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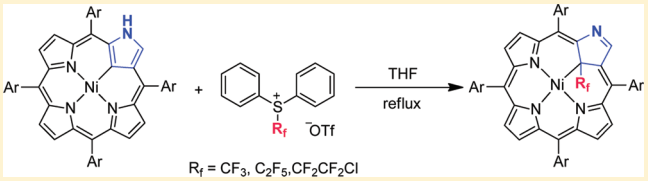
Electrophilic Fluoroalkylation of Ni(II) *N*-Confused Porphyrins with Fluoroalkylarylsulfonium Salts

Fei Hao, Hua-Wei Jiang, Guoqiang Zong, Zhiguo Zhou, Ruo-Bing Du, Qing-Yun Chen, and Ji-Chang Xiao*

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road 200032, P. R. China

Supporting Information

ABSTRACT: Experimental studies showed that Ni(II) *N*-confused porphyrins, treated with fluoroalkylarylsulfonium salts, can undergo an electrophilic fluoroalkylation at the inner 21-C position, leading to 21-fluoroalkylated Ni(II) *N*-confused porphyrins.



The fluorinated porphyrin derivatives have been widely investigated because of their unique properties.[1] Importantly, when localized to a tumor tissue, fluorinated porphyrin derivatives can be used as a tracer by ^{19}F NMR imaging.[1g,2] What is more, the introduction of fluorine substituent to the porphyrin macrocycle might give additional stability and lipophilicity and therefore increase their antitumor activity.[3] These advantages over ordinary porphyrins make fluorinated porphyrin derivatives potential candidates for photodynamic therapy (PDT). The fluorinated porphyrin derivatives have also been proven to be effective catalysts. In 1989, Tsuchiya's group found that perfluorinated Fe(III) porphyrin, which could resist the porphyrin skeleton to oxidative degradation, effectively catalyzed the cyclooxidation of alkenes and the hydroxylation of benzene.[4] There is a special advantage of fluorinated porphyrins over the common porphyrins in organometallic catalysis field. That is, (*β*-perfluoroalkylated tetraphenylporphyrin)cobalt complex, which could dissolve in the perfluorinated solvents, could catalyze the epoxidation of different alkenes with atmospheric air under fluorous biphasic system other than pure oxygen or high pressure air.[5] Besides these advantages in catalysis, the fluorine-containing porphyrins have also been applied in semiconductor materials, molecular devices, etc.[6] However, the synthesis of fluorine-containing metalloporphyrins was very challenging. The traditional method,[7] starting from fluorinated pyrrole or aldehyde, usually took several steps, leading to very low yields.

In 1999, the Tsudzuki group realized the direct electrophilic trifluoromethylation of porphyrins with Umemoto's reagent, *S*-(trifluoromethyl)-3,7-dinitrobenzothiophenium trifluoromethanesulfonate.[8] Introduction of a fluoroalkyl group onto the porphyrin macrocycle through direct fluoroalkylation was much more effective than the traditional procedure. We have been interested in fluorine-containing porphyrin chemistry. Several efficient methods for direct fluoroalkylation of porphyrins such as modified sulfinatodehalogenation,[9] copper-induced fluoroalkylation,[10] and Pd-catalyzed fluoroalkylation[11] have been developed. Some of the fluoroalkylated porphyrins showed interesting properties and potential application in catalysis and material science. For example, we observed the self-assembly and thermal behavior of 5-fluoroalkyl-10,20-diarylporphyrins[12] and documented the synthesis and unique properties of the nonaromatic 20 *π*-electron *β*-tetrakis-(trifluoromethyl)-*meso*-tetraphenylporphyrins.[13] Then we extended our research from normal porphyrins to *N*-confused porphyrins, which were first reported by Furuta[14] and Latos-Grażyński[15] in 1994, respectively, focusing on the application of fluoroalkylated *N*-confused metalloporphyrins in catalysis. In 2008, we successfully synthesized the inner fluoroalkylated Ni(II) *N*-confused porphyrins.[16] However, perfluoroalkyl iodides should be added in large excess, and high temperature (100 °C) was required for the fluoroalkylation. Moreover, trifluoromethyl Ni(II) *N*-confused porphyrins could not be obtained from this procedure.

Recently, we investigated the synthesis of fluoroalkylarylsulfonium salts and their electrophilic fluoroalkylations.[17] Considering the electronic properties of *N*-confused porphyrins, we assumed that the electrophilic fluoroalkylation of Ni(II) *N*-confused porphyrins with fluoroalkylarylsulfonium salts would similarly happen. Herein, we report our results.

We initiated this study with the reaction of Ni(II) *N*-confused porphyrins (**Ni1**) with 5 equiv of trifluoromethyldiphenylsulfonium salt ($CF_3SPh_2^+OTf^-$, **a**) in anhydrous THF for 3 days. **Ni1** disappeared completely and afforded a purple compound in 60% yield after flash chromatography. The chemical shift at −58.73 ppm observed in ^{19}F NMR and the $[M + H]^+$ peak at 739.2 in MALDI-MS implied that the trifluoromethyl group linked to the Ni(II) NCP macrocycle. The chemical shift at *δ* 10.07 ppm in ^{1}H NMR indicated that C(3)H was retained and the six *β*-pyrrole protons could be observed at *δ* 8.44−8.70 ppm in the ^{1}H NMR. These data together showed that the trifluoromethyl group was introduced into the inner 21-C of **Ni1** (Scheme 1). The inner trifluoromethyl Ni(II) *N*-confused porphyrins was not obtained previously from the copper-induced fluoroalkylation, as the

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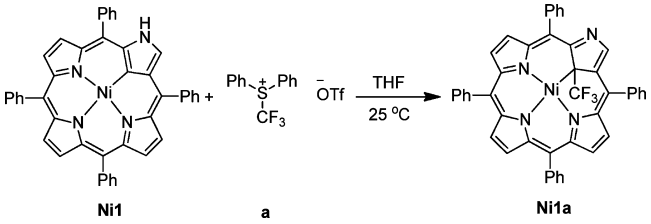
Scheme 1. Synthesis of Inner 21-C Trifluoromethyl Ni(II)NCP (Ni1a)



trifluoromethyl iodide is a gas at 100 °C and therefore escaped from the reaction mixture.

The single-crystal X-ray structure (CCDC 833912) further confirmed that the trifluoromethyl group was attached to the inner 21-C. From the side view, it was observed that the trifluoromethyl group was almost perpendicular to the macrocycle plane (Figure 1). Selected bond lengths of inner

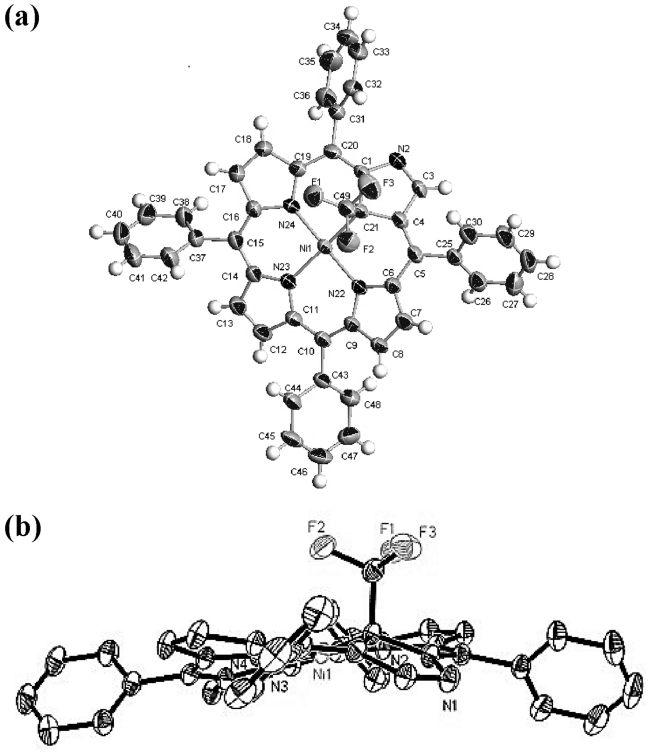


Figure 1. Molecular structure of compound **Ni1a**. The solvent $CDCl_3$ was omitted for clarity: (a) top view; (b) side view.

21-C are shown in Table 1. It was found that the C(21)−Ni bond length (2.015 Å) is in the length range of a Ni(II)−C

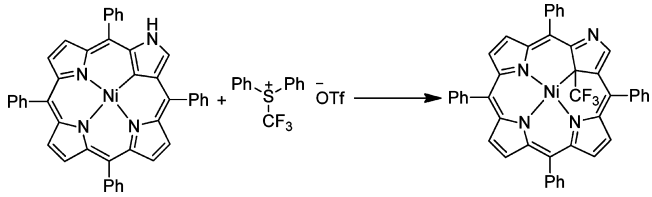
Table 1. Length of C21-Linked Four Bonds

bond	C(21)−C(1)	C(21)−C(4)	C(21)−C(49)	C(21)-Ni
bond length (Å)	1.505	1.478	1.526	2.015

single bond (1.81−2.02 Å).[18] That is to say, C(21) has been linked with four single bonds. This structure was very similar to the methylation product of NiNCP.[19a] Though the alkylation of the NiNCPs has been well established,[19] however, the fluoroalkylation could not be achieved by the reaction of NiNCP and perfluoroalkyl iodide under the alkylation reaction conditions because of the totally different chemical properties of the perfluoroalkyl halide from alkyl halide. The work further showed that fluoroalkylarylsulfonium salts were effective fluoroalkylation reagents[17] and could be applied in the synthesis the fluoroalkylated NiNCPs.

The reaction conditions were optimized by screening the amount of $CF_3SPh_2^+OTf^-$, temperature, concentration, and solvents (Table 2). It was found that 10 equiv of

Table 2. Fluoroalkylation of Ni1 with $CF_3SPh_2^+OTf^-$ under Various Conditions[a]



entry	solvent (mL)	$CF_3SPh_2^+O$-Tf$^-$ (equiv)	temp (°C), time	yield[b] (%)
1	THF (10)	5	rt, 3 d	60
2	THF (10)	10	rt, 3 d	61
3	THF (10)	15	rt, 3 d	43
4	THF (10)	20	rt, 2 d	40
5	THF (10)	30	rt, 2 d	39
6	THF (10)	5	reflux, 8 h	44
7	THF (10)	10	reflux, 8 h	61
8	THF (10)	30	reflux, 8 h	51
9	THF (5)	10	reflux, 8 h	75
10	THF (20)	10	reflux, 8 h	53
11	dioxane (5)	10	reflux, 8 h	52
12	toluene (5)	10	reflux, 8 h	11
13	DCE (5)	10	reflux, 8 h	55

[a]33.6 mg (0.05 mmol) of **Ni1** was used. [b]Isolated yield.

$CF_3SPh_2^+OTf^-$ was needed to facilitate the reaction (Table 2, entries 1−5). A smaller amount of $CF_3SPh_2^+OTf^-$ would slow the reaction, while a larger excess of $CF_3SPh_2^+OTf^-$ would lead to the degradation of the product **Ni1**. When the reaction was conducted at reflux temperature (Table 2, entries 6−8), the reaction time was shortened to only 8 h. The concentration also had great influence on the yield. Thus, suitable amounts of solvent were necessary for the reaction (Table 2, entries 7, 9, and 10). Then, different solvents such as dioxane, toluene, and DCE were examined, but no obvious improvement was observed. On the basis of these results, the optimized reaction conditions were 33.6 mg (0.05 mmol) of **Ni1** and 10 equiv of sulfonium salt in 5 mL of refluxing THF.

With the optimal reaction conditions in hand, the scope of this reaction was then examined. As shown in Table 3, the desired fluoroalkylated NiNCPs were obtained smoothly for each substrate. It is worth mentioning that the substituent at the para-position of the phenyl moiety had a great influence on the reaction yield. The yield for **Ni3a−c** (Table 3, entries 3, 6, and 9) was lower than that for **Ni1a−c** (Table 3, entries 1, 4, and 7), which might be due to the decreased electron density of the porphyrin macrocycle with a para electron-withdrawing group (-Cl) in **Ni3a−c**. It might be expected that the yields for **Ni2a−c** with a methyl group at the para-position on the phenyl ring would be higher. However, the yields for **Ni2a−c** (Table 3, entries 2, 5, and 8) were much lower compared to those for **Ni1a−c** and **Ni3a−c**. This might be because of the higher susceptibility of **Ni2** to oxidation[20] and the fluoroalkyl

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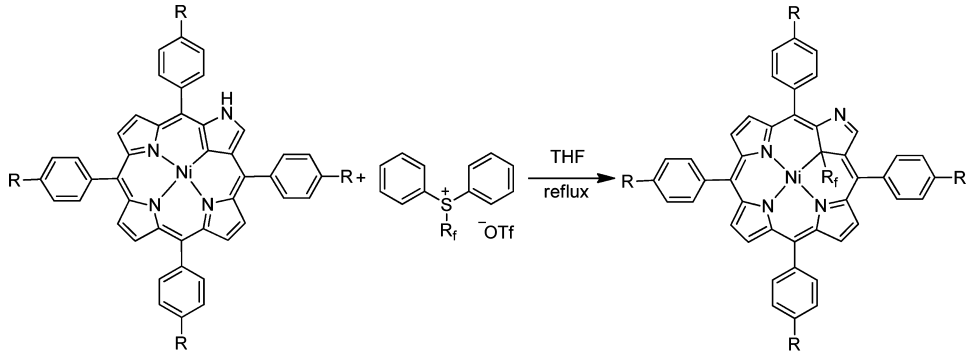
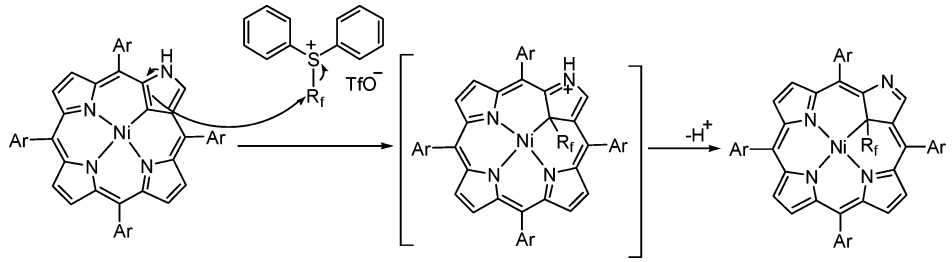
Table 3. Fluoroalkylation of Ni(II) NCPs with Fluoroalkylarylsulfonium Salts[a]



entry	Ni(II) NCP	sulfonium salt	time (h)	product	yield[b] (%)
1	**Ni1**	**a**	8	**Ni1a**	75
2	**Ni2**	**a**	5	**Ni2a**	60
3	**Ni3**	**a**	9	**Ni3a**	65
4	**Ni1**	**b**	2.5	**Ni1b**	43
5	**Ni2**	**b**	2	**Ni2b**	36
6	**Ni3**	**b**	3	**Ni3b**	39
7	**Ni1**	**c**	2.5	**Ni1c**	38
8	**Ni2**	**c**	2	**Ni2c**	33
9	**Ni3**	**c**	3	**Ni3c**	35

[a]General conditions: 0.05 mmol of NiNCP, 0.5 mmol of fluoroalkylarylsulfonium salt, 5 mL of THF. [b]Isolated yield.

Scheme 2. Proposed Mechanism



sulfonium salts **a**–**c** used in the reaction are somewhat oxidative.[17a] The substituents on the phenyl ring affected the electrophilic fluoroalkylation through their effects on the electron density of the macrocyclic system, and also influenced the oxidizability of NiNCPs. Compared with our previous copper-induced fluoroalkylation method, in which 100 equiv of fluoroalkyl iodide is necessary when preparing **Ni1c**–**Ni3c**,[16] much smaller amounts of fluoroalkylation reagent (10 equiv) were needed for the completion of the reaction according to the present procedure (Table 3, entries 7–9).

A possible mechanism was proposed as shown in Scheme 2. First, 21-C attacks the fluoroalkyl group of the sulfonium salt, leading to the opening of the carbon–carbon double bond. Subsequently, the release of the proton yields the inner fluoroalkylated Ni(II) NCP. This direct electrophilic fluoroalkylation was quite different from the previous fluoroalkylcopper mechanism.[16]

In conclusion, the direct and mild electrophilic fluoroalkylation of Ni(II) *N*-confused porphyrins was realized by using fluoroalkylarylsulfonium salts. The inner trifluoromethyl Ni(II) *N*-confused porphyrins was successfully obtained through this approach. The interesting substitution effect at the para-position of the phenyl moiety was found. Further studies on the properties and applications of fluoroalkylated *N*-confused porphyrins are now underway.

■ EXPERIMENT SECTION

THF was distilled over sodium with benzophenone as oxygen presence indicator in argon atmosphere. NiNCPs and fluoroalkylarylsulfonium salts were prepared according to the reported literatures.[15,17a,b,21] Other chemicals were used without purification.

Typical Procedure for the Synthesis of 21-Fluoroalkylated Ni(II) *N*-Confused Porphyrins. A mixture of **Ni1** (33.6 mg, 0.05 mmol) and **a** (202.3 mg, 0.5 mmol) was heated in 5 mL of THF under reflux for 3–8 h. The reaction course was monitored by TLC. When **Ni1** was totally consumed, the reaction mixture was evaporated by rotary evaporator to dryness. After column chromatography on silica gel using CH_2Cl_2 as an eluent (the first band was collected) and crystallization from CH_2Cl_2/hexane, a purple solid **Ni1a** was obtained.

Ni1a: amorphous solid, 27.8 mg, yield 75%, melting point over 300 °C. A single crystal of **Ni1a** was obtained by recrystallization from $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 8.68 (d, J = 4.8 Hz, 1H), 8.65 (d, J = 5.6 Hz, 1H), 8.54 (d, J = 2.8, 1H), 8.53 (d, J = 2.8, 1H), 8.48 (d, J = 5.2 Hz, 1H), 8.44 (d, J = 4.8 Hz, 1H), 7.66 - 8.12

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(m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ172.9, 160.0, 157.5, 155.6, 149.6, 148.7, 147.9, 146.9, 146.8, 140.7, 140.6, 140.3, 140.2, 136.1, 135.4, 135.2, 135.0, 134.1, 134.0, 133.9, 133.8, 133.7, 133.6, 133.6, 133.5, 133.4, 133.4, 133.1, 133.0, 132.6, 132.0, 129.2, 129.1, 128.9, 128.3, 128.2, 128.2, 128.2, 127.97, 127.6, 126.9, 126.9, 126.7, 124.9, 121.4 (q, J = 281 Hz, CF_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ −58.73 (s, 3F). UV/vis (CH_2Cl_2): λ_{max} (relative intensity) = 318 (2.8), 434 (8.8), 551 (1.0) nm. HRMS (MALDI): calcd for $[C_{45}H_{27}N_4F_3Ni + H]^+$ 739.1614, found 739.1606.

Ni1b: amorphous solid, 17.0 mg, yield 43%, melting point over 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 8.58−8.61 (m, 2H), 8.49−8.50 (m, 2H), 8.45−8.47 (m, 1H), 8.42−8.43 (m, 1H), 7.68−8.12 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 160.3, 157.2, 156.4, 156.1, 149.9, 148.9, 148.8, 148.1, 148.0, 147.8, 146.8, 140.8, 140.7, 140.5, 140.4, 135.7, 135.6, 134.7, 134.6, 134.0, 133.8, 133.1, 133.0, 132.4, 132.2, 132.1, 129.8, 129.1, 129.1, 128.4, 128.3, 128.2, 128.2, 128.1, 127.9, 127.9, 126.9, 126.5, 124.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −80.83 (s, 3F), −99.12, −100.26 (AB, J_{AB} = 256.4 Hz, 2F). UV/vis (CH_2Cl_2): λ_{max} = 435 nm. HRMS (MALDI): calcd for $[C_{46}H_{27}N_4F_5Ni + H]^+$ 789.1582, found 789.1558.

Ni1c: amorphous solid, 15.3 mg, yield 38%, melting point over 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 8.61 (m, 2H), 8.43−8.50 (m, 4H), 7.69−8.12 (m, 20H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.30, −65.38 (AB, J_{AB} = 167.7 Hz, 2F), −92.18 to −92.14 (m, 2F). HRMS (MALDI): calcd for $[C_{46}H_{27}N_4F_4ClNi + H]^+$ 805.1287, found 805.1289.

Ni2a: amorphous solid, 23.9 mg, yield 60%, melting point over 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 8.68−8.65 (m, 2H), 8.53 (d, J = 5.2 Hz, 2H), 8.48 (d, J = 4.4 Hz, 1H), 8.44 (d, J = 4.4 Hz, 1H), 7.48−8.12 (m, 16H), 2.62−2.66 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 160.0, 157.5, 155.7, 149.7, 148.7, 147.9, 147.1, 146.8, 139.1, 138.2, 138.0, 137.9, 137.9, 137.8, 137.7, 137.6, 135.8, 135.4, 135.3, 134.8, 133.7, 133.1, 132.8, 132.4, 131.8, 128.9, 128.9, 128.7, 127.7, 127.6, 127.6, 126.6, 124.8, 21.6, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −58.78 (s, 3F). UV/vis (CH_2Cl_2): λ_{max} (relative intensity) = 338 (9.4), 437 (2.8), 551 (1.0) nm. HRMS (MALDI): calcd for $[C_{49}H_{35}N_4F_3Ni + H]^+$ 795.2240, found 795.2215.

Ni2b: amorphous solid, 15.2 mg, yield 36%, melting point over 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (d, J = 0.8 Hz, 1H), 8.58−8.61 (m, 2H), 8.50 (d, J = 5.2 Hz, 2H), 8.45−8.47 (m, 1H), 8.41−8.43 (m, 1H), 7.49−8.00 (m, 16H), 2.61−2.65 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 160.2, 156.9, 156.2, 149.9, 149.0, 147.8, 146.9, 139.2, 139.1, 138.3, 138.2, 138.0, 138.0, 137.9, 137.9, 137.8, 137.8, 135.4, 135.3, 134.4, 134.3, 133.9, 133.0, 132.8, 132.3, 131.9, 129.7, 129.0, 128.9, 128.8, 128.7, 127.7, 127.6, 126.4, 124.7, 21.5, 21.5, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −80.92 (s, 3F), −99.28, −100.45 (AB, J_{AB} = 186.1 Hz, 2F). UV/vis (CH_2Cl_2): λ_{max} (relative intensity) = 338 (2.7), 438 (8.2), 562 (1.0) nm. HRMS (MALDI): calcd for $[C_{50}H_{35}N_4F_5Ni + H]^+$ 845.2208, found 845.2187.

Ni2c: amorphous solid, 14.2 mg, yield 33%, melting point over 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 8.9 (m, 2H), 8.42−8.50 (m, 4H), 7.48−8.00 (m, 16H), 2.61−2.64 (m, 12H). ^{19}F NMR (376 MHz, $CDCl_3$): δ = −63.70, −65.79 (AB, J_{AB} = 225.2 Hz, 2F), −92.73 to −92.67 (m, 2F). HRMS (MALDI): calcd for $[C_{50}H_{35}N_4F_4ClNi + H]^+$ 861.1913, found 861.1924.

Ni3a: amorphous solid, 28.5 mg, yield 65%, melting point over 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 8.65 (m, 2H), 8.44−8.52 (m, 4H), 7.68−8.02 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9, 161.5, 159.2, 157.2, 151.3, 150.3, 149.5, 148.7, 148.4, 140.6, 140.4, 140.2, 140.1, 138.2, 137.8, 137.7, 137.7, 136.9, 136.8, 136.8, 136.7, 136.6, 135.1, 134.7, 134.4, 134.1, 133.8, 130.3, 130.0, 129.6, 129.0, 129.0, 127.2, 125.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −58.68 (s, 3F). UV/vis (CH_2Cl_2): λ_{max} (relative intensity) = 330 (2.8), 436 (8.7), 540 (1.0) nm. HRMS (MALDI): calcd for $[C_{45}H_{23}N_4F_3Cl_4Ni + H]^+$ 875.0055, found 875.0066.

Ni3b: amorphous solid, 18.1 mg, yield 39%, melting point over 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (d, J = 0.8 Hz, 1H), 8.58−8.62 (m, 2H), 8.41−8.50 (m, 4H), 7.68−8.05 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 173.9, 160.0, 157.0, 156.2, 155.9, 149.9, 149.8, 148.9, 148.8, 148.1, 148.0, 147.7, 147.6, 146.7, 139.0, 138.9, 138.8, 138.7, 138.6, 138.6, 138.6, 136.1, 136.0, 135.7, 135.6, 135.2, 135.2, 134.9, 134.9, 134.8, 134.7, 134.6, 134.3, 133.2, 133.0, 132.7, 132.5, 132.2, 132.2, 128.6, 128.6, 128.4, 128.3, 127.3, 125.2, 123.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −80.99 (s, 3F), −99.35, −100.42 (AB, J_{AB} = 145.1 Hz, 2F). UV/vis (CH_2Cl_2): λ_{max} = 418 nm. HRMS (MALDI): calcd for $[C_{46}H_{23}N_4F_5Cl_4Ni + H]^+$ 925.0023, found 925.0023.

Ni3c: amorphous solid, 16.5 mg, yield 35%, melting point over 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (s, 1H), 8.58 (d, J = 4.8 Hz, 2H), 8.47 (d, J = 5.2 Hz, 2H), 8.45 (d, J = 4.8 Hz, 1H), 8.41 (d, J = 5.2 Hz, 1H), 7.67−8.04 (m, 16H). ^{19}F NMR (376 MHz, $CDCl_3$): δ = −63.64, −65.75 (AB, J_{AB} = 169.6 Hz, 2F), −92.33 (m, 2F). HRMS (MALDI): calcd for $[C_{46}H_{23}N_4F_4Cl_5Ni + H]^+$ 940.9728, found 940.9711.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystal structure of compound **Ni1a** and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jchxiao@sioc.ac.cn.

Notes

The authors declare no competing financial interest.

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