblies comprising alternately stacking positively and negatively charged species[5h,9] are currently underway.

EXPERIMENTAL SECTION

General Procedures. Commercially available starting materials were used without further purification unless otherwise stated. Assignments of ^{1}H NMR for **2b**, **2c**, and **3c** were performed on the basis of 2D NMR (COSY, NOESY, and ROESY).

BF_2 Complex of 1,3-Bis(3,4-dimethyl-5-iodopyrrol-2-yl)-1,3-propanedione, 2a-I_2. To an acetone (100 mL) solution of **2a**[5g] (205.0 mg, 0.67 mmol) at room temperature was added *N*-iodosuccinimide (360.8 mg, 1.47 mmol). The mixture was stirred at room temperature for 3 h. After consumption of the starting material was confirmed by TLC analysis, the mixture was washed with water and extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and evaporated to dryness. The residue was then chromatographed over a silica gel flash column (eluent: 3% MeOH/CH_2Cl_2) and recrystallized from CH_2Cl_2/hexane to afford **2a-I_2** (344.3 mg, 92%). R_f = 0.49 (CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.40 (s, 2H), 6.28 (s, 1H), 2.36 (s, 6H), 2.06 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 167.6, 129.8, 127.7, 127.5, 90.6, 86.4, 12.6, 11.9. MALDI-TOF-MS: *m*/*z* (% intensity) 556.9 (100), calcd for $C_{15}H_{14}BF_2I_2N_2O_2$ ([M − H]$^-$) 556.92. HRMS (ESI-TOF): *m*/*z* (% intensity) 556.9213, calcd for $C_{15}H_{14}BF_2I_2N_2O_2$ ([M − H]$^-$) 556.9214.

BF_2 Complex of 1,3-Bis(3,4-dimethyl-5-phenylpyrrol-2-yl)-1,3-propanedione, 2b. A Schlenk tube placed with **2a-I_2** (80.0 mg, 0.143 mmol), phenylboronic acid (52.45 mg, 0.430 mmol), tetrakis(triphenylphosphine)palladium(0) (34.67 mg, 0.03 mmol), and Cs_2CO_3 (140 mg, 0.43 mmol) was flushed with nitrogen and charged with a mixture of degassed DMF (3 mL) and water (0.3 mL). The mixture was heated at 95 °C for 17 h, cooled, and then partitioned between water and CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated. The residue was then chromatographed over a silica gel flash column (eluent: 0.5% MeOH/CH_2Cl_2) to give **2b** (32.6 mg, 50%) as a pink solid. R_f = 0.52 (0.5% MeOH/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.32 (s, 2H, NH), 7.53 (d, *J* = 7.2 Hz, 4H, Ar-*o*-CH), 7.49 (t, *J* = 7.2 Hz, 4H, Ar-*m*-CH), 7.41 (t, *J* = 7.2 Hz, 4H, Ar-*p*-CH), 6.50 (s, 1H, CH), 2.42 (s, 6H, inner-CH_3), 2.22 (s, 6H, outer-CH_3). ^{13}C NMR (151 MHz, DMSO-d_6, 20 °C): δ (ppm) 166.8, 137.8, 131.5, 130.8, 129.2, 128.7, 127.7, 123.7, 121.0, 92.3, 12.5, 10.4. UV/vis (CH_2Cl_2, λ_{max} (nm) (ε, 10^5 M^{-1} cm^{-1})): 499.0 (1.0). Fluorescence (CH_2Cl_2, λ_{em} (nm) (λ_{ex} (nm))): 533.6 (499). MALDI-TOF-MS: *m*/*z* (% intensity) 457.2 (100), calcd for $C_{27}H_{24}BF_2N_2O_2$ ([M − H]$^-$) 457.19. HRMS (ESI-TOF): *m*/*z* (% intensity) 457.1909, calcd for $C_{27}H_{24}BF_2N_2O_2$ ([M − H]$^-$) 457.1909.

3,4,5-Trihexadecyloxyphenylboronic Acid Pinacol Ester. A Schlenk tube placed with 5-bromo-1,2,3-trihexadecyloxybenzene (878.3 mg, 1 mmol), dichlorobis(triphenylphosphine)palladium (23.16 mg, 0.033 mmol), bis(pinacolato)diboron (380.4 mg, 1.5 mmol), and potassium acetate (294.2 mg, 3 mmol) was flushed with nitrogen and charged with a mixture of degassed dioxane (13 mL). The mixture was heated at 80 °C for 12 h, cooled, and then partitioned between water and CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated. The residue was then chromatographed over a flash silica gel column (eluent: 3% EtOAc/hexane) to give the desired product (613.3 mg, 66%) as a white solid. R_f = 0.25 (3% EtOAc/hexane). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 6.99 (s, 2H), 4.00 (t, *J* = 6.6 Hz, 4H), 3.97 (t, *J* = 6.6 Hz, 2H), 1.81−1.77 (tt, *J* = 7.2 and 6.6 Hz, 4H), 1.75−1.70 (tt, *J* = 7.2 and 6.6 Hz, 2H), 1.48−1.43 (m, 6H), 1.33 (s, 12H), 1.30−1.25 (m, 72H), 0.88 (t, *J* = 6.6 Hz, 9H). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 152.9, 141.1, 112.7, 73.3, 69.0, 31.9, 30.4, 29.7−29.4, 26.1, 24.8, 22.7, 14.1 (some of the signals for hexadecyl chains were overlapped). MALDI-TOF-MS: *m*/*z* (% intensity) 924.8 (100), calcd for $C_{60}H_{113}BO_5$ ([M]$^+$) 924.87. HRMS (ESI-TOF): *m*/*z* (% intensity) 925.8765, calcd for $C_{60}H_{114}BO_5$ ([M + H]$^+$) 925.8764.

BF_2 Complex of 1,3-Bis(3,4-dimethyl-5-(3,4,5-trihexadecyloxyphenyl)pyrrol-2-yl)-1,3-propanedione, 2c. A Schlenk tube placed with **2a-I_2** (64.7 mg, 0.116 mmol), 3,4,5-trihexadecyloxyphenylboronic acid pinacol ester (266.7 mg, 0.267 mmol), tetrakis(triphenylphosphine)palladium(0) (28.0 mg, 0.024 mmol), and Cs_2CO_3 (113.4 mg, 0.348 mmol) was flushed with nitrogen and charged with a mixture of degassed DMF (3 mL), toluene (1.5 mL), and water (0.1 mL). The mixture was heated at 95 °C for 21 h, cooled, and then partitioned between water and CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated. The residue was then chromatographed over a silica gel flash column (eluent: hexane/CH_2Cl_2 = 2: 1 and CH_2Cl_2) to give **2c** (99.6 mg, 45%) as a reddish brown solid. R_f = 0.44 (CH_2Cl_2/hexane =2: 1). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.27 (s, 2H, NH), 6.66 (s, 1H, CH), 6.47 (s, 4H, Ar-H), 4.02 (m, 12H, OCH_2), 2.04 (s, 6H, inner-CH_3), 2.21 (s, 6H, outer-CH_3), 1.84 (tt, *J* = 7.8 and 7.2 Hz, 8H, OCH_2CH_2), 1.77 (tt, *J* = 7.8 and 7.2 Hz, 4H, OCH_2CH_2), 1.50 (m, 12H, $OC_2H_4CH_2$), 1.36−1.25 (m, 144H, $OC_3H_6C_{12}H_{24}$), 0.89−0.83 (m, 18H, $OC_{15}H_{30}CH_3$). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 166.20, 153.5, 138.8, 138.0, 130.6, 126.2, 123.2, 120.5, 106.2, 92.1, 73.6, 69.4, 31.9, 30.4, 29.76, 29.74, 29.72, 29.68, 29.65, 29.62, 29.44, 29.41, 29.37, 26.1, 22.7, 14.1, 12.4, 10.3 (some of the signals for hexadecyl chains were overlapped). UV/vis (CH_2Cl_2, λ_{max} (nm) (ε, 10^5 M^{-1} cm^{-1})) 512.5 (1.2). Fluorescence (CH_2Cl_2, λ_{em} (nm) (λ_{ex} (nm))): 560.2 (512.0). MALDI-TOF-MS (% intensity): *m*/*z* 1899.6 (84), 1900.6 (100), calcd for $C_{123}H_{217}N_2O_8BF_2$ ([M]$^-$) 1899.67. HRMS (ESI-TOF): *m*/*z* (% intensity) 1898.6628, calcd for $C_{123}H_{216}N_2O_8BF_2$ ([M − H]$^-$) 1898.6628.

BF_2 Complex of 1,3-Bis(3,4-diethyl-5-(3,4,5-trihexadecyloxyphenyl)pyrrol-2-yl)-1,3-propanedione, 3c. A Schlenk tube placed with **3a-I_2**[5f] (92.1 mg, 0.150 mmol), 3,4,5-trihexadecyloxyphenylboronic acid pinacol ester (319.3 mg, 0.345 mmol), tetrakis(triphenylphosphine)palladium(0) (32.36 mg, 0.028 mmol), and Cs_2CO_3 (146.6 mg, 0.45 mmol) was flushed with nitrogen and charged with a mixture of degassed DMF (2 mL), toluene (1 mL), and water (0.1 mL). The mixture was heated at 95 °C for 23 h, cooled, and then partitioned between water and CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated. The residue was then chromatographed over a silica gel flash column (eluent: 5% EtOAc/hexane and 10% hexane/$CHCl_3$) to give **3c** (170.0 mg, 57%) as a reddish-brown solid. R_f = 0.62 (20% hexane/$CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.25 (s, 2H, NH), 6.66 (s, 1H, CH), 6.53 (s, 4H, Ar-H), 4.02 (m, 12H, OCH_2), 2.84 (q, *J* = 7.8 Hz, 4H, inner-CH_2CH_3), 2.61 (q, *J* = 7.8 Hz, 4H, outer-CH_2CH_3), 1.84 (tt, *J* = 7.8 and 7.2 Hz, 8H, OCH_2CH_2), 1.77 (tt, *J* = 7.8 and 7.2 Hz, 4H, OCH_2CH_2), 1.50 (m, 12H, $OC_2H_4CH_2$), 1.35 (t, *J* = 7.8 Hz, 6H, inner-CH_2CH_3), 1.36−1.25 (m, 144H, $OC_3H_4C_{12}H_{24}$), 1.19 (t, *J* = 7.8 Hz, 6H, outer-CH_2CH_3), 0.89−0.83 (m, 18H, $OC_{15}H_{30}CH_3$). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 166.3, 153.5, 138.8, 138.0, 136.8, 126.5, 126.2, 122.5, 106.1, 90.7, 73.6, 69.3, 31.9, 30.4, 29.76, 29.74, 29.72, 29.68, 29.66, 29.62, 29.44, 29.40, 29.37, 26.1, 22.7, 19.2, 17.5, 16.2, 15.4, 14.1 (some of the signals for hexadecyl chains were overlapped). UV/vis (CH_2Cl_2, λ_{max} (nm) (ε, 10^5 M^{-1} cm^{-1})): 512.0 (1.1). Fluorescence (CH_2Cl_2, λ_{em} (nm) (λ_{ex} (nm))): 562.8 (512.0). MALDI-TOF-MS (% intensity): *m*/*z* 1955.8 (76), 1956.7 (100), calcd for $C_{127}H_{225}N_2O_8BF_2$ ([M]$^-$) 1955.73. HRMS (ESI-TOF): *m*/*z* (% intensity) 1954.7255, calcd for $C_{127}H_{224}N_2O_8BF_2$ ([M − H]$^-$) 1954.7254.

BF_2 Complex of 1,3-Bis(3,4-difluoro-5-iodopyrrol-2-yl)-1,3-propanedione, 4a-I_2. To a dioxane solution (10 mL) of **4a**[5b] (46.5 mg, 0.144 mmol) was added *N*-iodosuccinimide (299 mg, 1.33 mmol) under dark, N_2 gas, with stirring for 3 h at reflux temperature. After removal of the solvent, the residue was chromatographed over a silica gel column (eluent: 12% EtOAc/CH_2Cl_2), and recrystallization

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Table 2. Crystallographic Details for Anion Receptors and Anion Complexes

	2b	4b	2b·TPACl	4b·TBACl	$4b^{-}\cdot TBA^{+}$
formula	$C_{27}H_{25}BF_2N_2O_2$	$C_{23}H_{13}BF_2N_2O_2\cdot 2C_4H_8O$	$C_{27}H_{25}BF_2N_2O_2\cdot C_{12}H_{28}NCl\cdot$ 0.5dichloroethane·[a] 0.26water[a]	$C_{23}H_{13}BF_6N_2O_2\cdot C_{16}H_{36}NCl$	$C_{23}H_{12}BF_6N_2O_2\cdot C_{16}H_{36}N\cdot C_6H_{14}O$
FW	458.30	618.37	731.75	752.07	817.79
crystal size, mm	0.30 × 0.10 × 0.10	0.50 × 0.20 × 0.20	0.50 × 0.30 × 0.20	0.70 × 0.40 × 0.35	0.40 × 0.20 × 0.15
crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a, Å	8.236(3)	24.8973(6)	16.897(3)	12.052(4)	8.626(2)
b, Å	16.744(6)	11.4380(2)	23.457(2)	12.904(6)	9.917(4)
c, Å	17.667(7)	9.8194(2)	21.571(2)	13.351(4)	28.029(8)
α, deg	109.518(12)	90	90	79.952(16)	96.182(13)
β, deg	101.221(13)	92.5677(14)	113.294(5)	86.514(15)	91.135(12)
γ, deg	95.073(12)	90	90	66.794(15)	112.602(13)
V, Å^3	2221.4(13)	2793.51(10)	7852.6(16)	1878.9(12)	2195.6(12)
ρ_{calcd}, g cm^{-3}	1.388	1.470	1.238	1.329	1.237
Z	2	4	8	2	2
T, K	123(2)	93(2)	123(2)	123(2)	123(2)
μ, mm^{-1}	0.098 (Mo Kα)	1.059 (Cu Kα)	0.213 (Mo Kα)	0.17 (Mo Kα)	0.094 (Mo Kα)
no. of reflns	21375	14125	117426	18566	19315
no. of unique reflns	9822	2555	34687	8532	9056
variables	621	200	1843	473	615
λ_{α}, Å	0.71075 (Mo Kα)	1.54187 (Cu Kα)	0.71075 (Mo Kα)	0.71075 (Mo Kα)	0.71075 (Mo Kα)
R_1 ($I > 2\sigma(I)$)	0.0624	0.0389	0.0597	0.0363	0.0479
wR_2 ($I > 2\sigma(I)$)	0.1527	0.0963	0.1451	0.1067	0.1508
GOF	0.980	1.096	1.041	1.073	1.038

[a] Some of the cocrystallized solvents cannot locate their hydrogen atom appropriately, resulting in the description of them as the compound name.

from CH_2Cl_2/hexane afforded bisiodinated derivative **4a-I$_2$** (46.1 mg, 57%) as a brown solid. R_f = 0.60 (10% EtOAc/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 9.03 (s, 2H), 6.54 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6, 20 °C): δ (ppm) 166.8, 141.8 140.1, 113.0, 90.7, 71.0. ^{19}F NMR (564 MHz, $CDCl_3$, 20 °C): δ (ppm) −142.13 (s, 2F), −155.42 (s, 2F), −163.89 (s, 2F). MALDI-TOF-MS (% intensity): m/z 572.8 (100), calcd for $C_{11}H_2I_2N_2O_2BF_6$ ($[M - H]^-$) 572.82. HRMS (ESI-TOF): m/z (% intensity): 572.8211, calcd for $C_{11}H_2I_2N_2O_2BF_6$ ($[M - H]^-$) 572.8210.

BF$_2$ Complex of 1,3-Bis(3,4-difluoro-5-phenylpyrrol-2-yl)-1,3-propanedione, 4b. A two necked flask containing **4a-I$_2$** (28.1 mg, 0.049 mmol), phenylboronic acid (15.0 mg, 0.12 mmol), tetrakis(triphenylphosphine)palladium(0) (4.6 mg, 3.98 μmol), and Na_2CO_3 (42.6 mg, 0.40 mmol) was flushed with nitrogen and charged with a mixture of degassed 1,2-dimethoxyethane (0.9 mL) and water (0.09 mL). The mixture was refluxed for 14 h, cooled, and then partitioned between water and CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated. The residue was chromatographed over a silica gel column (eluent: 10% EtOAc/CH_2Cl_2) to give **4b** (4.6 mg, 20%) as a red solid. R_f = 0.46 (3% MeOH/CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 8.85 (s, 2H, NH), 7.69 (d, J = 7.8 Hz, 4H, Ar-H), 7.53 (t, J = 7.8 Hz, 4H), 7.46 (t, J = 7.2 Hz, 2H), 6.73 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6, 20 °C): δ (ppm) 167.1, 141.6, 136.2, 129.7, 129.1, 127.4, 127.1, 125.0, 108.5, 92.4. UV/vis (CH_2Cl_2, λ_{max} (nm) (ε, 10^5 M^{-1}cm^{-1})): 492.0 (1.2). Fluorescence (CH_2Cl_2, λ_{em} (nm) (λ_{ex} (nm))): 520.6 (492.0). MALDI-TOF-MS (% intensity): m/z 474.1 (100), calcd for $C_{23}H_{13}N_2O_2BF_6$ ($[M]^-$) 474.10. HRMS (ESI-TOF): m/z (% intensity) 473.0908, calcd for $C_{23}H_{13}N_2O_2BF_6$ ($[M - H]^-$) 473.0906.

BF$_2$ Complex of 1,3-Bis(3,4-difluoro-5-(3,4,5-trihexadecyloxyphenyl)pyrrol-2-yl)-1,3-propanedione, 4c. A two-necked flask containing **4a-I$_2$** (120.2 mg, 0.21 mmol), 3,4,5-trihexadecyloxyphenylboronic acid pinacol ester (537.2 mg, 0.58 mmol), tetrakis(triphenylphosphine)palladium(0) (58.2 mg, 0.050 mmol), and Na_2CO_3 (190.5 mg, 1.80 mmol) was flushed with nitrogen and charged with a mixture of degassed 1,2-dimethoxyethane (3.6 mL) and water (0.36 mL). The mixture was refluxed for 14 h, cooled, then partitioned between water and CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated. The residue was then chromatographed over a silica gel flash column (eluent: 5% EtOAc/hexane) to give **4c** (78.4 mg, 20%) as a red solid. R_f = 0.56 ($CHCl_3$/hexane =3: 1). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 8.72 (s, 2H), 6.82 (s, 1H), 6.69 (s, 4H), 4.04 (t, J = 6.6 Hz, 12H), 4.01 (t, J = 6.6 Hz, 4H), 1.85 (tt, J = 7.2 and 6.6 Hz, 8H), 1.75 (tt, J = 7.2 and 6.6 Hz, 4H), 1.53−1.46 (m, 12H), 1.39−1.26 (m, 144H), 0.89−0.86 (m, 18H). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 165.5, 153.7, 143.3, 139.7, 136.0, 124.4, 121.8, 107.9, 103.9, 92.8, 73.4, 69.3, 31.7, 30.1, 29.52, 29.46, 29.44, 29.39, 29.22, 29.16, 25.9, 22.5, 13.9 (some of the signals for hexadecyl chains were overlapped). UV/vis (CH_2Cl_2, λ_{max} (nm) (ε, 10^5 M^{-1} cm^{-1})): 518.0 (1.2). Fluorescence (CH_2Cl_2, λ_{em} (nm) (λ_{ex} (nm))): 577.4 (518). MALDI-TOF-MS (% intensity): m/z 1915.5 (80), 1916.6 (100), calcd for $C_{119}H_{205}N_2O_8BF_6$ ($[M]^-$) 1915.57. HRMS (ESI-TOF): m/z (% intensity) 1914.5625, calcd for $C_{119}H_{204}N_2O_8BF_6$ ($[M - H]^-$) 1914.5625.

Method for X-ray analysis. Crystallographic data are summarized in Table 2. The data were collected at 123 K on a Rigaku RAXIS-RAPID diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71075 Å) for **2b**, **2b**·TPACl, **4b**·TBACl, and $\mathbf{4b}^{-}\cdot TBA^{+}$ and at 93 K on a Rigaku RAXIS-RAPID diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.54187 Å) for **4b**, and the structures were solved by direct methods. A single crystal of **2b** was obtained by vapor diffusion of hexane into a CH_2ClCH_2Cl solution. The data crystal was a red prism of approximate dimensions 0.30 mm × 0.10 mm × 0.10 mm. A single crystal of **4b** was obtained by vapor diffusion of heptane into a THF/toluene solution. The data crystal was a red prism of approximate dimensions 0.50 mm × 0.20 mm × 0.20 mm. A single crystal of **2b**·TPACl was obtained by vapor diffusion of hexane into a CH_2ClCH_2Cl solution of **2b** with 1 equiv of TPA chloride. The data crystal was an orange prism of approximate dimensions 0.50 mm × 0.30 mm × 0.20 mm. A single crystal of **4b**·TBACl was obtained by vapor diffusion of octane into i-Pr_2O and CD_2Cl_2 solutions of **4b** and 1 equiv of TBA chloride. The data crystal was an orange prism of approximate dimensions 0.70 mm × 0.40 mm × 0.35 mm. A single crystal of

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4b$^-$·TBA$^+$ was obtained by vapor diffusion of *i*-Pr_2O into a CH_2Cl_2 solution of **4b** and 1 equiv of TBA acetate. The data crystal was an orange prism of approximate dimensions 0.40 mm × 0.20 mm × 0.15 mm. In each case, the non-hydrogen atoms were refined anisotropically. The calculations were performed using the Crystal Structure crystallographic software package of Molecular Structure Corp.[10] The CIF files (CCDC-781979, 827559, and 781980−781982) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Determination of Anion-Binding Constants. Anion-binding constants (K_a) were estimated by fitting the 1:1 binding curves for the changes of absorbance in UV/vis absorption spectra upon the addition of CH_2Cl_2 solutions of anions as TBA salts to CH_2Cl_2 solutions of the host molecules (1×10^{-5} M).

Supramolecular Gel Formation. Examination of formation of supramolecular gels was conducted by addition of solvent (octane) to examined molecules in the absence or presence of Cl^- as a TBA salt, heating to solution, and cooling for a while. Formation of gelated states was checked by whether the gel could remain stable when the tube was turned upside down.

Computational Methods. Ab initio calculations were carried out by using the Gaussian 03 program.[7] The structures were optimized, and the total electronic energies were calculated at the B3LYP level using a 6-31G** basis set. Molecular orbitals were determined by single-point calculations at the B3LYP level using a 6-31+G** basis set of the optimized structures at the B3LYP level using a 6-31G** basis set.

Scanning Electron Microscopy (SEM). SEM images were obtained with a HITACHI S-4800 scanning electron microscope at acceleration voltages of 10 kV. Silicon (100) was used as substrate, and a platinum coating was applied using a HITACHI E-1030 ion sputter.

■ ASSOCIATED CONTENT

Supporting Information. Optimized structures, anion-binding behavior, and X-ray structural analysis of **2b**, **4b**, **2b**·TPACl, **4b**·TBACl, and **4b**$^-$·TBA$^+$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Selected books for supramolecular gels: (a) *Low Molecular Mass Gelators, Topics in Current Chemistry*; Fages, F., Ed.; Springer-Verlag: Berlin, 2005; Vol. 256, p 283. (b) Ishi-i, T.; Shinkai, S. In *Supramolecular Dye Chemistry, Topics in Current Chemistry*; Würthner, F., Ed.; Springer-Verlag: Berlin, 2005; Vol. 258, pp 119−160. (c) *Molecular Gels*; Weiss, R. G., Terech, P., Eds.; Springer: Dordrecht, 2006.

(2) Selected books for anion binding: (a) *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., Gracía-España, E., Eds.; Wiley-VCH: New York, 1997. (b) *Fundamentals and Applications of Anion Separations*; Singh, R. P., Moyer, B. A., Eds.; Kluwer Academic/Plenum Publishers: New York, 2004. (c) *Anion Sensing*; Stibor, I., Ed.; Topics in Current Chemistry; Springer-Verlag: Berlin, 2005; Vol. 255, p 238. (d) Sessler, J. L.; Gale, P. A.; Cho, W.-S. *Anion Receptor Chemistry*; RSC: Cambridge, 2006. (e) *Recognition of Anions*; Vilar, R., Ed.; Structure and Bonding; Springer-Verlag: Berlin, 2008; Vol. 129, p 252.

(3) Reviews for anion-responsive supramolecular gels: (a) Maeda, H. *Chem.—Eur. J.* **2008**, *14*, 11274–11282. (b) Lloyd, G. O.; Steed, J. W. *Nature Chem.* **2009**, *1*, 437–442. (c) Piepenbrock, M.-O. M.; Lloyd, G. O.; Clarke, N.; Steed, J. W. *Chem. Rev.* **2010**, *110*, 1960–2004. (d) Steed, J. W. *Chem. Soc. Rev.* **2010**, *39*, 3689–3699. (e) Maeda, H. In *Supramolecular Soft Matter: Applications in Materials and Organic Electronics*; Nakanishi, T., Ed.; Wiley: New York, 2011; Chapter 6, in press.

(4) (a) Maeda, H. In *Handbook of Porphyrin Science*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; World Scientific: Hackensack, NJ, 2010; Vol. 8, Chapter 38. (b) Maeda, H. In *Anion Complexation by Heterocycle Based Receptors, Topics in Heterocyclic Chemistry*; Gale, P. A., Dehaen, W., Eds.; Springer-Verlag: Berlin, 2010; Vol. 24, pp 103−144.

(5) (a) Maeda, H.; Kusunose, Y. *Chem.—Eur. J.* **2005**, *11*, 5661–5666. (b) Maeda, H.; Ito, Y. *Inorg. Chem.* **2006**, *45*, 8205–8210. (c) Maeda, H.; Kusunose, Y.; Mihashi, Y.; Mizoguchi, T. *J. Org. Chem.* **2007**, *72*, 2612–2616. (d) Maeda, H.; Haketa, Y.; Nakanishi, T. *J. Am. Chem. Soc.* **2007**, *129*, 13661–13674. (e) Maeda, H.; Terasaki, M.; Haketa, Y.; Mihashi, Y.; Kusunose, Y. *Org. Biomol. Chem.* **2008**, *6*, 433–436. (f) Maeda, H.; Haketa, Y. *Org. Biomol. Chem.* **2008**, *6*, 3091–3095. (g) Maeda, H.; Haketa, Y.; Bando, Y.; Sakamoto, S. *Synth. Met.* **2009**, *159*, 792–796. (h) Haketa, Y.; Sasaki, S.; Ohta, N.; Masunaga, H.; Ogawa, H.; Araoka, F.; Takezoe, H.; Maeda, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 10079–10083.

(6) Some examples of β-fluorinated oligopyrrole systems: (a) Anzenbacher, P., Jr.; Try, A. C.; Miyaji, H.; Jurseíková, K.; Lynch, V. M.; Marquez, M; Sessler, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 10268–10272. (b) Sessler, J. L.; Cho, W.-S.; Gross, D. E.; Shriver, J. A.; Lynch, V. M.; Marquez, M. *J. Org. Chem.* **2005**, *70*, 5982–5986. (c) Shimizu, S.; Shin, J.-Y.; Furuta, H.; Ismael, R.; Osuka, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 78–82.

(7) All calculations were carried out using the Gaussian 03 program. *Gaussian 03*, Revision C.01: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford, CT, 2004.

(8) (a) Maeda, H.; Fujii, Y.; Mihashi, Y. *Chem. Commun.* **2008**, 4285–4287. (b) Maeda, H.; Takayama, M.; Kobayashi, K.; Shinmori, H. *Org. Biomol. Chem.* **2010**, *8*, 4308–4315. (c) Maeda, H.; Bando, Y.; Shimomura, K.; Yamada, I.; Naito, M.; Nobusawa, K.; Tsumatori, H.; Kawai, T. *J. Am. Chem. Soc.* **2011**, *133*, 9266–9269.

(9) Modified benzoate anions afford supramolecular structures containing charge-by-charge assemblies by combination with the anion

receptors **1a**,**b**: Maeda, H.; Naritani, K.; Honsho, Y.; Seki, S. *J. Am. Chem. Soc.* **2011**, *133*, 8896–8899.

(10) CrystalStructure (Ver. 3.8), Single Crystal Structure Analysis Software, Rigaku/MSC and Rigaku Corp., 2006.