Ion-Pair-Based Assemblies Comprising Pyrrole–Pyrazole Hybrids

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a) i)

Abstract: Modified 3,5-dipyrrolylpyrazole (DPP) derivatives in their protonated form produce planar [2+2]-type complexes with trifluoroacetate (TFA) ions. These complexes serve as constituent components of ion-pair-based assemblies. An essential strategy for the construction of dimension-controlled organized structures based on these [2+2]-type complexes is the introduction of aryl rings bearing long alkyl chains, which enables the formation of 2D patterns at interfaces, supramolecular gels, and mesophases.

Keywords: assembled structures . ion pairs · pi-conjugated molecules · pyrrole derivatives · soft materials · supramolecular chemistry

1a ($R^1 = R^2 = H$)

Introduction

Assemblies of π -conjugated molecules have attracted much attention for the fabrication of functional materials.^[1] Among various protocols for assembling molecules, arrangement of appropriately designed charged *n*-conjugated species and counterions would enable the formation of dimension-controlled organized structures, such as crystals or soft materials.^[2-4] Ion pairs as components of supramolecular assemblies provide various modes of structural organization according to the combination of cations and anions. Exchanging the components in the assemblies may then afford a variety of ion-based electronic and optical materials. Among ion-pair-based discrete assemblies, planar complexes of cations and anions can also be considered as effective subunits for the construction of highly organized structures through stacking interactions. Planar geometries are also suitable for the fabrication of 2D patterns on appropriate surfaces. 3,5-Dipyrrolylpyrazoles (DPPs; e.g., 1a and 2a, Figure 1 a)^[5] are potential precursor candidates for positively charged π -conjugated units as they form planar [2+2]-type

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Figure 1. a) i) 3,5-Dipyrrolylpyrazoles (DPPs) and ii) their [2+2]-type complexes with CF₃CO₂⁻ in their protonated form and b) solid-state packing structures of i) 1a·H⁺ and ii) 2a·H⁺ as CF₃CO₂⁻ salts.

complexes in their protonated forms (1a·H⁺ and 2a·H⁺) by combination with trifluoroacetate (TFA; CF₃CO₂⁻).^[6] Although DPPs are small and structurally very simple, their [2+2]-type complexes may be envisaged as serving as constituent subunits of a variety of ordered assembled structures. In our previous report,^[6] [2+2]-type complexes of

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1a•H⁺ and **2a**•H⁺ with $CF_3CO_2^-$ were shown to form herringbone-like stacking assemblies in the solid state (Figure 1 b). Therefore, appropriate arrangement of [2+2]-type complexes of modified DPPs may lead to ordered structures, such as stacked columnar assemblies, to give functional soft materials. Herein, we report the synthesis, assembly behavior, and charge-carrier transport properties of DPP derivatives possessing aryl rings at the pyrrole α -positions.

Results and Discussion

 α -Aryl-substituted DPPs **1b-f** (Figure 1 ai) were obtained in 38-78% yields from the corresponding 1,3-dipyrrolyl-1,3propanedione^[7] by treatment with excess hydrazine in AcOH at reflux. In addition, to examine the effect of pyrrole β -substituents, as seen in **2a**, β -fluorinated α -aryl-substituted **2b-f** (Figure 1 ai) were prepared from the dipyrrolyldiketone derivatives through the corresponding BF2 complexes.^[8] Addition of TFA to solutions of the α -aryl-substituted DPPs (0.01 mm in CH₂Cl₂) at RT resulted in UV/Vis spectral changes,^[9] suggesting the formation of protonated species. As observed in the α -unsubstituted derivatives, protonated DPPs form complexes with $CF_3CO_2^-$ in the bulk state. Furthermore, the single-crystal X-ray structure of methoxy-substituted 1c in the presence of TFA (1 equiv) revealed the formation of unexpected tetrameric box-like complexes held together by hydrogen bonding between the pyrrole/pyrazole NH and CF₃CO₂⁻ as well as between the pyrrole/pyrazole NH and methoxy O atoms (Figure 2). The solid-state structure of $[1c \cdot H^+]_4 [CF_3CO_2^-]_4$, as a unique ex-



Figure 2. Single-crystal X-ray structure of $[1c\cdot H^+][CF_3CO_2^-]$ as a) a top view and b) a side view of the tetrametric box-like complex.

ample of ion-pair-based assemblies, is far from a planar [2+2]-type structure, presumably because of the methoxy substituents, which act as hydrogen-bonding accepting units, on the α -aryl moieties. The box-like complexes, possessing inner cavities of 96 Å³, form tube-like assemblies. The single-crystal X-ray structure indicated the formation of the complex of 1c·H⁺ and CF₃CO₂⁻ in a 1:1 ratio from a mixture of 1c and TFA. On the other hand, longer alkoxy chains would interfere with the formation of such a box-like structure. In addition, aliphatic chains on the α -aryl moieties would interact with one another, resulting in the formation of columnar structures based on the [2+2]-type ion-pair complexes, as discussed below.^[10]

Planar [2+2]-type complexes of α -aryl-substituted DPPs under the appropriate conditions were observed by scanning tunneling microscopy (STM) measurements^[11] at the interface of a 1,2,4-trichlorobenzene (TCB) solution and a highly oriented pyrolytic graphite (HOPG) substrate. Bright parts and lamellar patterns in dark trough areas are ascribable to π -conjugated core units and alkoxy side chains, respectively. TFA-free hexadecyloxy-substituted **1f** showed an STM image of offset dimers in a parallelogram pattern (Figure 3 ai) with lattice parameters of 4.3 ± 0.1 nm (*a*) and $3.3 \pm$



Figure 3. a) STM images (TCB, HOPG) and b) proposed model structures of i) $\mathbf{1} \mathbf{f}$ and ii) $[\mathbf{1} \mathbf{f} \cdot \mathbf{H}^+][CF_3CO_2^-]$. Some of the alkyl chains that are missing in b) can be considered to show weak interactions with the surface.

0.1 nm (*b*; Figure 3 bi).^[12] On the other hand, in the presence of TFA (1 equiv), rectangular patterns consisting of dimers arranged in parallel were observed (Figure 3 a ii). The parallel pairs of bright rods were in contrast to the pairs of TFA-free **1f**. The lattice parameters of 3.7 ± 0.3 nm (*a*) and 3.5 ± 0.3 nm (*b*) strongly suggested the formation of a [2+2]-type assembly of [**1f**·H⁺]₂[CF₃CO₂⁻]₂ (Figure 3 bii) at the interface. The observed difference between the 2D patterns of **1f** and **1f**·H⁺ as a CF₃CO₂⁻ complex was induced by protonation and subsequent anion binding.

In addition to the extension of the [2+2]-type planar structures in the direction parallel to the planes, as observed by STM, their stacking behaviors were also examined.^[13] Longer alkyl chains attached to aryl rings can serve as van

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Figure 4. a) Photographs (under $UV_{365 nm}$ light) of i) **1 f** as a precipitate and ii) **2 f** as a supramolecular gel from 1,4-dioxane (20 mg mL⁻¹) exhibiting the changes upon the addition of 1 equivalent of TFA, b) SEM images of xerogels of i) [**1 f**·H⁺][CF₃CO₂⁻] and ii) [**2 f**·H⁺][CF₃CO₂⁻], and c) synchrotron XRD pattern of [**1 f**·H⁺][CF₃CO₂⁻] as a xerogel (from 1,4dioxane) at 25 °C.

der Waals interaction sites, supporting the formation of columnar structures based on the [2+2]-type complexes. The DPPs 1d,e and 2d,e proved to be soluble in 1,4-dioxane both in the absence and presence of TFA, whereas 1f formed a precipitate. On the other hand, TFA-free 2 f, along with $1 \text{ f} \cdot \text{H}^+$ and $2 \text{ f} \cdot \text{H}^+$ as CF_3CO_2^- complexes, afforded 1,4dioxane gels (Figure 4a), suggesting the formation of dimension-controlled organized structures. SEM measurements of the xerogels indicated the formation of structures with the appearance of crumpled paper (Figure 4b).^[14] Furthermore, synchrotron XRD analysis of the xerogels of 2f, $[1f \cdot H^+]$ - $[CF_3CO_2^-]$, and $[2f \cdot H^+][CF_3CO_2^-]$ revealed the formation of lamellar structures with repeat distances of 5.46, 5.46, and 5.63 nm, respectively (Figure 4c). The observed distances in the xerogels are consistent with AM1-estimated lengths in the long-axis directions of 2 f, 1 f·H⁺, and 2 f·H⁺ (ca. 5.7, 5.5, and 5.7 nm, respectively),^[15] suggesting that the building units are aligned almost vertically with respect to the layer structures.

Next, the mesophases of DPPs 1d-f and 2d-f and their protonated species as $CF_3CO_2^-$ complexes were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) measurements. In contrast to 1d-f, which show no mesophases, the DSC data for 2d-f re-

vealed monotropic mesophases at 84-134, 69-110, and 63-109°C, respectively, during the heating processes. On the other hand, $1 f \cdot H^+$ and $2 f \cdot H^+$ as $CF_3 CO_2^-$ complexes, which were purified as precipitates from octane,^[16] exhibited enantiotropic mesophases at 66-85°C (M1) and 85-96°C (M2; $[1 f \cdot H^+][CF_3CO_2^-])$ and at 68–131 °C ($[2 f \cdot H^+][CF_3CO_2^-]$) during cooling processes from isotropic liquids (Iso).^[17] POM measurements of $1 f \cdot H^+$ as a $CF_3CO_2^-$ complex also suggested two types of mesophases, showing a broken-fanlike texture and no texture for M1 and M2, respectively, whereas $[2 f \cdot H^+][CF_3CO_2^-]$ as a mesophase exhibited a sand-like POM texture (Figure 5a). Synchrotron XRD analysis of TFA-free **2d–f** showed Col_h phases ($Z \approx 2$ for $\rho = 1$), with a = 3.04 (110 °C), 3.54 (90 °C), and 4.00 nm (80 °C), respectively, which were formed from disk-like units consisting of two rod-like molecules. Furthermore, upon cooling from Iso, $[1 f \cdot H^+][CF_3CO_2^-]$ as M2 at 90 °C appeared to form a Cub ($Pn\bar{3}m$) phase, which is consistent with the POM result, with a = 10.9 nm (Figure 5 bi). $[1 \text{ f} \cdot \text{H}^+][\text{CF}_3\text{CO}_2^-]$ as M1 at 80°C showed a slightly complicated phase as a mixed state





Figure 5. a) POM images and b) synchrotron XRD patterns with proposed assembling models (insets) of i) $[1 f \cdot H^+][CF_3CO_2^-]$ and ii) $[2 f \cdot H^+]-[CF_3CO_2^-]$ as mesophases at 90 and 120 °C, respectively, during cooling from the Iso.

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of a Col_r phase (a=7.32, b=3.52 nm, $Z\approx 2$ for $\rho=1$) and another phase such as Cub. The M1 mesophase can be considered as a transient state from Cub to a crystal state at lower temperature. These mesophases differed from the lamellar structures seen in the xerogel from 1,4-dioxane and the precipitate from octane. On the other hand, $[2f \cdot H^+]$ - $[CF_3CO_2^-]$ as a mesophase appeared to form a Col_h phase (a=3.91 nm at 120 °C) based on a [2+2]-type complex (Z ≈ 2 for $\rho = 1$; Figure 5 bii). These observations for **1 f** and **2 f** suggest anion-driven control of the assembled structures. In this case, the anion (CF₃CO₂⁻) serves as a bridging unit connecting two cationic π -conjugated species, resulting in the formation of a larger planar area as a building subunit of the columnar structures. Furthermore, the differences between **1 f** and **2 f** can be attributed to the planarity of the π conjugated systems and the differences in the dipole moments in the presence and absence of electron-withdrawing groups.

When assembled with TFA in the bulk state, 1f and 2f change not only their structural order, but also their electronic states. Analogous to the absorption spectral changes in solution upon addition of TFA, $[1 f \cdot H^+][CF_3CO_2^-]$ and $[2 f \cdot H^+][CF_3CO_2^-]$ in the solid state exhibited redshifted absorption bands, indicating smaller band gaps than those of 1f and 2f alone.^[9] Photoelectron yield spectroscopy of $[1 f \cdot H^+][CF_3CO_2^-]$ and $[2 f \cdot H^+][CF_3CO_2^-]$ in the solid state indicated shallow HOMO energy levels of -5.3 and -5.2 eV, respectively.^[9] Based on the advantageous HOMO energy levels and low band gap for positive-charge-conducting pathways, we performed flash-photolysis time-resolved microwave conductivity (FP-TRMC)^[18,19] measurements to investigate the effect of ion-pair-based directional assembly on hole mobility. This method allows us to evaluate the local-scale motion of the photochemically generated chargecarrier species. When photoexcited by a 355 nm laser pulse at RT, powder samples of 1f and 2f on a quartz plate showed transient conductivity, with maximum signal values of $(0.7 \pm 0.2) \times 10^{-5}$ and $(1.1 \pm 0.2) \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively (Figure 6). Upon complexation with TFA, the solidstate structures of $[1 f \cdot H^+][CF_3CO_2^-]$ and $[2 f \cdot H^+][CF_3CO_2^-]$ exhibited higher conductivities of $(1.2\pm0.2)\times10^{-5}$ and $(1.4 \pm 0.2) \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively (Figure 6).^[9] In these cases, it was challenging to examine the electrical conductivities in the mesophases, since they were susceptible to partial loss of TFA upon heating. Considering the increase in TRMC signals as a result of ion-pair assembly for both $1\,f$ and 2 f, we can conclude that directional assembly achieved by modifying side chains and one-step ion-pair complexation is effective for harnessing the semiconducting properties of nonplanar π -conjugated units such as DPP.

Conclusion

Modified 3,5-dipyrrolylpyrazole (DPP) derivatives in their protonated forms have been found to fabricate supramolecular structures such as gels and mesophases by combining



Figure 6. Conductivity transients observed for a) 1 f and $[1 f \cdot H^+]$ -[CF₃CO₂^{-]} and b) 2 f and $[2 f \cdot H^+]$ [CF₃CO₂^{-]} in the solid state at RT.

with TFA anions in [2+2]-type ion-pair complexes. β -Substitution of DPPs can be used to control the assembly of the [2+2]-type complexes into structures such as Cub and Col_h mesophases. Furthermore, improved charge-transfer character has been observed for DPP units upon ion-pair complexation. Protonated DPP is a useful moiety that achieves hydrogen-bonding-based ion-pair formation and provides highly ordered organized structures. Even more highly ordered arrangement of DPP units with a view to obtaining functional materials is currently being investigated.

Experimental Section

General procedures: Starting materials were purchased from Wako Pure Chemical Industries Ltd., Nacalai Tesque Inc., and Sigma-Aldrich Co. and were used without further purification unless otherwise stated. UV/ Vis spectra were recorded on a Hitachi U-3500 spectrometer. Fluorescence spectra of solutions were recorded on a Hitachi F-4500 fluorescence spectrometer. NMR spectra used to characterize the products were recorded on a JEOL ECA-600 600 MHz spectrometer. All NMR spectra were referenced to the solvent used. Matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF-MS) were recorded on a Shimadzu Axima-CFRplus operating in negative-ion mode. TLC analyses were carried out on aluminum sheets coated with silica gel 60 (Merck 5554). Fast atom bombardment mass spectrometric (FAB-MS) studies were carried out on a JEOL-HX110 instrument in positive-ion mode by using a 3-nitrobenzyl alcohol matrix, with the help of Prof. Tomohiro Miyatake, Ryukoku University. Column chromatography was performed on Sumitomo alumina KCG-1525, Wakogel C-200/C-300, or Merck silica gel 60/60 H.

3,5-Di(5-phenylpyrrol-2-yl)pyrazole (1b): Following a literature procedure,^[6] hydrazine monohydrate ($450 \,\mu$ L, 8.73 mmol) was added to a solution of 1,3-di(5-phenylpyrrol-2-yl)-1,3-propanedione^[7] ($43.0 \,\text{mg}$,

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0.12 mmol) in AcOH (9 mL) and the mixture was stirred at reflux for 9 h. When TLC monitoring showed complete consumption of the starting diketone, the solvent was removed and the residue was chromatographed on a column of silica gel (Wakogel C-300; eluent: 5% MeOH/CH2Cl2). Concentration of the appropriate fraction and recrystallization of the residue from CH₂Cl₂/n-hexane gave 1b as a pale-yellow solid (32.9 mg, 0.094 mmol, 78%). $R_{\rm f} = 0.28$ (eluent: 5% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, [D₆]DMSO, 20 °C): $\delta = 12.79$ (brs, 1H; pyrazole-NH), 11.40 (brs, 2H; pyrrole-NH), 7.79-7.72 (m, 4H; Ar-H), 7.41-7.33 (m, 4H; Ar-H), 7.22-7.14 (m, 2H; Ar-H), 6.87 (s, 1H; pyrazole-CH), 6.63 (br s, 1H; pyrrole-H), 6.59 (brs, 1H; pyrrole-H), 6.57 (brs, 1H; pyrrole-H), 6.42 ppm (brs, 1H; pyrrole-H); UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 325.5 nm $(3.8 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1});$ fluorescence $(CH_2Cl_2): \lambda_{ex} = 326 \text{ nm}; \lambda_{em} = 375,$ 446 nm (sh); MALDI-TOF-MS: m/z (%): calcd for C₂₃H₁₈N₄: 350.15 [*M*]⁺; found: 350.1 (100), 351.2 (82).

3,5-Bis[5-(3,4,5-trimethoxyphenyl)pyrrol-2-yl]pyrazole (1c): Hydrazine monohydrate (267 µL, 5.50 mmol) was added to a solution of 1,3-bis-[5-(3,4,5-trimethoxyphenyl)pyrrol-2-yl]-1,3-propanedione^[7] (115.8 mg, 0.22 mmol) in AcOH (4 mL) and the mixture was stirred at reflux for 15 h. When TLC monitoring showed complete consumption of the starting diketone, the solvent was removed and the residue was flash chromatographed on a column of silica gel (eluent: 2% MeOH/CH2Cl2). Concentration of the appropriate fraction and recrystallization of the residue from CH2Cl2/n-hexane gave 1c as a pale-yellow solid (49.1 mg, 0.093 mmol, 42%). $R_{\rm f} = 0.37$ (eluent: 5% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, $[D_6]$ DMSO, 20°C): $\delta = 12.83$ (brs, 1H; pyrazole-NH), 11.37 (brs, 2H; pyrrole-NH), 7.05 (s, 4H; Ar-H), 6.80 (s, 1H; pyrazole-CH), 6.60 (s, 3H; pyrrole-CH), 6.43 (brs, 1H; pyrrole-CH), 3.90-3.82 (m, 12H; OCH₃), 3.77–3.72 ppm (m, 6H; OCH₃); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 329.0 nm (4.7×10⁴ M⁻¹ cm⁻¹); fluorescence (CH₂Cl₂): $\lambda_{ex} = 329$ nm; $\lambda_{em} =$ 364, 378, 494 nm; MALDI-TOF-MS: m/z (%) calcd for $C_{29}H_{30}N_4O_6$: 530.22 [M]⁺; found: 530.2 (100), 531.2 (28).

3,5-Bis[5-(3,4,5-trioctyloxyphenyl)pyrrol-2-yl]pyrazole (1d): Hydrazine monohydrate (1.63 mL, 33.6 mmol) was added to a solution of 1,3-bis-[5-(3,4,5-trioctyloxyphenyl)pyrrol-2-yl]-1,3-propanedione^[7] (467 mg, 0.42 mmol) in AcOH (4 mL) and the mixture was stirred at reflux for 35 h. When TLC monitoring showed complete consumption of the starting diketone, the solvent was removed and the residue was flash chromatographed on a column of silica gel (eluent: 1% MeOH/CH2Cl2). Concentration of the appropriate fraction and recrystallization of the residue from CH₂Cl₂/MeOH gave 1d as a brown solid (309.1 mg, 0.28 mmol, 67%). $R_{\rm f} = 0.22$ (eluent: 1% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, $[D_6]DMSO, 20^{\circ}C): \delta = 12.79$ (brs, 1H; pyrazole-NH), 11.33 (brs, 1H; pyrrole-NH), 11.27 (brs, 1H; pyrrole-NH), 7.00 (s, 4H; Ar-H), 6.80 (s, 1H; pyrazole-CH), 6.55 (s, 3H; pyrrole-CH), 6.40 (brs, 1H; pyrrole-CH), 4.02 (t, J=6.6 Hz, 8H; OCH₂), 3.83 (t, J=6.0 Hz, 4H; OCH₂), 1.75–1.73 (tt, J=7.8, 6.6 Hz, 8H; OCH₂CH₂), 1.65–1.63 (tt, J=7.8, 6.6 Hz, 4H; OCH₂CH₂), 1.48–1.42 (m, 12H; OC₂H₄CH₂), 1.36–1.26 (m, 48H; OC₃H₆C₄H₈CH₃), 0.86–0.84 ppm (m, 18H; OC₇H₁₄CH₃); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 329.5 nm (6.1 × 10⁴ m⁻¹ cm⁻¹); fluorescence (CH₂Cl₂): λ_{ex} = 329 nm; λ_{em} = 363, 380, 497 nm; MALDI-TOF-MS: m/z (%) calcd for $C_{71}H_{115}N_4O_6$: 1119.88 $[M+H]^+$; found: 1119.9 (100).

3,5-Bis[5-(3,4,5-tridodecyloxyphenyl)pyrrol-2-yl]pyrazole (1e): Hydrazine monohydrate (953 µL, 19.6 mmol) was added to a solution of 1,3-bis-[5-(3,4,5-tridodecyloxyphenyl)pyrrol-2-yl]-1,3-propanedione^[7] (817.2 mg, 0.56 mmol) in AcOH (3 mL) and the mixture was stirred at reflux for 7 h. When TLC monitoring showed complete consumption of the starting diketone, the solvent was removed and the residue was flash chromatographed on a column of silica gel (eluent: 0.5% MeOH/CH2Cl2). Concentration of the appropriate fraction and recrystallization of the residue from CH₂Cl₂/MeOH gave 1e as a brown solid (305.8 mg, 0.21 mmol, 38%). $R_f = 0.20$ (eluent: 0.5% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, 20°C; the pyrazole-NH signal could not be observed at this temperature because of fast proton exchange between the adjacent N atoms; other solvents such as [D₆]DMSO make the pyrazole-NH signal more evident, as observed for **1b-d** and **2d**): $\delta = 8.87$ (brs, 2H; pyrrole-NH), 6.70 (s, 4H; Ar-H), 6.55 (s, 1H; pyrazole-CH), 6.52 (s, 2H; pyrrole-CH), 6.46 (s, 2H; pyrrole-CH), 4.03–3.95 (m, 12H; OCH₂), 1.84–1.80 (m, 8H; OCH₂CH₂), 1.77-1.73 (m, 4H; OCH₂CH₂), 1.48-1.47 (m, 12H; OCH₂CH₂CH₂), 1.36–1.26 (m, 96 H; OC₃H₆C₈H₁₆CH₃), 0.89–0.87 ppm (m, 18H; OC₁₁H₂₂CH₃); UV/Vis (CH₂Cl₂): λ_{max} (ϵ)=329.5 nm (7.0× $10^4 \text{ m}^{-1} \text{ cm}^{-1}$; fluorescence (CH₂Cl₂): $\lambda_{\text{ex}} = 330 \text{ nm}$; $\lambda_{\text{em}} = 363, 379, 501 \text{ nm}$; MALDI-TOF-MS: m/z (%) calcd for C₉₅H₁₆₂N₄O₆: 1455.25 [M]⁺; found: 1455.3 (100).

3,5-Bis[5-(3,4,5-trihexadecyloxyphenyl)pyrrol-2-yl]pyrazole (1 f): Hydrazine monohydrate (50 µL, 1.03 mmol) was added to a solution of 1,3-bis[5-(3,4,5-trihexadecyloxyphenyl)pyrrol-2-yl]-1,3-propanedione^[7]

(89.5 mg, 0.05 mmol) in AcOH (3 mL) and the mixture was stirred at reflux for 5 h. When TLC monitoring showed complete consumption of the starting diketone, the solvent was removed and the residue was flash chromatographed on a column of silica gel (eluent: 1% MeOH/CH₂Cl₂). Concentration of the appropriate fraction and recrystallization of the residue from CH2Cl2/MeOH gave 1f as a pale-yellow solid (44.0 mg, 0.025 mmol, 77%). $R_{\rm f} = 0.43$ (eluent: 1% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, 20°C; the pyrazole-NH signal could not be observed at this temperature because of fast proton exchange between the adjacent N atoms): $\delta = 9.11$ (brs, 2H; pyrrole-NH), 6.70 (s, 4H; Ar-H), 6.55 (s, 1H; pyrazole-CH), 6.52 (s, 2H; pyrrole-CH), 6.45 (s, 2H; pyrrole-CH), 4.00-3.94 (m, 12H; OCH2), 1.82-1.80 (m, 8H; OCH2CH2), 1.77-1.72 (m, 4H; OCH₂CH₂), 1.47-1.46 (m, 12H; OC₂H₄CH₂), 1.34-1.25 (m, 144H; OC₃H₆C₁₂H₂₄CH₃), 0.89–0.86 ppm (m, 18H; OC₁₅H₃₀CH₃); UV/ Vis (CH₂Cl₂): λ_{max} (ϵ) = 329.0 nm (6.2 × 10⁴ m⁻¹ cm⁻¹); fluorescence (CH₂Cl₂): $\lambda_{ex} = 330 \text{ nm}$; $\lambda_{em} = 381$, 508 nm; MALDI-TOF-MS: m/z (%) calcd for C₁₁₉H₂₁₀N₄O₆: 1792.63 [M+H]⁺; found: 1791.6 (98), 1792.6 (100).

4-Bromo-1,2,3-trihexadecyloxybenzene: A mixture of K₂CO₃ (6.11 g, 44.2 mmol), 4-bromo-1,2,3-trihydroxybenzene^[20] (1.30 g, 6.32 mmol), and 1-bromohexadecane (6.56 g, 21.5 mmol) in dry DMF (50 mL) was stirred at reflux for 3 days. After cooling, the solvent was evaporated. The crude product was taken up in CH₂Cl₂, and the solution was washed with water, dried over MgSO4, and concentrated to dryness. The residue was then chromatographed on a column of silica gel (Wakogel C-300; eluent: CH2Cl2/n-hexane, 1:5) to give 4-bromo-1,2,3-trihexadecyloxybenzene as a white solid (4.65 g, 5.29 mmol, 84%). $R_{\rm f}$ =0.45 (eluent: CH₂Cl₂/*n*-hexane, 1:5); ¹H NMR (600 MHz, CDCl₃, 20 °C): $\delta = 7.15$ (d, J = 9.0 Hz, 1H; Ar-H), 6.54 (d, J=9.0 Hz, 1H; Ar-H), 4.02 (t, J=6.0 Hz, 2H; OCH₂), 3.96 (t, J=6.0 Hz, 2H; OCH₂), 3.92 (t, J=6.0 Hz, 2H; OCH₂), 1.83-1.72 (m, 6H; OCH₂CH₂), 1.50–1.43 (m, 6H; OC₂H₄CH₂), 1.34–1.25 (m, 72H; OC₃H₆C₁₂H₂₄CH₃), 0.89–0.87 ppm (m, 9H; OC₁₅H₃₀CH₃); MALDI-TOF-MS: m/z (%) calcd for C₅₄H₁₀₁BrO₃: 876.69 [M]⁺; found: 876.7 (100).

1-tert-Butoxycarbonyl-2-(2,3,4-trihexadecyloxyphenyl)pyrrole and 2-(2,3,4-trihexadecyloxyphenyl)pyrrole: A solution of Na₂CO₃ (1.98 g, 18.7 mmol) in water (4 mL) was added to a solution of 4-bromo-1,2,3-trihexadecyloxybenzene (4.55 g, 5.18 mmol), 1-tert-butoxycarbonylpyrrole-2-boronic acid (1.31 g, 6.22 mmol), and [Pd(PPh₃)₄] (370.0 mg, 0.32 mmol) in 1,2-dimethoxyethane (40 mL) at RT under nitrogen. The mixture was heated at reflux for 6 h, cooled, and then partitioned between water and CH₂Cl₂. The organic phase was dried over anhydrous MgSO4 and concentrated to give an oil, which was chromatographed on a column of silica gel (Wakogel C-300; eluent: CH₂Cl₂/n-hexane, 1:2) to give 1-tert-butoxycarbonyl-2-(2,3,4-trihexadecyloxyphenyl)pyrrole (1.91 g, 1.98 mmol, 38%) as a colorless oil. $R_f = 0.31$ (eluent: CH₂Cl₂/n-hexane, 1:2); ¹H NMR (600 MHz, CDCl₃, 20°C): $\delta = 7.31-7.30$ (m, 1H; pyrrole-CH), 6.92 (d, J=9.0 Hz, 1H; Ar-H), 6.62 (d, J=8.4 Hz, 1H; Ar-H), 6.19-6.18 (m, 1H; pyrrole-CH), 6.09-6.08 (m, 1H; pyrrole-CH), 4.00-3.94 (m, 6H; OCH₂), 1.81-1.74 (m, 6H; OCH₂CH₂), 1.50-1.42 (m, 6H; OC₂H₄CH₂), 1.36 (s, 9H; Boc), 1.34-1.25 (m, 72H; OC₃H₆C₁₂H₂₄CH₃), 0.89-0.86 ppm (m, 9H; OC₁₅H₃₀CH₃); MALDI-TOF-MS: m/z (%) calcd for C₆₃H₁₁₃NO₅: 963.86 [M]⁺; found: 963.3 (100). The product 1-tert-butoxycarbonyl-2-(2,3,4-trihexadecyloxyphenyl)pyrrole (1.91 g, 1.98 mmol) was heated at 190°C for 30 min. The residue was then chromatographed on a column of silica gel (Wakogel C-300; eluent: CH2Cl2/n-hexane, 1:3) to give 2-(2,3,4-trihexadecyloxyphenyl)pyrrole as a white solid (1.24 g, 1.43 mmol, 73%). $R_f = 0.33$ (eluent: CH₂Cl₂/*n*-hexane, 1:3); ¹H NMR (600 MHz, CDCl₃, 20°C): $\delta = 9.78$ (s, 1H; pyrrole-NH), 7.25 (d, J =9.0 Hz, 1H; Ar-H), 6.81-6.80 (m, 1H; pyrrole-CH), 6.67 (d, J=9.0 Hz,

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1H; Ar-H), 6.46–6.45 (m, 1H; pyrrole-CH), 6.26–6.24 (m, 1H; pyrrole-CH), 4.02–3.95 (m, 6H; OCH₂), 1.84–1.73 (m, 6H; OCH₂CH₂), 1.51–1.39 (m, 6H; OC₂H₄CH₂), 1.38–1.25 (m, 72H; OC₃H₆C₁₂H₂₄CH₃), 0.89–0.86 ppm (m, 9H; OC₁₅H₃₀CH₃); MALDI-TOF-MS: m/z (%) calcd for C₅₈H₁₀₅NO₅: 863.81 [*M*]⁺; found: 863.8 (100).

1,3-Bis[5-(2,3,4-trihexadecyloxyphenyl)pyrrol-2-yl]-1,3-propanedione

(1g'): Malonyl chloride (62.4 mg, 0.44 mmol) was added to a solution of 2-(2,3,4-trihexadecyloxyphenyl)pyrrole (633.1 mg, 0.73 mmol) in CH₂Cl₂ (20 mL) at RT and the mixture was stirred for 10 min at the same temperature. After TLC monitoring showed complete consumption of the starting pyrrole, the mixture was washed with saturated aqueous Na₂CO₃ and water, dried over anhydrous MgSO4, filtered, and concentrated to dryness. The residue was then chromatographed on a column of silica gel (Wakogel C-300; eluent: CH₂Cl₂/n-hexane, 2:1) to give 1g' (361.1 mg, 0.20 mmol, 55%) as an orange solid. $R_f = 0.30$ (eluent: CH₂Cl₂/n-hexane, 2:1); ¹H NMR (600 MHz, CDCl₃, 20 °C; the diketone was obtained as a mixture of keto and enol tautomers in a ratio of 1:0.41): keto form: $\delta =$ 10.66 (s, 2H; pyrrole-NH), 7.28 (d, J=9.0 Hz, 2H; Ar-H), 7.11-7.10 (m, 2H; pyrrole-CH), 6.67 (d, J=9.0 Hz, 2H; Ar-H), 6.52-6.51 (m, 2H; pyrrole-CH), 4.19 (s, 2H; CH), 4.02-3.96 (m, 12H; OCH2), 1.87-1.75 (m, 12H; OCH₂CH₂), 1.50-1.44 (m, 12H; OCH₂CH₂CH₂), 1.39-1.23 (m, 144H; OC₃H₆C₈H₁₆CH₃), 0.88–0.85 ppm (m, 18H; OC₁₅H₃₀CH₃); enol form: $\delta = 10.63$ (s, 2H; pyrrole-NH), 7.30 (d, J=9.0 Hz, 2H; Ar-H), 6.90-6.89 (m, 2H; pyrrole-H), 6.69 (d, J=9.0 Hz, 2H; Ar-H), 6.55-6.54 (m, 2H; pyrrole-H), 6.31 (s, 1H; CH), 4.12-4.06 (m, 12H; OCH₂), 1.87-1.75 (m, 12H; OCH₂CH₂), 1.50–1.44 (m, 12H; OC₂H₄CH₂), 1.39–1.23 (m, 144 H; $OC_3H_6C_8H_{16}CH_3$), 0.88–0.85 ppm (m, 18 H; $OC_{15}H_{30}CH_3$); MALDI-TOF-MS: *m*/*z* (%) calcd for C₁₁₉H₂₁₀N₂O₈: 1795.61 [*M*]⁺; found: 1795.6 (100).

3,5-Bis[5-(2,3,4-trihexadecyloxyphenyl)pyrrol-2-yl]pyrazole (1g): Hydrazine monohydrate (258 µL, 5.3 mmol) was added to a solution of 1g' (106.9 mg, 0.06 mmol) in AcOH (3 mL) and the mixture was stirred at reflux for 46 h. When TLC monitoring showed complete consumption of the starting diketone, the solvent was removed and the residue was flash chromatographed on a column of silica gel (eluent: CH2Cl2/n-hexane, 4:1). Concentration of the appropriate fraction and recrystallization of the residue from CH2Cl2/MeOH gave 1g as a white solid (34.9 mg, 0.019 mmol, 33%). $R_{\rm f} = 0.28$ (eluent: CH₂Cl₂/*n*-hexane, 4:1); ¹H NMR (600 MHz, CDCl₃, 20°C; the pyrazole-NH signal could not be observed at this temperature because of fast proton exchange between the adjacent N atoms): $\delta = 10.22$ (brs, 2H; pyrrole-NH), 7.28 (d, J = 8.4 Hz, 2H; Ar-H), 6.67 (d, J=8.4 Hz, 2H; Ar-H), 6.50-6.49 (m, 2H; pyrrole-CH), 6.48–6.47 (m, 2H; pyrrole-CH), 6.44 (s, 1H; pyrazole-CH), 4.08 (t, J =6.6 Hz, 4H; OCH₂), 4.02 (t, J=6.6 Hz, 4H; OCH₂), 3.98 (t, J=6.6 Hz, 4H; OCH₂), 1.87-1.77 (m, 12H; OCH₂CH₂), 1.52-1.43 (m, 12H; OC₂H₄CH₂), 1.36–1.21 (m, 144 H; OC₃H₆C₁₂H₂₄CH₃), 0.89–0.86 ppm (m, 18H; OC₁₅H₃₀CH₃); UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 329.0 nm (1.1× $10^4 \text{ m}^{-1} \text{ cm}^{-1}$; fluorescence (CH₂Cl₂): $\lambda_{\text{ex}} = 329 \text{ nm}$; $\lambda_{\text{em}} = 376 \text{ nm}$; MALDI-TOF-MS: *m*/*z* (%) calcd for C₁₁₉H₂₁₀N₄O₆: 1791.63 [*M*]⁺; found: 1791.6 (100).

1,3-Bis(3,4-difluoro-5-phenylpyrrol-2-yl)-1,3-propanedione (2b'): AlCl₃ (38.7 mg, 0.29 mmol) was added to a solution of the BF2 complex of 2b' $(2b'')^{[8]}$ (27.5 mg, 0.058 mmol) in CH₂Cl₂ (3 mL) and the mixture was stirred at reflux for 10 min. After cooling to RT, tert-butyl alcohol (1.36 mL, 14.5 mmol) was added and the resulting mixture was stirred at the same temperature for 10 min. Water (2.72 mL) was then added and the mixture was stirred at the same temperature for 26 h. It was then partitioned between water and CH2Cl2. The organic phase was dried over anhydrous MgSO4 and concentrated. The residue was then chromatographed on a column of silica gel (Wakogel C-300; eluent: 1 % MeOH/CH2Cl2). Concentration of the appropriate fraction and removal of impurities by repeated rinsing with n-hexane gave 2b' (6.0 mg, 0.014 mmol, 24%) as an orange solid. $R_f = 0.27$ (eluent: 1 % MeOH/CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, 20°C; the diketone was obtained as a mixture of keto and enol tautomers in a ratio of 0.78:1): keto form: $\delta = 8.77$ (brs, 2H; pyrrole-NH), 7.83–7.37 (m, 10H; Ar-H), 4.31 ppm (s, 2H; CH); enol form: $\delta =$ 8.61 (brs, 2H; NH), 7.83-7.37 (m, 10H; Ar-H), 6.50 ppm (s, 1H; CH); MALDI-TOF-MS: m/z (%) calcd for $C_{23}H_{13}F_4N_2O_2$: 425.09 $[M-H]^-$; found: 425.1 (100).

3,5-Bis(3,4-difluoro-5-phenylpyrrol-2-yl)pyrazole (2b): Hydrazine monohydrate (10 µL, 0.21 mmol) was added to a solution of 2b' (3.8 mg, 8.9 µmol) in AcOH (1 mL) and the mixture was stirred at reflux for 10 h. When TLC monitoring showed complete consumption of the starting diketone, the solvent was removed and the residue was flash chromatographed on a column of silica gel (eluent: 3% MeOH/CH2Cl2). Concentration of the appropriate fraction and recrystallization of the residue from CH_2Cl_2/n -hexane gave **2b** as a brown solid (2.1 mg, 5.0 µmol, 56%). $R_{\rm f}$ =0.15 (eluent: 3% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, 20°C; the pyrazole-NH signal could not be observed at this temperature because of fast proton exchange between the adjacent N atoms): $\delta = 8.31$ (brs, 2H; pyrrole-NH), 7.58 (d, J=7.8 Hz, 4H; Ar-H), 7.42 (t, J=7.8 Hz, 4H; Ar-H), 7.28 (d, J=7.2 Hz, 4H; Ar-H), 6.67 ppm (s, 1H; pyrazole-CH); UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 321.0 nm (3.4×10⁴ m⁻¹ cm⁻¹); fluorescence (CH₂Cl₂): $\lambda_{ex} = 321$ nm; $\lambda_{em} = 374$, 444 nm (sh); MALDI-TOF-MS: m/z (%) calcd for C₂₃H₁₄F₄N₄: 423.12 [*M*+H]⁺; found: 423.1 (100).

3,4,5-Trimethoxyphenylboronic acid pinacol ester: A two-necked flask containing 5-bromo-1,2,3-trimethoxybenzene (686 mg, 2.78 mmol), [PdCl₂(PPh₃)₂] (64.4 mg, 0.03 mmol), bis(pinacolato)diboron (1.06 g, 4.17 mmol), and KOAc (818 mg, 8.34 mmol) was flushed with nitrogen and charged with degassed 1,4-dioxane (35 mL). The mixture was heated at 80 °C for 18 h, cooled, and then partitioned between water and CH₂Cl₂. The organic phase was dried over anhydrous MgSO₄ and concentrated. The residue was flash chromatographed on a column of silica gel (eluent: 1% MeOH/CH₂Cl₂) to give the desired product (661 mg, 2.25 mmol, 81 %) as a white solid. $R_{\rm f}$ =0.27 (eluent: 1% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, 20°C): δ =7.03 (s, 2H; Ar-H), 3.90 (s, 6H; OCH₃), 3.87 (s, 3H; OCH₃), 1.34 ppm (s, 12H; pinacol-CH₃); FAB-MS: m/z (%) calcd for C₁₅H₂₃BO₅: 294.16 [*M*]⁺; found: 294.1 (100).

BF2 complex of 1,3-bis[3,4-difluoro-5-(3,4,5-trimethoxyphenyl)pyrrol-2yl]-1,3-propanedione (2c"): A two-necked flask containing the BF2 complex of 1,3-bis(3,4-difluoro-5-iodopyrrol-2-yl)-1,3-propanedione^[8] (146 mg, 0.25 mmol), 3,4,5-trimethoxyphenyl boronic acid pinacol ester (185 mg, 0.63 mmol), [Pd(PPh₃)₄] (28.9 mg, 0.03 mmol), and Na₂CO₃ (489 mg, 1.50 mmol) was flushed with nitrogen and charged with DMF (5.0 mL). The mixture was heated at reflux for 4 h, cooled, and then partitioned between water and CH2Cl2. The organic phase was dried over anhydrous MgSO4 and concentrated. The residue was flash chromatographed on a column of silica gel (eluent: 1% MeOH/CH2Cl2). Evaporation of the solvent from the appropriate fraction gave 2c" (52.3 mg, 0.08 mmol, 32%) as a red solid. $R_f = 0.27$ (eluent: 1% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, 20 °C): $\delta = 8.84$ (s, 2H; pyrrole-NH), 6.88 (s, 4H; Ar-H), 6.73 (s, 1H; CH), 3.97 (s, 12H; OCH₃), 3.92 ppm (s, 6H; OCH₃); UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 512.0 nm (1.3×10⁴ M⁻¹ cm⁻¹); MALDI-TOF-MS: m/z (%) calcd for C₂₉H₂₄BF₆N₂O₈: 653.15 [M-H]⁻; found: 653.2 (100).

1,3-Bis[3,4-difluoro-5-(3,4,5-trimethoxyphenyl)pyrrol-2-yl]-1,3-propane-

dione (2c'): AlCl₃ (40.0 mg, 0.30 mmol) was added to a solution of 2c" (19.9 mg, 0.030 mmol) in THF (6 mL) and the mixture was stirred at reflux for 30 min. It was then cooled to RT, whereupon tert-butyl alcohol (704 µL, 7.5 mmol) was added and the resulting mixture was stirred at the same temperature for 10 min. Water (1.4 mL) was then added and the mixture was stirred at the same temperature for 1 h. It was then partitioned between water and CH2Cl2. The organic phase was dried over anhydrous MgSO4 and concentrated. The residue was flash chromatographed on a column of silica gel (eluent: 2% MeOH/CH2Cl2) to give **2c'** (6.0 mg, 9.9 μ mol, 33%) as an orange solid. R_f =0.33 (eluent: 2%) MeOH/CH2Cl2); ¹H NMR (600 MHz, CDCl3, 20°C; the diketone was obtained as a mixture of keto and enol tautomers in a ratio of 0.71:1): keto form: $\delta = 8.87$ (brs, 2H; pyrrole-NH), 6.82 (s, 4H; Ar-H), 4.30 (s, 2H; CH), 3.93 (s, 12H; OCH₃), 3.92 ppm (s, 6H; OCH₃); enol form: $\delta = 8.65$ (brs, 2H; pyrrole-NH), 6.81 (s, 4H; Ar-H), 6.51 (s, 1H; CH), 3.93 (s, 12H; OCH₃), 3.92 ppm (s, 6H; OCH₃); MALDI-TOF-MS: *m*/*z* (%) calcd for $C_{29}H_{25}F_4N_2O_8$: 605.15 $[M-H]^-$; found: 605.2 (100).

3,5-Bis[3,4-difluoro-5-(3,4,5-trimethoxyphenyl)pyrrol-2-yl]pyrazole (2c): Hydrazine monohydrate (78 μL, 1.6 mmol) was added to a solution of 2c'

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(6.0 mg, 9.9 µmol) in AcOH (1 mL) and the mixture was stirred at reflux for 29 h. When TLC monitoring showed complete consumption of the starting diketone, the solvent was removed and the residue was chromatographed on a column of silica gel (eluent: 2% MeOH/CH₂Cl₂). Concentration of the appropriate fraction and recrystallization of the residue from CH₂Cl₂/MeOH gave **2c** as a brown solid (1.4 mg, 2.3 µmol, 23%). R_f =0.07 (eluent: 2% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, 20°C; the pyrazole-NH signal could not be observed at this temperature because of fast proton exchange between the adjacent N atoms): δ =8.42 (brs, 2H; pyrrole-NH), 6.78 (s, 4H; Ar-H), 6.70 (s, 1H; pyrazole-CH), 3.92 (s, 12H; OCH₃), 3.87 ppm (s, 6H; OCH₃); UV/Vis (CH₂Cl₂): λ_{max} (ε)=327.0 nm (5.5×10⁴ m⁻¹ cm⁻¹); fluorescence (CH₂Cl₂): λ_{ex} =327 nm; λ_{em} =387 nm; MALDI-TOF-MS: *m/z* (%) calcd for C₂₉H₂₆F₄N₄O₆: 602.18 [*M*]⁺; found: 602.2 (100).

3,4,5-Trioctyloxyphenylboronic acid pinacol ester: A two-necked flask containing 5-bromo-1,2,3-trioctyloxybenzene (1.79 g, 3.30 mmol), [PdCl₂-(PPh₃)₂] (122 mg, 0.17 mmol), bis(pinacolato)diboron (1.26 g, 4.95 mmol), and KOAc (972 mg, 9.90 mmol) was flushed with nitrogen and charged with degassed 1,4-dioxane (45 mL). The mixture was heated at 80 °C for 48 h, cooled, and then partitioned between water and CHCl₃. The organic phase was dried over anhydrous MgSO₄ and concentrated. The residue was flash chromatographed on a column of silica gel (eluent: CHCl₃/*n* hexane, 1:1) to give the desired product (1.78 g, 3.02 mmol, 92 %) as a colorless oil. R_t =0.17 (eluent: CHCl₃/*n*-hexane, 1:1); ¹H NMR (600 MHz, CDCl₃, 20°C): δ =6.99 (s, 2 H; Ar-H), 4.01 (t, *J* = 6.6 Hz, 4H; OCH₂), 3.97 (t, *J* = 6.6 Hz, 2H; OCH₂), 1.81–1.71 (m, 6H; OCH₂CH₂), 1.49–1.44 (m, 6H; OC₂H₄CH₂), 1.35–1.22 (m, 24H; OC₃H₆C₄H₈), 1.33 (s, 12 H; pinacol-CH₃), 0.89–0.87 ppm (m, 9H; OC₇H₁₄CH₃); MALDI-TOF-MS: m/z (%) calcd for C₃₆H₆₅BO₅: 588.49 [M^+]; found: 588.5 (100).

BF2 complex of 1,3-bis[3,4-difluoro-5-(3,4,5-trioctyloxyphenyl)pyrrol-2yl]-1,3-propanedione (2d"): A two-necked flask containing the BF₂ complex of 1,3-bis(3,4-difluoro-5-iodopyrrol-2-yl)-1,3-propanedione^[8] (247 mg, 0.43 mmol), 3,4,5-trioctyloxyphenyl boronic acid pinacol ester (633 mg, 1.08 mmol), [Pd(PPh₃)₄] (104 mg, 0.09 mmol), and Na₂CO₃ (365 mg, 3.44 mmol) was flushed with nitrogen and charged with a mixture of degassed 1,2-dimethoxyethane (6 mL) and water (0.6 mL). The mixture was heated at reflux for 18 h, cooled, and then partitioned between water and CH2Cl2. The organic phase was dried over anhydrous $MgSO_4$ and concentrated. The residue was flash chromatographed on a column of silica gel (eluent: CHCl₃/n-hexane, 3:1) to give 2d" (26.7 mg, 0.02 mmol, 5%) as a red solid. The deboronated compound 2d' was also obtained (116 mg, 0.10 mmol, 23 %; see below). $R_{\rm f}$ =0.24 (eluent: CHCl₃/ *n*-hexane, 3:1); ¹H NMR (600 MHz, CDCl₃, 20 °C): $\delta = 8.72$ (s, 2H; pyrrole-NH), 6.83 (s, 4H; Ar-H), 6.70 (s, 1H; CH), 4.05 (t, J=6.6 Hz, 8H; OCH₂), 4.02 (t, J=6.6 Hz, 4H; OCH₂), 1.88–1.74 (m, 12H; OCH₂CH₂), 1.52–1.46 (m, 12H; $OC_2H_4CH_2$), 1.38–1.30 (m, 48H; $OC_3H_6C_4H_8CH_3$), 0.89 ppm (t, J = 6.6 Hz, 18H; OC₇H₁₄CH₃); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 518.0 nm $(1.1 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1})$; MALDI-TOF-MS: m/z (%) calcd for $C_{71}H_{109}BF_6N_2O_8$: 1241.81 $[M-H]^-$; found: 1241.8 (100).

1,3-Bis[3,4-difluoro-5-(3,4,5-trioctyloxyphenyl)pyrrol-2-yl]-1,3-propanedione (2d'): AlCl₃ (14.7 mg, 0.11 mmol) was added to a solution of 2d" (26.7 mg, 0.021 mmol) in CH₂Cl₂ (3 mL) and the mixture was stirred at reflux for 10 min. After cooling to RT, tert-butyl alcohol (490 µL, 5.23 mmol) was added and the resulting mixture was stirred at the same temperature for 10 min. Water (0.98 mL) was then added and the mixture was stirred at the same temperature for 26 h. It was then partitioned between water and CH_2Cl_2 . The organic phase was dried over anhydrous MgSO4 and concentrated. The residue was flash chromatographed on a column of silica gel (eluent: CHCl₃/n-hexane, 3:1) to give 2d' (7.1 mg, 5.9 μ mol, 28%) as an orange solid. $R_f = 0.13$ (eluent: CHCl₃/n-hexane, 3:1); ¹H NMR (600 MHz, CDCl₃, 20 °C; the diketone was obtained as a mixture of keto and enol tautomers in a ratio of 0.81:1): keto form: $\delta =$ 8.64 (brs, 2H; pyrrole-NH), 6.77 (s, 4H; Ar-H), 4.29 (s, 2H; CH), 4.03-3.98 (m, 12H; OCH2), 1.86-1.73 (m, 12H; OCH2CH2), 1.51-1.46 (m, 12H; OC₂H₄CH₂), 1.36–1.29 (m, 48H; OC₃H₆C₄H₈CH₃), 0.90–0.87 (m, 18H; $OC_7H_{14}CH_3$); enol form: $\delta = 8.50$ (brs, 2H; NH), 6.77 (s, 4H; Ar-H), 6.48 (s, 1H; CH), 4.03-3.98 (m, 12H; OCH₂), 1.86-1.73 (m, 12H; OCH₂CH₂), 1.51–1.46 (m, 12H; OC₂H₄CH₂), 1.36–1.29 (m, 48H; $OC_3H_6C_4H_8CH_3$), 0.90–0.87 ppm (m, 18H; $OC_7H_{14}CH_3$); MALDI-TOF-MS: m/z (%) calcd for $C_{71}H_{109}F_4N_2O_8$: 1195.83 $[M+H]^+$; found: 1195.8 (100).

3,5-Bis[3,4-difluoro-5-(3,4,5-trioctyloxyphenyl)pyrrol-2-yl]pyrazole (2d): Hydrazine monohydrate (423 µL, 8.73 mmol) was added to a solution of 2d' (116 mg, 0.097 mmol) in AcOH (0.5 mL) and the mixture was stirred at reflux for 63 h. When TLC monitoring showed complete consumption of the starting diketone, the solvent was removed and the residue was flash chromatographed on a column of silica gel (eluent: 1% MeOH/ CH₂Cl₂). Concentration of the appropriate fraction and recrystallization of the residue from CH_2Cl_2/MeOH gave 2d as a brown solid (36.5 mg, 0.031 mmol, 32%). $R_{\rm f} = 0.15$ (eluent: 1% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, $[D_6]DMSO$, 50 °C): $\delta = 13.02$ (brs, 1H; pyrazole-NH), 11.23 (br s, 1 H; pyrrole-NH), 11.12 (br s, 1 H; pyrrole-NH), 7.00 (s, 2 H; Ar-H), 6.93 (s, 2H; Ar-H), 6.77 (s, 1H; pyrazole-CH), 4.02-4.00 (m, 8H; OCH₂), 3.90-3.86 (m, 4H; OCH₂), 1.77-1.72 (m, 8H; OCH₂CH₂), 1.70-1.62 (m, 4H; OCH₂CH₂), 1.49–1.43 (m, 12H; OC₂H₄CH₂), 1.36–1.27 (m, 48H; $OC_3H_6C_4H_8CH_3$), 0.87–0.85 ppm (m, 18H; $OC_7H_{14}CH_3$); UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 327.5 nm (6.8×10⁴ M⁻¹ cm⁻¹); fluorescence (CH₂Cl₂): $\lambda_{ex} = 328 \text{ nm}; \ \lambda_{em} = 385 \text{ nm}; \ \text{MALDI-TOF-MS:} \ m/z \ (\%) \ \text{calcd} \ \text{for}$ $C_{71}H_{110}F_4N_4O_6[M+H]^+$: 1191.84; found: 1191.8 (100).

3,4.5-Tridodecyloxyphenylboronic acid pinacol ester: A two-necked flask containing 5-bromo-1,2,3-tridodecyloxybenzene (2.34 g, 3.30 mmol), [PdCl₂(PPh₃)₂] (122 mg, 0.17 mmol), bis(pinacolato)diboron (1.26 g, 4.95 mmol), and KOAc (972 mg, 9.90 mmol) was flushed with nitrogen and charged with degassed 1,4-dioxane (45 mL). The mixture was heated at 80°C for 48 h, cooled, and then partitioned between water and CHCl₃. The organic phase was dried over anhydrous MgSO4 and concentrated. The residue was flash chromatographed on a column of silica gel (eluent: 5% EtOAc/n-hexane) to give the desired product (2.39 g, 3.16 mmol, 96%) as a white solid. $R_f = 0.39$ (eluent: CHCl₃/*n*-hexane, 1:1); ¹H NMR (600 MHz, CDCl₃, 20 °C): $\delta = 6.99$ (s, 2H; Ar-H), 4.00 (t, J = 6.6 Hz, 4H; OCH₂), 3.97 (t, J=6.6 Hz, 2H; OCH₂), 1.80-1.72 (m, 6H; OCH₂CH₂), 1.46-1.43 (m, 6H; OC₂H₄CH₂), 1.33 (s, 12H; pinacol-CH₃), 1.31-1.28 (m, 48H; $OC_{3}H_{6}C_{8}H_{16}CH_{3}$), 0.88 ppm (t, J=6.6 Hz, 9H; $OC_{11}H_{22}CH_{3}$); MALDI-TOF-MS: m/z (%) calcd for C₃₆H₆₅BO₅: 756.68 [M^+]; found: 756.7 (100).

BF2 complex of 1,3-bis[3,4-difluoro-5-(3,4,5-tridodecyloxyphenyl)pyrrol-2-yl]-1,3-propanedione (2e"): A two-necked flask containing the BF₂ complex of 1,3-bis(3,4-difluoro-5-iodopyrrol-2-yl)-1,3-propanedione^[8] (625 mg, 1.09 mmol), 3,4,5-tridodecyloxyphenyl boronic acid pinacol ester (2.09 g, 2.76 mmol), [Pd(PPh₃)₄] (254 mg, 0.22 mmol), and Na₂CO₃ (936 mg, 8.83 mmol) was flushed with nitrogen and charged with a mixture of degassed 1,2-dimethoxyethane (15 mL) and water (1.5 mL). The resulting mixture was heated at reflux for 17 h, cooled, and then partitioned between water and CH2Cl2. The organic phase was dried over anhydrous MgSO4 and concentrated. The residue was flash chromatographed on a column of silica gel (eluent: CHCl₃/n-hexane, 2:1) to give 2e" (78.8 mg, 0.05 mmol, 5%) as a red solid. The deboronated compound 2e' was also obtained (112 mg, 0.09 mmol, 9%; see below). $R_{\rm f}$ =0.29 (eluent: CHCl₃/*n*-hexane, 2:1); ¹H NMR (600 MHz, CDCl₃, 20°C): $\delta = 8.74$ (s, 2H; pyrrole-NH), 6.83 (s, 4H; Ar-H), 6.70 (s, 1H; CH), 4.05 (t, J= 6.6 Hz, 4H; OCH₂), 4.02 (t, J=6.6 Hz, 2H; OCH₂), 1.86–1.74 (m, 12H; OCH₂CH₂), 1.52–1.48 (m, 12H; OC₂H₄CH₂), 1.38–1.26 (m, 96H; $OC_3H_6C_8H_{16}CH_3$), 0.88 ppm (t, J=6.6 Hz, 18H; $OC_{11}H_{22}CH_3$); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 518.0 nm (8.4×10⁴ m⁻¹ cm⁻¹); MALDI-TOF-MS: m/z(%) calcd for $C_{95}H_{157}BF_6N_2O_8$: 1578.19 [*M*-H]⁻; found: 1578.2 (100).

1,3-Bis[3,4-difluoro-5-(3,4,5-tridodecyloxyphenyl)pyrrol-2-yl]-1,3-pro-

panedione (2e'): AlCl₃ (33.3 mg, 0.25 mmol) was added to a solution of **2e''** (75.0 mg, 0.050 mmol) in CH₂Cl₂ (3 mL) and the mixture was stirred at reflux for 10 min. It was then cooled to RT, whereupon *tert*-butyl alcohol (1.17 mL, 12.5 mmol) was added and the resulting mixture was stirred at the same temperature for 10 min. Water (2.34 mL) was then added and the mixture was stirred at the same temperature for 24 h. It was then partitioned between water and CH₂Cl₂. The organic phase was dried over anhydrous MgSO₄ and concentrated. The residue was flash chromatographed on a column of silica gel (eluent: CHCl₃/n-hexane, 3:1) to give **2e'** (54.6 mg, 0.036 mmol, 72%) as an orange solid. R_t =0.20 (eluent:



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CHCl₃/*n*-hexane, 3:1); ¹H NMR (600 MHz, CDCl₃, 20 °C; the diketone was obtained as a mixture of keto and enol tautomers in a ratio of 0.77:1): keto form: $\delta = 8.63$ (brs, 2H; pyrrole-NH), 6.77 (s, 4H; Ar-H), 4.29 (s, 2H; CH), 4.03–3.98 (m, 12H; OCH₂), 1.85–1.73 (m, 12H; OCH₂CH₂), 1.51–1.46 (m, 12H; OC₂H₄CH₂), 1.37–1.26 (m, 96H; OC₃H₆C₈H₁₆CH₃), 0.89–0.86 ppm (m, 18H; OC₇H₁₄CH₃); enol form: $\delta = 8.48$ (brs, 2H; pyrrole-NH), 6.77 (s, 4H; Ar-H), 6.48 (s, 1H; CH), 4.03–3.98 (m, 12H; OCH₂CH₂), 1.35–1.73 (m, 12H; OCH₂CH₂), 1.51–1.46 (m, 12H; OC₂H₄CH₂), 1.51–1.46 (m, 12H; OC₂H₄CH₂), 1.51–1.46 (m, 12H; OC₂H₄CH₂), 1.51–1.46 (m, 12H; OC₂H₄CH₂), 1.37–1.26 (m, 96H; OC₃H₆C₈H₁₆CH₃), 0.89–0.86 ppm (m, 18H; OC₇H₄CH₃); MALDI-TOF-MS: *m/z* (%) calcd for C₉₅H₁₅₇BF₆N₂O₈: 1532.20 [*M*+H]⁺; found: 1532.2 (100).

3,5-Bis[3,4-difluoro-5-(3,4,5-tridodecyloxyphenyl)pyrrol-2-yl]pyrazole

(2e): Hydrazine monohydrate (414 $\mu L,\,8.46$ mmol) was added to a solution of 2e' (112 mg, 0.094 mmol) in AcOH (0.5 mL) and the mixture was stirred at reflux for 64 h. When TLC monitoring showed complete consumption of the starting diketone, the solvent was removed and the residue was flash chromatographed on a column of silica gel (eluent: 1% MeOH/CH2Cl2). Concentration of the appropriate fraction and recrystallization of the residue from $CH_2Cl_2\!/MeOH$ gave $2\,e$ as a brown solid (41.3 mg, 0.027 mmol, 29%). $R_{\rm f} = 0.18$ (eluent: 1% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, 20 °C; the pyrazole-NH signal could not be observed at this temperature because of fast proton exchange between the adjacent N atoms): $\delta = 8.04$ (brs, 2H; pyrrole-NH), 6.73 (s, 4H; Ar-H), 6.66 (s, 1H; pyrazole-CH), 4.02 (t, J=6.0 Hz, 8H; OCH₂), 3.97 (t, J= 6.0 Hz, 4H; OCH₂), 1.85-1.80 (m, 8H; OCH₂CH₂), 1.78-1.73 (m, 4H; $OCH_2CH_2), \ 1.51-1.45 \ (m, \ 12\,\mathrm{H}; \ OC_2H_4CH_2), \ 1.37-1.26 \ (m, \ 96\,\mathrm{H};$ OC₃H₆C₈H₁₆CH₃), 0.89–0.87 ppm (m, 18H; OC₁₁H₂₂CH₃); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 327.0 nm (5.1 × 10⁴ M⁻¹ cm⁻¹); fluorescence (CH₂Cl₂): $\lambda_{ex} = 327 \text{ nm}; \lambda_{em} = 386 \text{ nm}; \text{ MALDI-TOF-MS: } m/z$ (%) calcd for $C_{95}H_{157}BF_6N_2O_8$: 1527.20 [*M*+H]⁺; found: 1527.2 (100).

1,3-Bis[3,4-difluoro-5-(3,4,5-trihexadecyloxyphenyl)pyrrol-2-yl]-1,3-pro-

panedione (2 f'): AlCl₃ (26.0 mg, 0.20 mmol) was added to a solution of the BF₂ complex of **2**f' $(2 f'')^{[8]}$ (73.5 mg, 0.039 mmol) in CH₂Cl₂ (3 mL) and the mixture was stirred at reflux for 10 min. After cooling to RT, tert-butyl alcohol (915 $\mu L,\,9.75\,\text{mmol})$ was added and the resulting mixture was stirred at the same temperature for 10 min. Water (1.83 mL) was then added and the mixture was stirred at the same temperature for 19 h. It was then partitioned between water and CH2Cl2. The organic phase was dried over anhydrous MgSO4 and concentrated. The residue was chromatographed on a column of silica gel (eluents: 8% EtOAc/nhexane and 5% EtOAc/n-hexane) to give 2f' (42.4 mg, 0.023 mmol, 27%) as an orange solid. $R_f = 0.27$ (eluent: CHCl₃/*n*-hexane, 3:1); ¹H NMR (600 MHz, CDCl₃, 20 °C; the diketone was obtained as a mixture of keto and enol tautomers in a ratio of 0.81:1): keto form: $\delta = 8.80$ (brs, 2H; pyrrole-NH), 6.78 (s, 4H; Ar-H), 4.29 (s, 2H; CH), 4.03-3.98 (m, 12H; OCH₂), 1.85–1.74 (m, 12H; OCH₂CH₂), 1.51–1.45 (m, 12H; OC₂H₄CH₂), 1.36–1.23 (m, 144 H; OC₃H₆C₁₂H₂₄CH₃), 0.89–0.86 ppm (m, 18H; OC₁₅H₃₀CH₃); enol form: $\delta = 8.59$ (brs, 2H; pyrrole-NH), 6.77 (s, 4H; Ar-H), 6.49 (s, 1H; CH), 4.03-3.98 (m, 12H; OCH₂), 1.85-1.74 (m, 12H; OCH₂CH₂), 1.51–1.45 (m, 12H; OC₂H₄CH₂), 1.36–1.23 (m, 144H; $OC_{3}H_{6}C_{12}H_{24}CH_{3}$), 0.89–0.86 ppm (m, 18H; $OC_{15}H_{30}CH_{3}$); MALDI-TOF-MS: m/z (%) calcd for C₁₁₉H₂₀₆F₄N₂O₈: 1867.57 [M]⁻; found: 1867.9 (100).

3,5-Bis[3,4-difluoro-5-(3,4,5-trihexadecyloxyphenyl)pyrrol-2-yl]pyrazole

(2 f): Hydrazine monohydrate (48 μ L, 0.99 mmol) was added to a solution of 2 f' (47.1 mg, 0.03 mmol) in AcOH (0.5 mL) and the mixture was stirred at reflux for 24 h. When TLC monitoring showed complete consumption of the starting diketone, the solvent was removed and the residue was flash chromatographed on a column of silica gel (eluent: 1% MeOH/CH₂Cl₂). Concentration of the appropriate fraction and recrystallization of the residue from CH₂Cl₂/MeOH gave 2f as a brown solid (16.7 mg, 9.0 μ mol, 36%). R_t =0.36 (eluent: 1% MeOH/CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃, 20°C; the pyrazole-NH signal could not be observed at this temperature because of fast proton exchange between the adjacent N atoms): δ =8.04 (brs, 2H; pyrrole-NH), 6.74 (s, 4H; Ar-H), 6.66 (s, 1H; pyrazole-CH), 4.04–3.97 (m, 12H; OCH₂), 1.85–1.81 (m, 8H; OCH₂CH₂), 1.78–1.73 (m, 4H; OCH₂CH₂), 1.50–1.48 (m, 12H; OC₂H₄CH₂), 1.38–1.26 (m, 144H; OC₃H₆Cl₂H₄CH₃), 0.89–0.86 ppm (m, 18H; OC₁₅H₃₀CH₃); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 327.5 nm (4.7× 10⁴ m⁻¹ cm⁻¹); fluorescence (CH₂Cl₂): λ_{ex} = 328 nm; λ_{em} = 387 nm; MALDI-TOF-MS: *m/z* (%) calcd for C₁₁₉H₂₀₆F₄N₄O₆: 1864.60 [*M*+H]⁺; found: 1864.6 (100).

Method for single-crystal X-ray diffraction analysis: Crystallographic data for the TFA complex of dipyrrolylpyrazole are summarized in Table 1. Single crystals of [1c-H⁺][CF₃CO₂⁻] were obtained by vapor diffusion of heptane into a solution in CH₂Cl₂ containing a small amount of toluene. The crystal selected for data collection was a brown prism of approximate dimensions $0.50 \times 0.30 \times 0.10$ mm. Data were collected at 93 K on a Rigaku RAXIS-RAPID diffractometer by using graphite-monochromated Cu_{Ka} radiation (λ = 1.54187 Å), and the structure was solved by direct methods. Nonhydrogen atoms were refined anisotropically. The calculations were performed by using the Crystal Structure crystallographic software package from Molecular Structure Corporation.^[21]

Table 1. Crystallographic details for compound $[1c \cdot H^+][CF_3CO_2^-]$.

	$[\mathbf{1c}\cdot\mathbf{H}^+][CF_3CO_2^-]\cdot$ water
formula	$C_{29}H_{31}N_4O_6 \cdot C_2F_3O_2 \cdot H_2O$
$M_{ m r}$	664.60
crystal size [mm]	$0.50 \times 0.30 \times 0.10$
crystal system	tetragonal
space group	$I4_1/a$ (no. 88)
a [Å]	27.2555(5)
b [Å]	27.2555(5)
c [Å]	16.2957(3)
α [°]	90
β[°]	90
γ [°]	90
V [Å ³]	12105.5(4)
$ ho_{ m calcd} [m g cm^{-3}]$	1.450
Ζ	16
T [K]	93(2)
$\mu(\mathrm{Cu}_{K\alpha}) \ [\mathrm{mm}^{-1}]$	1.022
no. of reflns	63199
no. of unique reflns	5556
variables	432
$\lambda(\mathrm{Cu}_{K\alpha})$ [Å]	1.54187
$R_1 (I > 2\sigma(I))$	0.0756
$wR_2 (I > 2\sigma(I))$	0.1980
GOF	1.148

CCDC-897964 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT and AM1 calculations: Ab initio and semi-empirical calculations on the π -conjugated molecules were carried out by using the Gaussian 03 program^[15] and an HP Compaq dc5100 SFF computer.

Scanning tunneling microscopy (STM): All STM investigations were carried out with a Nanoscope IIIa (Veeco Instruments, Santa Barbara, CA) at the solution/HOPG interface. Mechanically cut Pt/Ir (90:10) wires (0.25 mm) were used as STM tips. Solutions for STM investigation (ca. 1×10^{-3} M) were prepared by first dropping an appropriate volume of the original solution in CH₂Cl₂ into a vial. After evaporation of the CH₂Cl₂, an appropriate volume of solvent (anhydrous 1,2,4-trichlorobenzene) was dropped into the same vial. The scales of the images were calibrated after every investigation by using the visualized lattice of the underlying HOPG.

Scanning electron microscopy (SEM): SEM images were obtained with a Hitachi S-4800 scanning electron microscope at an acceleration voltage of 10 kV by using a silicon (100) substrate. A platinum coating was applied by using a Hitachi E-1030 ion sputter apparatus.

Differential scanning calorimetry (DSC): The phase-transition points were observed by means of differential scanning calorimetry (Perkin–Elmer Diamond DSC).

Polarizing optical microscopy (POM): POM measurements were carried out with a Nikon OPTIPHOT-POL polarizing optical microscope equipped with a Mettler FP82 HT hot stage.

Synchrotron X-ray diffraction analysis (XRD): High-resolution XRD analyses were carried out by using a synchrotron radiation X-ray beam with a wavelength of 1.00 Å on BL40B2 at SPring-8 (Hyogo, Japan). A large Debye-Scherrer camera with camera lengths of 535.481 mm for XRD of 2f (solid (from CH₂Cl₂/MeOH), Figure S16b in the Supporting Information), VT-XRD of 2f (Figure S17c in the Supporting Information) and [2 f·H⁺][CF₃CO₂⁻] (precipitate, Figure S19b in the Supporting Information); 532.704 mm for VT-XRD of [2f·H⁺][CF₃CO₂⁻] (Figure S19c in the Supporting Information); 531.034 mm for XRD of 1f (solid (from 1,4-dioxane), Figure S16a in the Supporting Information), VT-XRD of 2d (Figure S17a in the Supporting Information), 2e (Figure S17b in the Supporting Information), and 2f (xerogel, Figure S17d in the Supporting Information); 531.679 mm for XRD of [1 f·H⁺][CF₃CO₂⁻] (xerogel, Figure S18a in the Supporting Information) and [2 f·H⁺]- $[CF_3CO_2^-]$ (xerogel, Figure S19a in the Supporting Information); 541.500 mm for VT-XRD of [1f·H⁺][CF₃CO₂⁻] (Figure S18c in the Supporting Information); and 540.180 mm for XRD of [1f·H⁺][CF₃CO₂⁻] (precipitate, Figure S18b in the Supporting Information) and VT-XRD of $[1 f \cdot H^+][CF_3CO_2^-)$ (Figure S18d–f in the Supporting Information) for the heating process by using a quartz capillary were used with an imaging plate as a detector. The diffraction pattern was obtained with a 0.01° step in 2θ . The exposure time to the X-ray beam was 10–60 s.

Photoelectron yield spectroscopy (PYS): The highest occupied molecular orbital (HOMO) was estimated by UV photoelectron yield spectroscopy (PYS). PYS measurements were performed on a Sumitomo Heavy Industry model PCR-102 spectrometer, with the photon energy being adjusted from 4.0 to 7.0 eV in increments of 0.1 eV. Thin-film samples were prepared from [**1f**·H⁺][CF₃CO₂⁻] and [**2f**·H⁺][CF₃CO₂⁻] smeared on ITO-coated glass plates and loaded into the vacuum chamber evacuated to about 5×10^{-4} Pa. An anode was installed beside the sample holder to collect electrons emitted from the respective films. A deuterium lamp was used as an excitation source and the anode voltage was fixed at 10 V. The threshold photon energy was estimated from the photoelectron yield spectrum.

Flash-photolysis time-resolved microwave conductivity (FP-TRMC): Charge carrier mobility was measured by the FP-TRMC technique. Samples were prepared by attaching solid 1 f, $[1\,f\text{-}H^+][\mathrm{CF_3CO_2}^-],\,2\,f\!,$ and $[\mathbf{2}\,\mathbf{f}\cdot\mathbf{H}^+][CF_3CO_2^-]$ to a quartz plate with double-sided sticky tape. Charge carriers were photochemically generated by using the third harmonic ($\lambda = 355$ nm) of a Spectra Physics model GCR-130 Nd:YAG laser with a pulse duration of 5-8 ns. The photon density of a 355 nm pulse was 0.9×10^{16} photons cm⁻². The microwave frequency and power were set at \approx 9.1 GHz and 3 mW, respectively. The TRMC signal, picked up by a diode (rise time <1 ns), was monitored by a Tektronics model TDS3052B digital oscilloscope. The observed conductivities were normalized, and are given in terms of the photocarrier generation yield (ϕ) multiplied by the sum of the charge carrier mobilities ($\Sigma \mu$), according to Equation (1), in which e, A, I_0 , F_{light} , P_r and ΔP_r are the unit charge of a single electron, a sensitivity factor [S⁻¹ cm], the incident photon density of the excitation laser [photon cm⁻²], a correction (or filling) factor [cm⁻¹], and the reflected microwave power and its change, respectively. The experiments were carried out at RT.

$$\phi \Sigma \mu = (1/eAI_0 F_{\text{light}}) (\Delta P_{\text{r}}/P_{\text{r}})$$
⁽¹⁾

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FULL PAPER

Supramolecular ion-pair assemblies:

Modified 3,5-dipyrrolylpyrazole (DPP) derivatives in their protonated form produce planar [2+2]-type complexes with trifluoroacetate ions as the constituent components of ion-pair-based assemblies. An essential strategy for the construction of dimension-controlled organized structures based on the [2+2]-type complexes is the introduction of aryl rings bearing long alkyl chains, which enables the formation of 2D patterns at interfaces, supramolecular gels, and mesophases (see figure).



Supramolecular Chemistry -

H. Maeda,* K. Chigusa, T. Sakurai, K. Ohta, S. Uemura, S. Seki Ion-Pair-Based Assemblies Comprising **Pyrrole–Pyrazole Hybrids**

