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Nucleophilic Substitution Reactions of *meso*-5,10,15-Tris(pentafluorophenyl)-corrole; Synthesis of ABC-Type Corroles and Corrole-Based Organogels

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Nucleophilic substitution reactions of 5,10,15-tris(pentafluorophenyl)corrole (**1**) with amines were examined as a post-modification route to functional corroles. Reaction of **1** with an excess of amine nucleophiles led to exclusive formation of 5,10,15-tris(4-amino-2,3,5,6-tetrafluorophenyl)-substituted corroles. In this nucleophilic reaction, 5- and 15-pentafluorophenyl substituents were found to be more reactive than the substituent at the 10-position. This substitution reaction was applied for the preparation of ABC-type corroles and corrole-based organogels. The latter exhibited a blue-shifted Soret band and small fluorescence quantum yields in nonpolar hydrocarbon solvents due to the formation of H-type aggregates.

Introduction

Corroles are aromatic tetrapyrrolic macrocycles bearing a direct pyrrole–pyrrole linkage.[1] In recent years, corroles have been extensively studied in coordination chemistry,[2] as a catalyst of water oxidation,[3] in photophysics,[4] chemical transformations,[5] gas sensors,[6] and other properties have also been investigated.[7] Increasing attention has been focused on *meso*-triaryl-substituted corroles because convenient and effective synthetic methods have been developed for these molecules independently by Gross et al.,[8] Paolesse et al.,[9] and Gryko et al.[10] Owing to these and subsequent synthetic efforts,[11] *meso*-A_3-substituted and *trans*-A_2B-substituted corroles are accessible from acid-catalyzed condensation of pyrrole or dipyrromethane with aldehydes, respectively. However, the synthesis of ABC-type *meso*-substituted corroles was not straightforward and needed tedious and lengthy sequences involving: 1) two different acylation steps of *meso*-aryl-substituted dipyrromethane, 2) reduction to the dipyrromethane diol, 3) acid-catalyzed reaction with solvent pyrrole, and 4) final oxidative ring-closure.[12]

Nucleophilic substitution reactions at the *para*-position of *meso*-pentafluorophenyl substituents have been used to fabricate porphyrins.[13] Similar reactions have also been reported for *meso*-hexakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1) with alcohols.[14] On the other hand, similar substitution reactions with corroles have been quite limited. As a sole example, Gross et al. reported that the reaction of 5,10,15-tris(pentafluorophenyl)-substituted corrole (**1**) with 2-pyridyllithium gave the trisubstituted product.[8a] In contrast to tetrakis(pentafluorophenyl)-substituted porphyrins, corrole **1** has two different *meso*-aryl substituents (strictly speaking, the three *meso*-aryl substituents are different considering the location of the inner pyrrolic hydrogen atoms). The relative reactivities of these different *meso*-pentafluorophenyl substituents have not yet been examined.

With this background, we examined the nucleophilic substitution reaction of **1** with various amines and found that the *para*-fluorine atoms of 5- and 15-pentafluorophenyl substituents are more reactive than that of the 10-substituent. This nucleophilic aromatic substitution reaction was used for the synthesis of ABC-type *meso*-aryl-substituted corroles and corrole-based organogels.

Results and Discussion

As shown in Scheme 1, the reaction of **1** with an excess of benzylamine was investigated to optimize the reaction conditions. Initially, tetrahydrofuran (THF) was used as solvent and the reaction was performed at reflux. Under these conditions, the reaction was slow but gave 5,10,15-tris(4-benzylamino-2,3,5,6-tetrafluorophenyl)corrole (**2a**) in 57% yield after four days. To shorten the reaction time, the solvent was changed to dimethyl sulfoxide (DMSO) and the reaction was performed at 100 °C, which led to improvements in both the isolated yield of **2a** (70%) and the reaction time (5 h). Under these conditions, the reactions of **1** with various amines afforded tri-aminated products in good yields (Table 1). Primary amines and less sterically hindered secondary amines were used for this reaction and gave satisfactory yields, but diisopropylamine and dibenzylamine did

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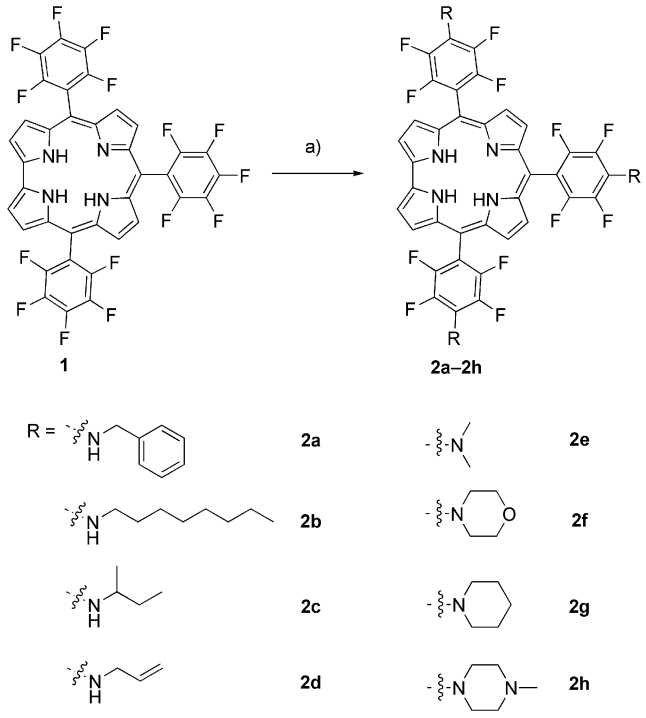
not afford any substituted products, probably due to steric hindrance (Table 1). All the tri-aminated products were characterized by ^1H and ^{19}F NMR spectroscopy, and high-resolution ESI-TOF-MS analyses.



Scheme 1. Synthetic scheme for tris-aminated corroles. *Reagents and conditions*: (a) amine, DMSO, 100 °C, 5 h.

Table 1. Synthesis of tri-aminated corroles.

Entry	Amine	Solvent	Temp. [°C]	Time [h]	Product	Yield [%]
1	benzylamine	THF	reflux	96	**2a**	57
2	benzylamine	DMSO	100	5	**2a**	70
3	octylamine	DMSO	100	5	**2b**	81
4	*sec*-butylamine	DMSO	100	5	**2c**	87
5	allylamine	DMSO	100	5	**2d**	89
6	dimethylamine[a]	DMSO	100	5	**2e**	92
7	morpholine	DMSO	100	5	**2f**	65
8	piperidine	DMSO	100	5	**2g**	95
9	*N*-methylpiperazine	DMSO	100	5	**2h**	70
10	diisopropylamine	DMSO	100	5	–	0
11	dibenzylamine	DMSO	100	5	–	0

[a] 50% aqueous solution.

Characteristically, the ^{19}F NMR spectra showed the disappearance of signals due to the *p*-fluorine atoms ($\delta \approx -155$ ppm), which evinced the high regioselectivity at the *para*-fluorine atoms (Figure 1). Care was needed for the analysis because the chemical shifts of the *meta*-fluorine atoms were sensitive to the structure of the amine nucleophiles. Namely, the signals due to the *meta*-fluorine atoms appear around $\delta = -160$ ppm for the products from primary amines (typically shown for **2a**, Figure 1, b), whereas they are down-field shifted by 10 ppm for the products from secondary amines (typically shown for **2f**, Figure 1, c).

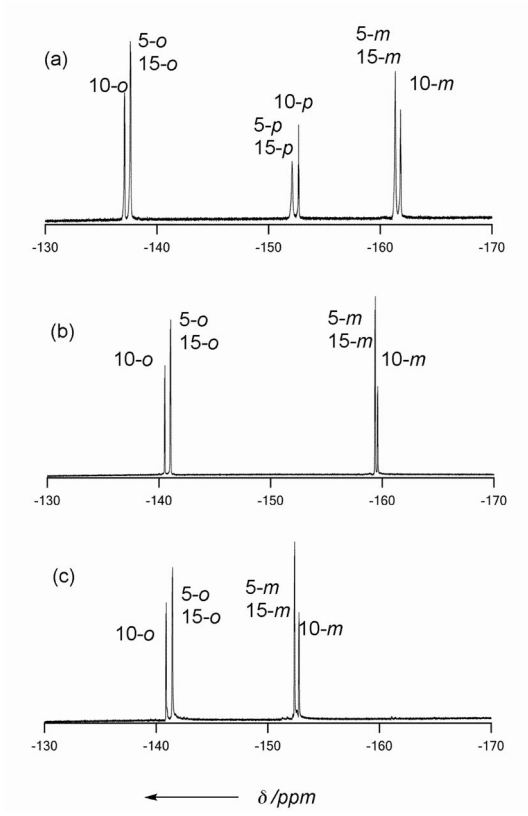
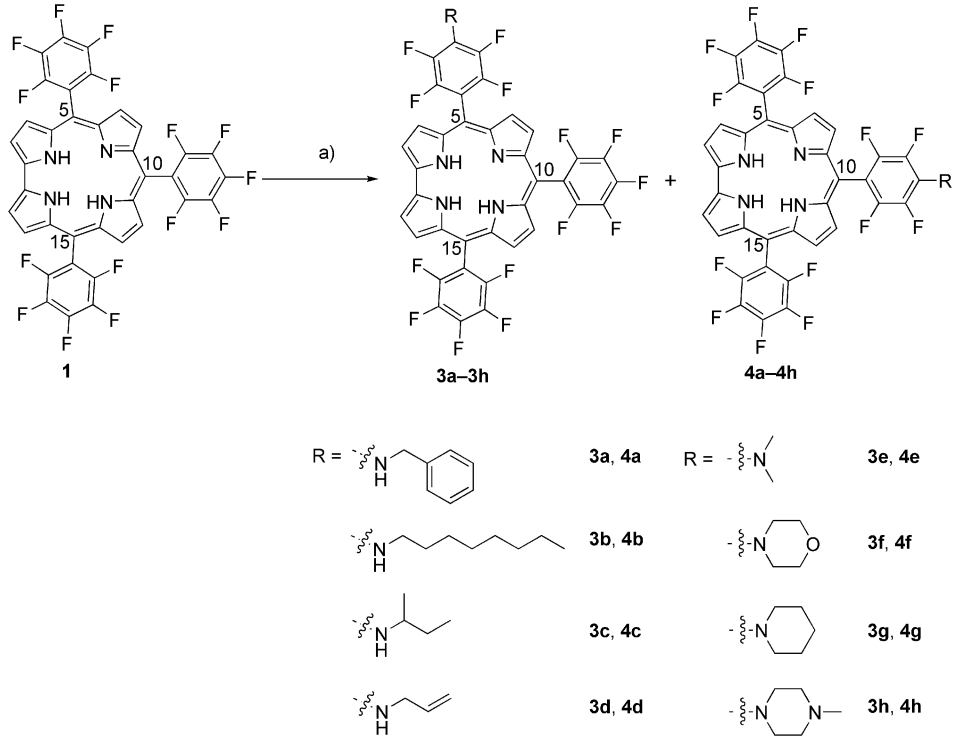


Figure 1. ^{19}F NMR spectra of (a) **1**, (b) **2a**, and (c) **2f** in $CDCl_3$.

In next step, the reaction of **1** with 2.2 equiv. of amine was examined to obtain mono-aminated products (Scheme 2). When the reaction was conducted in DMSO at 100 °C for 24 h, mono-aminated corroles **3a** and **4a** in a combined yield of 38%, along with the recovery of **1** (41%), were obtained. The ratio of **3a** to **4a** was determined to be 3.9:1 on the basis of the ^{19}F NMR spectrum (Figure 2a), indicating higher reactivities of the 5- and 15-pentafluorophenyl substituents than the substituent at the 10-position. The NMR signals were assigned after extensive ^{19}F-^{19}F COSY measurements. Unfortunately, we failed to separate isomers **3a** and **4a**. Under the same conditions, various amines were employed to obtain mono-aminated corroles in comparable yields and **3/4** ratios, despite the structural differences between the primary and secondary amines (Scheme 2 and Table 2).

To understand the preferential reactivity of the 5- or 15-pentafluorophenyl substituents in **1**, DFT calculations were performed at the B3LYP/6-31G* level[15] on the basis of the X-ray crystal structure.[16] It is well known that the lowest unoccupied molecular orbital (LUMO) is the key orbital that determines the reactivity of nucleophilic substitution reactions. Figure 3 shows the LUMO of **1**, which, in line with the experimental results, shows a large coefficient at the *para*-carbon atom in the 5-pentafluorophenyl substituent. LUMO coefficients at the *para*-carbon atom of the



Scheme 2. Syntheses of mono-aminated corroles. *Reagents and conditions:* (a) amine, DMSO, 100 °C, 24 h.

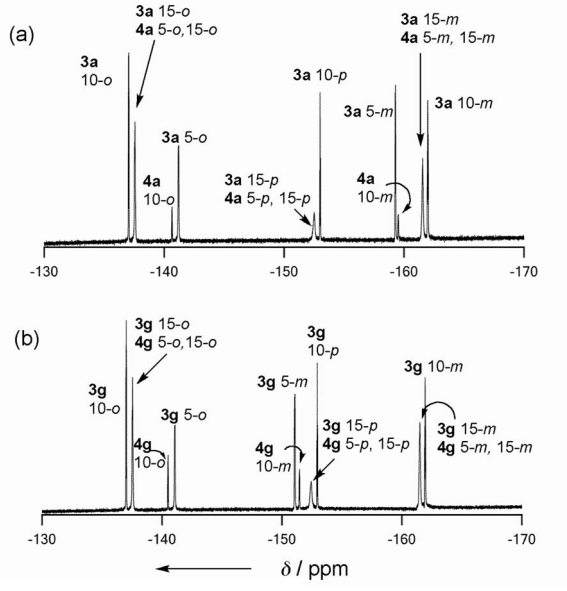


Figure 2. ^{19}F NMR spectra of (a) **3a** and **4a**, and (b) **3g** and **4g** in $CDCl_3$.

Table 2. Synthesis of mono-aminated corroles.

Entry	Amine	Product	Yield[a] [%]	Ratio of **3**/**4**[b]
1	benzylamine	**3a**, **4a**	38	3.9:1
2	octylamine	**3b**, **4b**	36	3.4:1
3	*sec*-butylamine	**3c**, **4c**	27	3.8:1
4	allylamine	**3d**, **4d**	28	3.4:1
5	dimethylamine[c]	**3e**, **4e**	15	4.5:1
6	morpholine	**3f**, **4f**	36	4.2:1
7	piperidine	**3g**, **4g**	38	4.0:1
8	*N*-methylpiperazine	**3h**, **4h**	35	3.8:1

[a] Yield refers to the sum of **3** and **4**. [b] Isomer ratio was determined by integration of ^{19}F NMR spectra. [c] 50% aqueous solution.

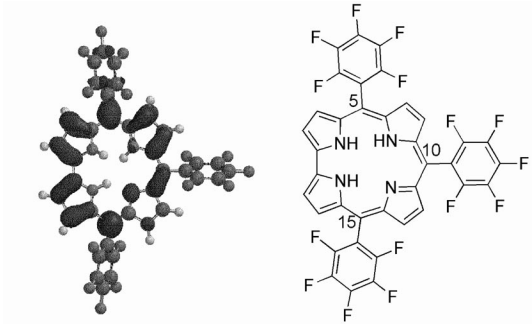
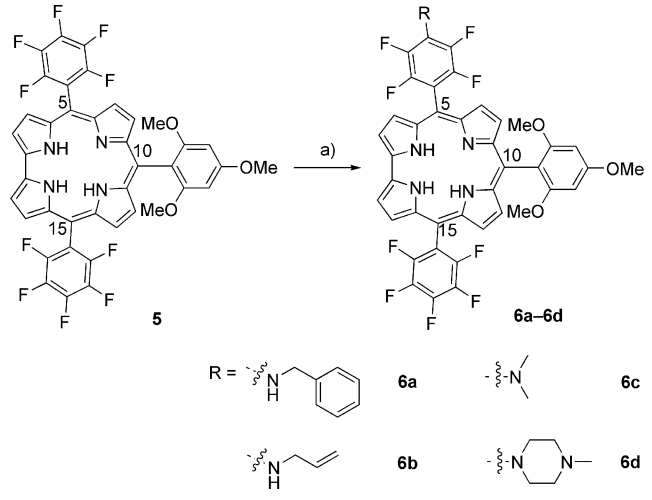


Figure 3. LUMO of **1** calculated at the B3LYP/6-31G* level.

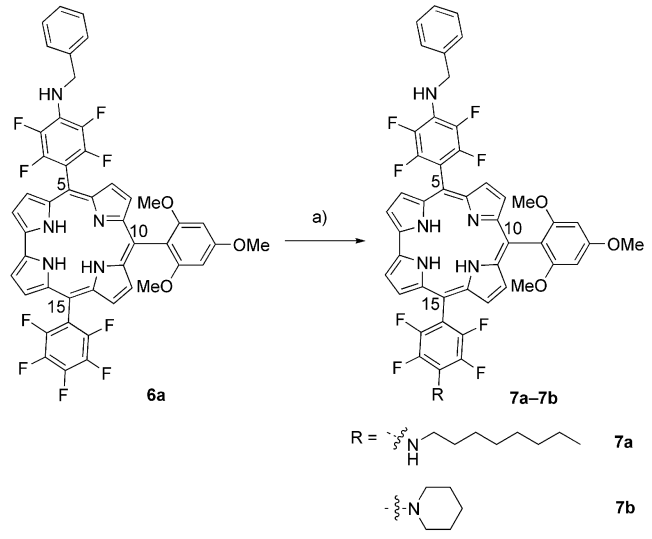
pentafluorophenyl substituents are highest at the 5-position (0.006087), decrease at the 15-position (0.004050), and are lowest at the 10-position (0.001552).

Next, the nucleophilic substitution reaction of corrole with two pentafluorophenyl groups was examined for stepwise amination (Scheme 3). 5,15-Bis(pentafluorophenyl)-10-(2,4,6-trimethoxyphenyl)corrole (**5**) reacted with benzylamine to afford 5-(4-benzylamino-2,3,5,6-tetrafluorophenyl)-10-(2,4,6-trimethoxyphenyl)-15-(pentafluorophenyl)corrole (**6a**) in 21% yield. Similarly, mono-aminated products **6b**, **6c**, and **6d** were obtained in 7, 8, and 6% yields, respectively, from the reaction of **5** with the corre-

sponding amines. Similar substitution reactions of **6a** were then examined so that a new substituent could be introduced to the 15-position. Indeed, ABC-type *meso*-aryl-substituted corroles **7a** and **7b** were prepared in 57 and 81% yields, respectively (Scheme 4).

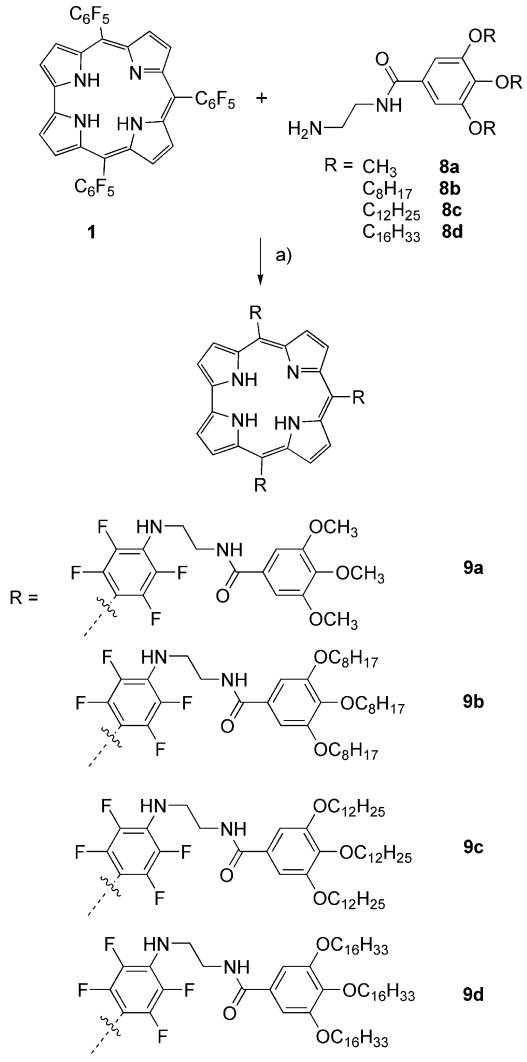


Scheme 3. Reactions of **5** with amines. *Reagents and conditions:* (a) amine, DMSO, 100 °C, 24 h.



Scheme 4. Reactions of **6a** with amines. *Reagents and conditions:* (a) amine, DMSO, 100 °C, 24 h.

As demonstrated above, the nucleophilic substitution reaction of *para*-fluorine atoms at the *meso*-pentafluorophenyl groups enabled the introduction of various substituents to the corrole skeleton. Therefore, we attempted to prepare corrole-based organogels by attaching long chains. In recent years, functional organogels have been explored by using porphyrins as a scaffold,[17] but no corrole-based organogel has yet been reported to the best of our knowledge. Scheme 5 illustrates a synthetic route to corrole derivatives **9**, which bear long alkoxy chains attached through an amide moiety that was designed to serve as a hydrogen-bonding interaction site. Nucleophilic substitution reactions of **1** with amine **8a**, **8b**, **8c**, and **8d** were conducted in 1,4-dioxane because these amines were not soluble in DMSO. The reactions went to completion in one week to give tri-aminated corroles **9a**, **9b**, **9c**, and **9d** in 87, 82, 87, and 69% yields, respectively.



Scheme 5. Syntheses of gelators. *Reagents and conditions:* (a) amine, 1,4-dioxane, reflux, 7 d.

The gelation ability of methoxy-substituted **9a**, octyloxy-substituted **9b**, dodecyloxy-substituted **9c**, and hexadecyloxy-substituted corroles **9d** was investigated in various solvents (Table 3). Corroles **9a** and **9b** did not show any ability to gelate in any of the solvents tested. In aromatic solvents, halogenated solvents, alcohols, and esters, corroles **9c** and **9d** did not form gels, probably due to interactions with solvents; however, they gave dark-green gels in hydrocarbon solvents such as hexane, octane, and cyclohexane. The critical gelation concentration was approximately 10 mg mL^{-1} in each of the hydrocarbon solvents. To study gel formation in detail, UV/Vis absorption spectra of **9d** at 50 mg mL^{-1} in cyclohexane were recorded with a 0.1 cm width cell (Figure 4). At this concentration, the system formed a solution at 70 °C but became a gel at 25 °C. As the temperature was

increased, the intensity of the Soret band at 400 nm decreased and a new peak appeared at 420 nm. The observed hypsochromic shift of the Soret band in the gel form suggests the formation of H-type aggregates. The fluorescence quantum yield of **9d** was 3% in non-gelation solvents such as THF and chloroform, but was only 0.6% in cyclohexane (Table 4).

Table 3. Organic solvents tested for gelation with **9a**, **9b**, **9c**, and **9d**.[a,b]

Solvent	9a	9b	9c	9d
Benzene	I	S	S	S
Toluene	I	S	S	S
p-Xylene	I	S	S	S
Pyridine	P	S	S	S
Anisole	I	S	S	S
Cyclohexane	I	S	G (10)	G (10)
Hexane	I	S	G (10)	G (10)
Octane	I	P	G (10)	G (10)
Hexafluorobenzene	I	I	P	P
1-Butanol	S	S	S	S
2-Propanol	S	S	S	P
1-Hexanol	S	S	S	S
Ethanol	S	S	P	I
Methanol	S	S	I	I
Acetonitrile	S	S	I	I
Ethyl acetate	S	S	S	S
THF	S	S	S	S
1,4-Dioxane	S	S	S	P
DMF	S	S	S	P
Acetone	P	S	S	P
Dichloromethane	P	S	S	S
Chloroform	P	S	S	S

[a] S, G, P, and I denote: solution, gel, precipitation, and insoluble solid, respectively. [b] The critical gelation concentrations [mg mL^{-1}] of gelators are shown in the parentheses.

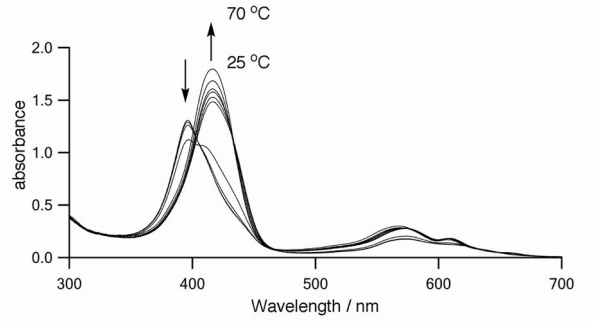


Figure 4. Temperature dependence of the UV/Vis spectra of the cyclohexane gel of **9d**.

Table 4. UV/Vis absorption and fluorescence data of **9d**.

Solvent	λ_{max} in Soret band [nm]	Fluorescence λ_{max} [nm][a]	Quantum yield
Cyclohexane	396	668	0.006
THF	420	673	0.034
$CHCl_3$	418	670	0.029
Toluene	424	667	0.033
EtOAc	416	672	0.043

[a] Excitation wavelength in the fluorescence spectra was λ_{max} in Soret band in each solvent.

Conclusions

In summary, we have explored the aromatic nucleophilic substitution reactions of corroles bearing pentafluorophenyl groups, with several nitrogen-centered nucleophiles. 5,10,15-Tris(pentafluorophenyl)corrole (**1**) reacted with an excess of amine to afford 5,10,15-tris(4-amino-2,3,5,6-tetrafluorophenyl)corroles in good yields. Reaction of **1** with 2.2 equiv. of amines mainly resulted in the formation of 5-(4-amino-2,3,5,6-tetrafluorophenyl)-10,15-bis(pentafluorophenyl)corrole. This selectivity can be explained in terms of the larger coefficients in the LUMO, which arises from effective electronic communication between the pentafluorophenyl group in the 5-position and the corrole core. 5,15-Bis(pentafluorophenyl)-10-(2,4,6-trimethoxyphenyl)corrole (**5**) reacted with amines to generate 5-(4-amino-2,3,5,6-tetrafluorophenyl)-10-(2,4,6-trimethoxyphenyl)-15-(pentafluorophenyl)corrole (**6**). Further amination of **6a** successfully led to the ABC-type corrole. The nucleophilic substitution reaction was applied to the preparation of corrole-based organogel materials of type **9**. Corrole derivatives **9c** and **9d** formed gels in hydrocarbon solvents, giving rise to H-aggregation, the extent of which was judged from hypsochromic shifts in UV/Vis absorption spectra. Consequently, the fluorine displacement methodology developed in this paper has great potential for the production of a wide range of functional corrole derivatives from simple corroles bearing pentafluorophenyl groups.

Experimental Section

General: All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. ^{1}H and ^{19}F NMR spectra were recorded with a JEOL ECA-delta-600 spectrometer operating at 600.17 MHz for ^{1}H and 564.73 MHz for ^{19}F nuclei; chemical shifts (δ) are reported in ppm relative to $CHCl_3$ (δ = 7.260 ppm for ^{1}H) and C_6F_6 (δ = –162.9 ppm for ^{19}F). Spectroscopic grade solvents were used for all spectroscopic studies. UV/Vis absorption spectra were recorded with Shimadzu UV-2550 and UV-3100 spectrometers. Steady-state fluorescence spectra were recorded with a Shimadzu RF-5300PC spectrometer, and a Hamamatsu Photonics C9920–02 spectrometer. High resolution ESI-TOF mass spectra were recorded with a Bruker microTOF instrument and MALDI-TOF mass spectra were recorded with a Bruker microflex instrument. Preparative separations were performed by silica gel gravity column chromatography (Wako-gel C-400). Preparative GPC-HPLC was carried out with a JAI LC-928 instrument by using preparative JAI-GEL-2.5H-40 and 3H-40 columns (eluent: THF; flow rate: 14 mL/min).

Gelation Test: The gelator and solvent were placed in a septum-capped test tube and heated until the solids dissolved completely. The sample vial was cooled to r.t. and left for 1 h. The state of material was evaluated by the test tube inversion method.

5,10,15-Tris(pentafluorophenyl)corrole (1): 5,10,15-Tris(pentafluorophenyl)corrole (**1**) was prepared according to the literature.[7b]

General Procedure for the Synthesis of Tris-Aminated Corroles: A test tube was charged with 5,10,15-tris(pentafluorophenyl)corrole (30 mg, 38 μmol), amine (0.1 mL), and DMSO (1 mL). The re-

sulting solution was stirred for 5 h at 100 °C. After this period, water and $CHCl_3$ were added and the organic layer was separated and dried with Na_2SO_4. Solvent was evaporated and the residue was purified by silica gel column chromatography.

5,10,15-Tris(4-benzylamino-2,3,5,6-tetrafluorophenyl)corrole (2a): The reaction mixture was purified by chromatography (silica; CH_2Cl_2/hexane = 1:1) to give the pure corrole (27 mg, 70%), which was recrystallized from CH_2Cl_2/hexane. ^{1}H NMR (600.17 MHz, $CDCl_3$): δ = 9.01 (d, J = 4.6 Hz, 2 H, β-H), 8.76 (d, J = 4.6 Hz, 2 H, β-H), 8.57 (d, J = 4.6 Hz, 2 H, β-H), 8.50 (br. s, 2 H, β-H), 7.54 (d, J = 7.4 Hz, 6 H, *o*-PhH), 7.48 (t, J = 7.1 Hz, 6 H, *m*-PhH), 7.41 (t, J = 7.3 Hz, 3 H, *p*-PhH), 4.84–4.83 (m, 6 H, benzyl), 4.53 (br. s, 2 H, NH), 4.49 (br. s, NH, 1 H) ppm. ^{19}F NMR (564.73 MHz, $CDCl_3$): δ = –140.5 (d, J = 15.6 Hz, 2 F, 10-*ortho*), –141.1 (d, J = 17.2 Hz, 4 F, 5-*ortho*, 15-*ortho*), –159.4 (d, J = 17.2 Hz, 4 F, 5-*meta*, 15-*meta*), –159.6 (d, J = 15.6 Hz, 2 F, 10-*meta*) ppm. ESI-MS: calcd. for $C_{58}H_{34}F_{12}N_7$ 1056.2679; found 1056.2676 [M – H]$^-$. UV/Vis ($CHCl_3$): λ_{max} (ε, $m^3 mol^{-1} cm^{-1}$) = 417 (142000), 569 (24400), 607 (14000) nm. Fluorescence ($CHCl_3$, λ_{ex} = 417 nm): λ_{em} = 653 nm.

General Procedure for the Synthesis of Mono-Aminated Tris-(pentafluorophenyl)corroles: A test tube was charged with 5,10,15-tris-(pentafluorophenyl)corrole (**1**) (30 mg, 38 μmol), amine (2.2 equiv. cf. **1**), and DMSO (1 mL). The resulting solution was stirred for 24 h at 100 °C. After this period, water and $CHCl_3$ were added and the organic layer was separated and dried with Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel chromatography.

Mono-Benzylaminated Corroles 3a and 4a: The reaction mixture was purified by chromatography (silica; CH_2Cl_2/hexane = 1:1) to give the mono-benzylaminated corrole (12 mg, 38% yield) as mixture of **3a** and **4a** (3.9:1) along with recovered **1** (12 mg, 41% yield). ^{1}H NMR (600.17 MHz, $CDCl_3$): δ = 9.01 [d, J = 4.1 Hz, 3 H (1 H, **3a** β-H; 2 H, **4a** β-H)], 9.05 (d, J = 4.1 Hz, 1 H, **3a** β-H), 8.56 (d, J = 4.1 Hz, 1 H, **3a** β-H), 8.73 [d, J = 4.6 Hz, 3 H (1 H, **3a** β-H; 2 H, **4a** β-H)], 8.67 (d, J = 4.6 Hz, 2 H, **4a** β-H), 8.56–8.54 [m, 6 H (2 H, **3a** β-H; 4 H, **4a** β-H)], 7.53 [d, J = 7.3 Hz, 4 H (2 H, **3a** *o*-PhH; 2 H, **4a** *o*-PhH)], 7.47 [t, J = 7.7 Hz, 4 H (2 H, **3a** *m*-PhH; 2 H, **4a** *m*-PhH)], 7.40 [t, J = 7.3 Hz, 2 H (1 H, **3a** *p*-PhH; 1 H, **4a** *p*-PhH)], 4.82 [m, 4 H (2 H, **3a** Ph-CH_2-; 2 H, **4a** Ph-CH_2-)], 4.55–4.50 [m, 2 H (1 H **3a** benzyl-N*H*-; 1 H, **4a** benzyl-N*H*-)] ppm. ^{19}F NMR (564.73 MHz, $CDCl_3$): δ = –137.06 (dd, J = 20.3, 8.6 Hz, 2 F, **3a** 10-*ortho*), –137.50 [d, J = 18.9 Hz, 6 F (2 F, **3a** 15-*ortho*; 4 F, **4a** 5-*ortho* and 15-*ortho*)], –140.68 (d, J = 20.6 Hz, 2 F, **4a** 10-*ortho*), –141.20 (J = 19.0 Hz, 2 F, **3a** 5-*ortho*), –152.53 [br. s, 3 F (1 F, **3a** 15-*para*; 2 F, **4a** 5-*para* and 15-*para*)], –153.00 (t, J = 20.7 Hz, 1 F, **3a** 10-*para*), –159.27 (d, J = 15.5 Hz, 2 F, **3a** 5-*meta*), –159.54 (d, J = 15.5 Hz, 2 F, **4a** 10-*meta*), –161.48 [br. s, 6 F (2 F, **3a** 15-*meta*; 4 F, **4a** 5-*meta* and 15-*meta*)], –161.98 (dt, J = 23.3, 6.9 Hz, 2 F, **3a** 10-*meta*) ppm. MALDI-TOF MS: calcd. for $C_{44}H_{18}F_{14}N_5$ 882.63; found 882.82 [M – H]$^-$.

5,15-Bis(pentafluorophenyl)-10-(2,4,6-trimethoxyphenyl)corrole (5): 5-Pentafluorophenyldipyrromethane (2.17 g, 6.97 mmol) and 2,4,6-trimethoxybenzaldehyde (0.684 g, 3.49 mmol) were added to CH_2Cl_2 (270 mL). TFA (60 μL) was added to the reaction mixture, which was was stirred for 24 h at r.t. in the dark. *p*-Chloranil (2.125 g) was added and the mixture was stirred for an additional 30 min. 5,15-Bis(pentafluorophenyl)-10-(2,4,6-trimethoxyphenyl)-corrole (**5**) (124 mg, 5%) was obtained after silica gel column chromatography (CH_2Cl_2/hexane = 1:1). ^{1}H NMR (600.17 MHz, $CDCl_3$): δ = 9.03 (d, J = 4.1 Hz, 2 H, β-H), 8.79 (d, J = 4.6 Hz, 2 H, β-H), 8.59 (br. s, 4 H, β-H), 8.49 (br. s, 2 H, β-H), 6.57 (s, 2 H, PhH), 4.10 (s, 3 H, *p*-OMe), 3.54 (s, 6 H, *o*-OMe) ppm. ^{19}F NMR (564.73 MHz, $CDCl_3$): δ = –137.6 (br. s, 4 F, 10-*ortho* and 15-*ortho*), –153.2 (br. s, 2 F, 5-*para* and 15-*para*), –161.9 (br. s, 10-*meta* and 15-*meta*, 4 F) ppm. ESI-MS: calcd. for $C_{40}H_{21}F_{10}N_4O_3$ 795.1448; found 795.1452 [M – H]$^-$. UV/Vis ($CHCl_3$): λ_{max} (ε, $m^3 mol^{-1} cm^{-1}$) = 415 (96500), 564 (19400), 614 (13600) nm. Fluorescence ($CHCl_3$, λ_{ex} = 415 nm): λ_{em} = 648 nm.

General Procedure for the Synthesis of Mono-Aminated 5,15-Bis-(pentafluorophenyl)-10-(2,4,6-trimethoxyphenyl)corroles: A test tube was charged with 5,15-bis(pentafluorophenyl)-10-(2,4,6-trimethoxyphenyl)corrole (30 mg, 38 μmol), amine (2.2 equiv. cf. corrole), and DMSO (1 mL). The resulting solution was stirred for 24 h at 100 °C. After this period, water and $CHCl_3$ were added and the organic layer was separated and dried with Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel chromatography.

5-(4-Benzylamino-2,3,5,6-tetrafluorophenyl)-10-(2,4,6-trimethoxyphenyl)-15-(pentafluorophenyl)corrole (6a): The reaction mixture was purified by chromatography (silica; CH_2Cl_2/hexane = 1:1) to give the pure corrole (7 mg, 21% yield), which was recrystallized from CH_2Cl_2/hexane. ^{1}H NMR (600.17 MHz, $CDCl_3$): δ = 9.00 (d, J = 4.1 Hz, 1 H, β-H), 8.97 (d, J = 4.1 Hz, 1 H, β-H), 8.67 (d, J = 4.6 Hz, 1 H, β-H), 8.57 (m, 3 H, β-H), 8.49 (d, J = 4.1 Hz, 1 H, β-H), 8.48 (d, J = 4.1 Hz, 1 H, β-H), 7.53 (d, J = 7.3 Hz, 2 H, *o*-PhH), 7.48 (t, J = 7.3 Hz, 2 H, *m*-PhH), 7.41 (t, J = 7.3 Hz, 1 H, *p*-PhH), 6.58 (s, 2 H, PhH), 4.84 (d, J = 6.4 Hz, 2 H, benzyl), 4.48 (br. s, 1 H, benzyl-N*H*), 4.09 (s, 3 H, *p*-OMe), 3.53 (s, 6 H, *o*-OMe) ppm. ^{19}F NMR (564.73 MHz, $CDCl_3$): δ = –137.6 (d, J = 19.0 Hz, 2 F, 15-*ortho*), –140.9 (d, J = 17.3 Hz, 2 F, 5-*ortho*), –153.8 (t, J = 18.9 Hz, 1 F, 15-*para*), –159.6 (d, J = 15.6 Hz, 2 F, 5-*meta*), –162.1 (t, J = 19.1 Hz, 2 F, 15-*meta*) ppm. ESI-MS: calcd. for $C_{47}H_{29}F_9N_5O_3$ 882.2121; found 882.2106 [M – H]$^-$. UV/Vis ($CHCl_3$): λ_{max} (ε, $m^3 mol^{-1} cm^{-1}$) = 415 (81500), 569 (15500), and 617 (11600) nm. Fluorescence ($CHCl_3$, λ_{ex} = 417 nm): λ_{em} = 650 nm.

General Procedure for the Synthesis of Mono-Aminated Benzyl-aminated Corroles: A test tube was charged with 5-(4-benzylamino-2,3,5,6-tetrafluorophenyl)-10-(2,4,6-trimethoxyphenyl)-15-(pentafluorophenyl)corrole (**6a**) (10 mg, 12 μmol), amine (5 equiv. cf. corrole), and DMSO (1 mL). The resulting solution was stirred for 5 h at 100 °C. After this period, water and $CHCl_3$ were added and the organic layer was separated and dried with Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel chromatography.

5-(4-Benzylamino-2,3,5,6-tetrafluorophenyl)-10-(2,4,6-trimethoxyphenyl)-15-(4-octylamino-2,3,5,6-tetrafluorophenyl)corrole (7a): The reaction mixture was purified by chromatography (silica; CH_2Cl_2/hexane = 2:1) to give the pure corrole (6 mg, 57% yield), which was recrystallized from CH_2Cl_2/hexane. ^{1}H NMR (600.17 MHz, $CDCl_3$): δ = 8.96 (d, J = 4.1 Hz, 1 H, β-H), 8.97 (d, J = 4.6 Hz, 1 H, β-H), 8.64 (d, J = 4.6 Hz, 1 H, β-H), 8.54 (d, J = 4.1 Hz, 2 H, β-H), 8.50 (br. s, 2 H, β-H), 7.54 (d, J = 7.3 Hz, 2 H, *o*-PhH), 7.48 (t, J = 7.4 Hz, 2 H, *m*-PhH), 7.40 (t, J = 6.9 Hz, 1 H, *p*-PhH), 6.57 (s, 2 H, PhH), 4.82 (d, J = 6.4 Hz, 2 H, benzyl), 4.48 (br. s, 1 H, benzyl-N*H*), 4.14 (br. s, 1 H, octyl-N*H*), 4.09 (s, 3 H, *p*-OMe), 3.65 (q, J = 6.9 Hz, 2 H, C_7H_{15}-CH_2-NH-), 3.52 (s, 6 H, *o*-OMe), 1.81 (quin, J = 7.3 Hz, 2 H, C_6H_{13}-CH_2-CH_2-NH-), 1.46–1.25 (m, 10 H, alkyl), 0.95 (t, J = 6.9 Hz, 3 H, CH_3-C_7H_{14}-NH-) ppm. ^{19}F NMR (564.73 MHz, $CDCl_3$): δ = –140.9 (d, J = 18.9 Hz, 2 F, *ortho*), –141.4 (d, J = 15.5 Hz, 2 F, *ortho*), –159.5 (d, J = 17.3 Hz, 2 F, *meta*), –160.7 (d, J = 17.1 Hz, 2 F, *meta*) ppm. ESI-MS: calcd. for $C_{55}H_{47}F_8N_6O_3$ 991.3576; found 991.3558 [M – H]$^-$. UV/Vis

($CHCl_3$): λ_{max} (ε, $m^3 mol^{-1} cm^{-1}$) = 418 (77000), 567 (13400), 614 (8800) nm. Fluorescence ($CHCl_3$, λ_{ex} = 418 nm): λ_{em} = 655 nm.

Corrole 9a: A test tube was charged with 5,10,15-tris(pentafluorophenyl)corrole (30 mg, 38 μmol), **8a** (0.41 g, 0.56 mmol), and 1,4-dioxane (1 mL). The resulting solution was stirred for a week at reflux temperature. After this period, the reaction mixture was passed through a short silica gel column with THF as eluent. The solvent was evaporated and the residue was purified by preparative GPC-HPLC to afford pure **9a** (75 mg, 87% yield). ^{1}H NMR (600.17 MHz, $CDCl_3$): δ = 8.95 (d, J = 3.7 Hz, 2 H, β-H), 8.70 (d, J = 4.6 Hz, 2 H, β-H), 8.52 (d, J = 4.1 Hz, 2 H, β-H), 8.45 (s, 2 H, β-H), 7.04 (s, 4 H, ArH), 7.03 (s, 2 H, ArH), 6.53 (s, 3 H, amide-N*H*), 4.82 (s, 2 H, amine-N*H*), 4.73 (s, 1 H, amine-N*H*), 3.93–3.79 [m, 39 H (27 H, -O-CH_3; 12 H, -NH-CH_2-CH_2-NH-)] ppm. ^{19}F NMR (564.73 MHz, $CDCl_3$): δ = –141.8 (d, J = 15.5 Hz, 2 F, 5-*ortho* and 15-*ortho*), –142.4 (s, 4 F, 10-*ortho*), –160.2 (d, J = 17.3 Hz, 4 F, 5-*meta* and 15-*meta*), –161.6 (s, 2 F, 10-*meta*) ppm. MALDI-TOF MS: calcd. for $C_{73}H_{62}F_{12}N_{10}O_{12}$ 1499; found 1499. UV/Vis ($CHCl_3$): λ_{max} (ε, $m^3 mol^{-1} cm^{-1}$) = 420 (119000), 575 (23400), 605 (16000) nm. Fluorescence ($CHCl_3$, λ_{ex} = 420 nm): λ_{em} = 659 nm.

Supporting Information (see also the footnote on the first page of this article): Compound data and experimental details.

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