

# A New Entry to Doubly N-Confused [26]Hexaphyrins(1.1.1.1.1.1) from Normal [26]Hexaphyrins(1.1.1.1.1.1) through an Unprecedented Double Pyrrolic Rearrangement

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**Abstract:** Treatment of hexakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1) (**1**) with CuCl in the presence of pyridine and molecular oxygen led to formation of doubly N-confused [26]hexaphyrin(1.1.1.1.1.1) **2** in a moderate yield through an unprecedented double pyrrolic rearrangement. Macrocycle **2** has been shown to serve as an effective bis-metal-coordinating ligand and exhibits attractive optical properties such as a sharp Soret-like band at 566 nm and low-energy fluorescence at 1058 nm.

**Keywords:** porphyrinoids • pyrrole rearrangement • structure elucidation • transition metals

## Introduction

N-Confused porphyrins (NCPs) exhibit attractive properties such as an ability to stabilize unusual oxidation states of metals, unique tautomerism between isomers bearing outer and inner NH, and supramolecular assembling through the interaction of the confused outer nitrogen atom with metal ions.<sup>[1,2]</sup> Extension of such NCP chemistry to expanded porphyrins<sup>[3]</sup> has been recently achieved by incorporating an N-

confused oligopyrrolic subunit into macrocycle, hence providing novel macrocycles including a doubly N-confused hexaphyrin (DNCH, **2**),<sup>[4a]</sup> a doubly N-fused pentaphyrin,<sup>[4b]</sup> and doubly N-confused pentaphyrins.<sup>[4c]</sup> Among these, the macrocycle **2** has been shown to be a useful bis-metal-coordinating ligand for Ni<sup>II</sup> and Cu<sup>II</sup> ions.<sup>[4a]</sup> DNCH and its bis-metal complexes are also attractive as near-infrared-absorbing dyes in the light of their expanded  $\pi$ -electronic systems, but have been only poorly explored, mainly due to its tedious multistep synthesis starting from an N-confused tripyrrene precursor. Such a synthetic difficulty precludes its large scale preparation, which would be needed for its further applications. Herein, we report on an unexpected but efficient route to DNCH **2** from [26]hexaphyrin(1.1.1.1.1.1) (**1**)<sup>[3c,5]</sup> by means of a double pyrrolic rearrangement, effected by Cu<sup>I</sup>-mediated aerobic oxidation.

## Results and Discussion

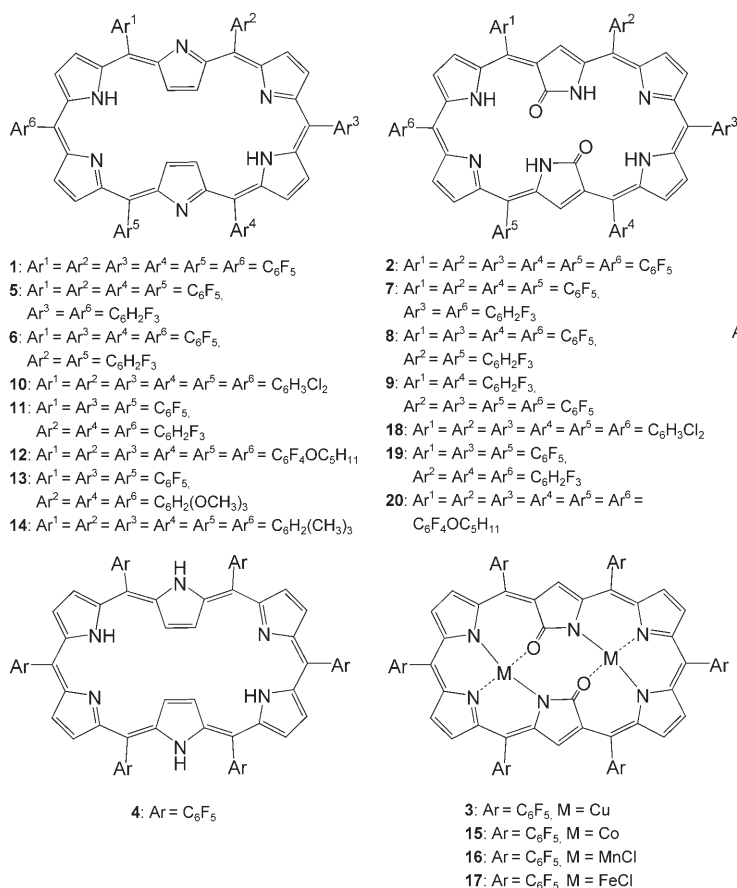
Under aerobic conditions, CuCl was added to a solution of **1** in pyridine and the resulting mixture was stirred for 3 h. TLC analysis of the reaction mixture revealed the appearance of a pale blue band moving faster than **1**. After usual workup followed by chromatographic separation through a silica gel column, a reddish solid was isolated as a sole major product. Positive-mode high-resolution electrospray ionization mass spectroscopy (HR-ESI-TOF-MS) exhibited the parent ion peak at  $m/z$ : 1616.9052  $[M+H]^+$  (calcd for

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C<sub>66</sub>H<sub>11</sub>F<sub>30</sub>N<sub>6</sub>O<sub>2</sub>Cu<sub>2</sub>: 1616.9050), thus demonstrating that two oxygen atoms are incorporated in addition to two copper ions. The structure of this complex has been revealed by single-crystal X-ray diffraction analysis to be bis-Cu<sup>II</sup>-DNCH (**3**; Figure 1), in which each of two Cu atoms is bound to three pyrrolic nitrogen atoms and a carbonyl oxygen atom with a Cu–Cu distance of 4.896(1) Å in a planar macrocycle with the mean plane deviation of only 0.079 Å and small Cu ion displacements of 0.059 Å. Bond

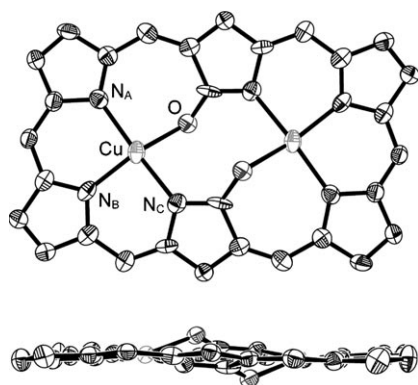
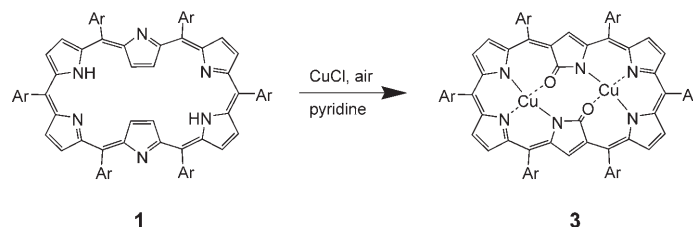


Figure 1. Crystal structures of **3**. The thermal ellipsoids were scaled to the 50% probability level. *meso*-Aryl substituents and hydrogen atoms were omitted for clarity.

lengths are Cu–N<sub>A</sub> 2.043(4) Å, Cu–N<sub>B</sub> 1.961(4) Å, Cu–N<sub>C</sub> 2.052(4) Å, and Cu–O 1.932(3) Å. Remarkably, both of the inverted pyrrole rings of **1** underwent simultaneous rearrangements to form N-confused pyrroles with concomitant oxygenation at the internal pyrrolic  $\alpha$ -position in **3** (Scheme 1). For structural confirmation, the complex **3** was



Scheme 1. Double pyrrolic rearrangements from **1** to **3**.

quantitatively demetallated to its free base **2** upon treatment with trifluoroacetic acid (TFA). Eventually, all the structural data of **2** including high-resolution ESI mass, the electronic absorption spectrum, <sup>1</sup>H- and <sup>19</sup>F NMR spectra, and single-crystal X-ray diffraction analysis, confirmed that this compound is exactly identical to that prepared by the previous stepwise synthesis.<sup>[4a]</sup> Although the yield of **3** is modest (24.4%), this reaction is far superior to the previous synthesis in terms of the easy procedure and ready availability of **1**. N-Confused porphyrinic macrocycles have been so far prepared by an accidental coupling reaction of an aryl aldehyde with pyrrole at the  $\beta$ -position or by means of a designed route using N-confused mono- or oligopyrrolic precursors.<sup>[1,6]</sup> In this respect, this procedure is quite attractive, since it opens up a new entry to N-confused expanded porphyrins from normal expanded porphyrins by means of an unprecedented pyrrole rearrangement.

We then examined the similar rearrangement reaction of hexaphyrins **5** and **6**, which have been shown to be conformationally stable at 0 °C, but start to show a caterpillar-like rotational isomerization around 20 °C.<sup>[7]</sup> When subjected to the similar metallation conditions (CuCl, pyridine, O<sub>2</sub>) at 0 °C followed by demetallation with TFA, hexaphyrin **5** gave **7** in 13% as a sole DNCH product, but at 20 °C it gave **7**, **8**, and **9** in 4.7, 14, and 4.7% yields. Similarly, the reaction of **6** at 0 °C gave a 1:1 mixture of **8** and **9** in 9%. These results suggest that the rearrangement occurs selectively at the inverted pyrroles at the long side. DNCH products were formed from hexaphyrins bearing electron-deficient aryl substituents such as **10**, **11**, and **12** (**18**, **19**, and **20**, respectively), but not from those with electron-rich aryl substituents like **13** and **14**. Modest yields of DNCH products suggest that the rearrangements may occur independently in either direction to give several rearranged products, of which only DNCH-type products are stabilized through the coordination of two Cu<sup>II</sup> ions.

At present, we know very little about the mechanistic course from **1** to **3**. Several experimental facts are given below:

- 1) The initial reaction is a reduction of **1** to [28]hexaphyrin **4** probably with Cu<sup>I</sup> ions, since in the beginning of reaction the purple color of **1** changed immediately to the blue color of **4**, and **4** underwent similar double rearrangements under the same conditions.
- 2) The gable-type bis-Cu complexes<sup>[8]</sup> of **1** that were prepared from the metallation of **1** with Cu<sup>II</sup> ion were not precursors for this rearrangement, since these Cu<sup>II</sup>-complexes did not undergo any rearrangements under the same conditions.
- 3) The reaction needed molecular oxygen, since the reaction did not proceed under anaerobic conditions but was initiated upon introduction of air or molecular oxygen.
- 4) Both Cu<sup>I</sup> ions and pyridine are essential for the reaction.
- 5) The parent ion peak of **2** was increased by four mass units when the reaction was conducted in the presence of <sup>18</sup>O-labelled water, suggesting adventitious water and not molecular oxygen was the oxygen source.

We thus anticipated the involvement of CuCl-pyridine-O<sub>2</sub> oxidation<sup>[9]</sup> in this reaction.<sup>[10]</sup> Indeed, a pretreated green solution of CuCl-pyridine-O<sub>2</sub><sup>[9]</sup> was found to effect the transformation of **1** to **3** with 13% yield.

DNCH **2** provides two NNNO units and serves as an effective bis-metal chelate for various metal ions including Co<sup>II</sup>, Mn<sup>III</sup>, and Fe<sup>III</sup> ions besides Cu<sup>II</sup> and Ni<sup>II</sup> ions. Thus, bis-metal complexes of **2** were prepared quantitatively by simple metallation. The bis-Co<sup>II</sup> complex **15**, bis-Mn<sup>III</sup> complex **16**, and bis-Fe<sup>III</sup> complex **17** exhibited parent ion peaks at *m/z*: 1606.9130 (calcd for C<sub>66</sub>H<sub>11</sub>F<sub>30</sub>N<sub>6</sub>O<sub>2</sub>Co<sub>2</sub>: 1606.9123) for **15**, at *m/z*=1669.75 (calcd for C<sub>66</sub>H<sub>10</sub>F<sub>30</sub>N<sub>6</sub>O<sub>2</sub>Mn<sub>2</sub>Cl<sub>2</sub>: 1669.56) for **16**, and at *m/z*=1663.92 (calcd for C<sub>66</sub>H<sub>10</sub>F<sub>30</sub>N<sub>6</sub>O<sub>2</sub>Fe<sub>2</sub>Cl<sub>2</sub>: 1671.37) for **17**. These smooth metallation behaviors of **2** are in sharp contrast to unpredictable metallation behaviors of expanded porphyrins<sup>[11]</sup> including hexaphyrin **1**.<sup>[8,12]</sup> Crystals of **15** suitable for X-ray crystallography were grown by slow evaporation of a solution of the sample in THF/octane (Figure 2). The complex **15** shows a slightly distorted structure with the mean plane deviation of 0.117 Å defined by the 36 atoms in the macrocycle. The displacement of Co ion is 0.302 Å and the Co-Co distance is 4.802(9) Å. Water molecules coordinated at the axial position of the Co ion were found with a Co-O distance of 2.025(4) Å. In the complex **15**, bond lengths were Co-N<sub>A</sub> 2.139(4) Å, Co-N<sub>B</sub> 2.007(4) Å, Co-N<sub>C</sub> 2.052(4) Å, and Co-O 1.932(3) Å, respectively, which were almost the same as those of porphyrins.

Finally, promising attributes of **2** as a near-infrared absorbing dye are briefly described. DNCH **2** possesses a 26π-conjugated aromatic electronic network, which is comparable to that of the hexaphyrin **1**, but larger than the 18π-conjugated one of porphyrins. The absorption spectrum of **2** shows a Soret band at 566 nm with a shoulder at 586 nm and Q-bands at 722, 793, 911, and 1047 nm (Figure 3). The Soret band of **2** (ε=410000) is distinctly sharper than that of **1** (ε=260000; Figure 4). Interestingly, compound **2** exhibits fluorescence at 1058 nm with a vibronic structure and a

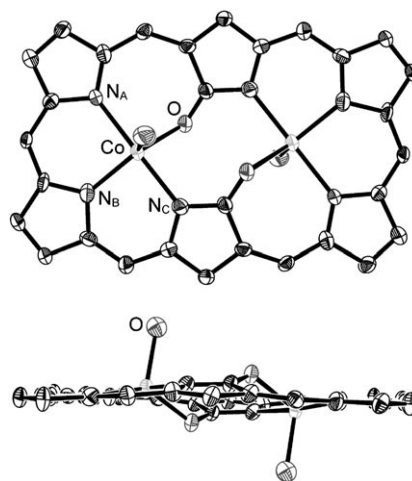


Figure 2. Crystal structures of **15**. The thermal ellipsoids were scaled to the 50% probability level. *meso*-Aryl substituents and hydrogen atoms were omitted for clarity.

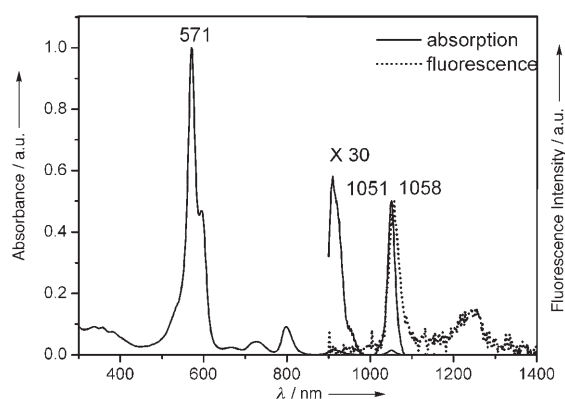


Figure 3. Absorption and fluorescence spectra of **2** in toluene at room temperature.

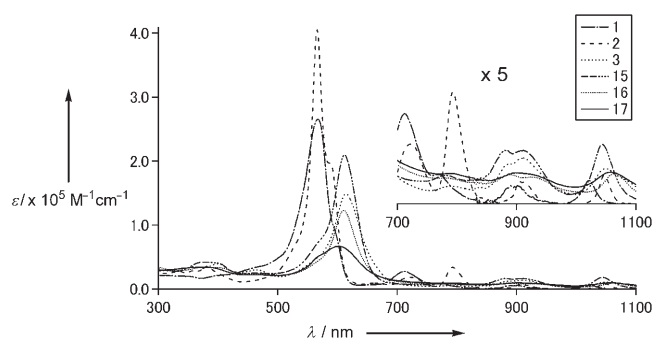


Figure 4. UV-visible absorption spectra of **1**, **2**, **3**, **15**, **16**, and **17** in CH<sub>2</sub>Cl<sub>2</sub>.

very small Stokes shift, suggesting a rigid structure (Figure 3). The fluorescence quantum yield of **2** was measured to be ~0.65 of that of **1**, which was roughly estimated to be less than 10<sup>-4</sup>.<sup>[13]</sup> These results may be rationalized in terms of a more rigid structure of **2** relative to that of **1**

owing to multiple intramolecular hydrogen-bonding interactions. Femtosecond time-resolved transient absorption spectroscopy was used to detect the  $S_1$ -state dynamics at 570 nm, which decays following a single exponential function with  $\tau = 62$  ps (Figure 5); this value is quite small rela-

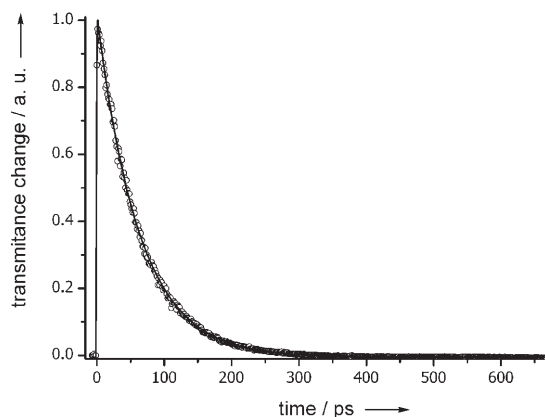


Figure 5. Temporal profile of **2** in toluene measured by transient absorption spectroscopy which has time-resolution of 150 fs. Obtained curve is well-fitted by single exponential decay with a time constant of  $62.05 \pm 0.05$  ps, which correspond to the  $S_1$ -state lifetime. Both pump and probe wavelengths are 570 nm.

tive to those of free-base porphyrins (ca. 10 ns), but almost comparable to 98 ps of the  $S_1$ -state of **1**.<sup>[13]</sup> The fluorescence in the near-infrared region is quite interesting, because of a variety of possible applications including biomedical imaging and sensing,<sup>[14]</sup> nonlinear optical materials,<sup>[15]</sup> and so forth, despite a limited number of fluorescent dyes in this region known.<sup>[16]</sup> The absorption spectra of **15–17** are shown in Figure 4, in which the Soret-like bands are observed at 614, 615, 610, and 602 nm for **3**, **15**, **16**, and **17**, respectively, showing 36–49 nm red shifts upon metallation.

## Conclusion

In summary, we found a facile entry to DNCH **2** from **1** by means of a double pyrrolic rearrangement, which can be performed in a large scale. The rearrangement was induced upon the treatment of [26]hexaphyrins(1.1.1.1.1.1) with  $\text{Cu}^{\text{I}}$  ions in pyridine in the presence of molecular oxygen. This pyrrolic-rearrangement strategy may be applied to other *meso*-aryl-substituted expanded porphyrins and may allow a new direct entry to other larger N-confused expanded porphyrins, which is a subject worthy of further investigations.

## Experimental Section

**General:** All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted.  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded on a JEOL ECA-600 spectrometer (operating as 600.17 MHz for  $^1\text{H}$  and 564.73 MHz for  $^{19}\text{F}$  NMR spectra) with

the residual solvent ( $\text{CHCl}_3$ ) as an internal reference for  $^1\text{H}$  spectra ( $\delta = 7.260$  ppm) and hexafluorobenzene as an external reference for  $^{19}\text{F}$  spectra ( $\delta = -162.9$  ppm). Spectroscopic grade  $\text{CH}_2\text{Cl}_2$  was used as solvents for all spectroscopic studies. UV-visible absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. Mass spectra were recorded on a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer, using positive-MALDI ionization method and on a BRUKER microTOF with the positive or negative mode ESI-TOF method in acetonitrile. Preparative separations were performed by silica gel flash column chromatography (Merck Kieselgel 60H Art. 7736), and silica gel gravity column chromatography (Wako gel C-400).

**Doubly N-confused hexaphyrin bis- $\text{Cu}^{\text{II}}$  complex 3:** Compound **1** (400 mg) and  $\text{CuCl}$  (2 g) in pyridine (100 mL) were stirred under aerobic conditions for 3 h at room temperature. The reaction mixture was diluted with  $\text{AcOEt}$ , and the organic layer was washed with brine three times, and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of solvent, the crude product was purified by silica gel column chromatography with  $\text{CH}_2\text{Cl}_2$ /hexane (3:7) as an eluent. The major blue-green fraction was collected. Recrystallization from a mixture of  $\text{CH}_2\text{Cl}_2$ /hexane gave reddish solids of **3** (108 mg, yield: 24.4%).

**Doubly N-confused [26]hexaphyrin(1.1.1.1.1.1) 2:** An excess amount of trifluoroacetic acid (TFA; 2 mL) was added to a solution of **3** (30 mg) in  $\text{CH}_2\text{Cl}_2$  (10 mL) and the resulting solution was stirred for 1 h. The reaction mixture was quenched with water. The organic layer was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Recrystallization from a mixture of  $\text{CH}_2\text{Cl}_2$ /acetonitrile gave **2** quantitatively as a greenish solid.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = -0.75$  (s, 2H; NH),  $-0.25$  (s, 2H; NH), 9.18 (d,  $J = 4.5$  Hz, 2H; outer  $\beta$ -H), 9.22 (d,  $J = 4.5$  Hz, 2H; outer  $\beta$ -H), 9.43 (d,  $J = 4.5$  Hz, 2H; outer  $\beta$ -H), 9.50 (d,  $J = 4.8$  Hz, 2H; outer  $\beta$ -H), 10.75 ppm (s, 2H; outer  $\beta$ -H);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ):  $\delta = -161.23$  (t,  $J = 17.5$  Hz, 4F; *meta*-F),  $-160.75$  (t,  $J = 17.5$  Hz, 4F; *meta*-F),  $-159.54$  (t,  $J = 17.5$  Hz, 4F; *meta*-F),  $-150.74$  (t,  $J = 17.5$  Hz, 2F; *para*-F),  $-149.70$  (t,  $J = 17.5$  Hz, 2F; *para*-F),  $-149.57$  (t,  $J = 17.5$  Hz, 2F; *para*-F),  $-136.56$  (d,  $J = 17.3$  Hz, 4F; *ortho*-F),  $-135.98$  (d,  $J = 17.3$  Hz, 4F; *ortho*-F),  $-135.78$  ppm (d,  $J = 17.5$  Hz, 4F; *ortho*-F); UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 1047 (9200), 911 (7500), 793 (38000), 722 (23000), 664 (13000), 586 (sh, 200000), 566 (410000), 382 (38000), 335 nm ( $30000\text{M}^{-1}\text{cm}^{-1}$ ); HR-ESI-TOF-MS (positive mode):  $m/z$  (%) calcd for  $\text{C}_{66}\text{H}_{15}\text{F}_{30}\text{N}_6\text{O}_2$  [ $M+H$ ] $^+$ : 1493.0772; found: 1493.0720 (100).

**General procedure for the synthesis of doubly N-confused hexaphyrin bis-metal complexes:** A solution of **2** in  $\text{CHCl}_3/\text{MeOH}$  (3:1) was refluxed in the presence of metal salt (large excess) under a nitrogen atmosphere overnight. The reaction mixture was quenched with water. The organic layer was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Recrystallization from a mixture of  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  gave bis-metallated complexes quantitatively. Complex **3** was obtained from the reaction of **2** with copper(II) acetate (**15** with cobalt(II) chloride; **16** with manganese(II) chloride; **17** with iron(II) chloride).

**Data for 3:** UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 1049 (11000), 911 (14000), 614 (150000), 465 (30000), 400 nm ( $40000\text{M}^{-1}\text{cm}^{-1}$ ); HR-ESI-TOF-MS (positive mode):  $m/z$  (%) calcd for  $\text{C}_{66}\text{H}_{11}\text{F}_{30}\text{N}_6\text{O}_2\text{Cu}_2$  [ $M+H$ ] $^+$ : 1616.9052; found: 1616.9050 (100).

**Data for 7:** Yield: 13%;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = -0.79$  (s, 2H; NH),  $-0.35$  (s, 2H; NH), 7.34 (m, 4H; phenyl), 9.19 (d,  $J = 4.1$  Hz, 2H; outer  $\beta$ -H), 9.24 (d,  $J = 4.6$  Hz, 2H; outer  $\beta$ -H), 9.47 (s, 4H; outer  $\beta$ -H), 10.73 ppm (s, 2H; outer  $\beta$ -H);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ):  $\delta = -161.01$  (t,  $J = 17.3$  Hz, 4F; *meta*-F),  $-159.80$  (t,  $J = 17.4$  Hz, 4F; *meta*-F),  $-150.14$  (t,  $J = 17.3$  Hz, 2F; *para*-F),  $-150.01$  (t,  $J = 17.3$  Hz, 4F; *para*-F),  $-136.59$  (m, 8F; *ortho*-F),  $-135.77$  (d,  $J = 17.3$  Hz, 4F; *ortho*-F),  $-138.2$  ppm (d,  $J = 17.3$  Hz, 4F; *ortho*-F); UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 1046 (5800), 905 (6000), 793 (25000), 722 (15000), 664 (7700), 590 (sh, 140000), 566 (280000), 381 (25000), 334 nm ( $20000\text{M}^{-1}\text{cm}^{-1}$ ); HR-ESI-TOF-MS (positive mode):  $m/z$  (%) calcd for  $\text{C}_{66}\text{H}_{19}\text{F}_{26}\text{N}_6\text{O}_2$  [ $M+H$ ] $^+$ : 1421.1149; found: 1421.1143 (100).

**Data for 8 and 9:** Yield: 4.5% + 4.5%;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = -0.83$  (s, 2H; NH),  $-0.64$  (s, 2H; NH),  $-0.37$  (s, 2H; NH),  $-0.13$  (s, 2H; NH), 7.42–7.45 (br, 4H; phenyl), 7.49–7.52 (br, 4H; phenyl), 9.13 (d,  $J = 4.6$  Hz, 2H; outer  $\beta$ -H), 9.20 (m, 4H; outer  $\beta$ -H), 9.25 (m, 4H; outer  $\beta$ -H).

H), 9.39 (d,  $J=3.7$  Hz, 2H; outer  $\beta$ -H), 9.42 (d,  $J=3.7$  Hz, 2H; outer  $\beta$ -H), 9.47 (d,  $J=4.6$  Hz, 2H; outer  $\beta$ -H), 9.58 (d,  $J=5.0$  Hz, 2H; outer  $\beta$ -H), 10.73 (s, 2H; outer  $\beta$ -H), 10.83 ppm (s, 2H; outer  $\beta$ -H);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ):  $\delta = -161.50$  (br, 8F; *meta*-F),  $-161.24$  (t,  $J=17.4$  Hz, 4F; *meta*-F),  $160.02$  (t,  $J=17.3$  Hz, 4F; *meta*-F),  $-151.16$  (m, 8F; *para*-F),  $-150.32$  (m, 4F; *para*-F),  $-136.57$  (d,  $J=17.3$  Hz, 4F; *ortho*-F),  $-135.96$  (br, 12F; *ortho*-F),  $-135.74$  ppm (d,  $J=17.3$  Hz, 8F; *ortho*-F); UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} = 1049, 911, 792, 721, 587$  (sh), 566, 382 nm.

**Data for 15:** UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} (\epsilon) = 1043$  (18000), 907 (16000), 879 (16000), 612 (210000), 379 nm ( $42000 \text{ M}^{-1} \text{ cm}^{-1}$ ); HR-ESI-TOF-MS (positive mode):  $m/z$  (%) calcd for  $\text{C}_{66}\text{H}_{11}\text{F}_{30}\text{N}_6\text{O}_2\text{Co}_2$  [ $M+H$ ] $^+$ : 1606.9123; found: 1606.9130 (100).

**Data for 16:** UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} (\epsilon) = 1065$  (9300), 887 (8900), 610 (120000), 304 nm ( $34000 \text{ M}^{-1} \text{ cm}^{-1}$ ); MALDI-TOF-MS (positive mode):  $m/z$  calcd for  $\text{C}_{66}\text{H}_{10}\text{F}_{30}\text{N}_6\text{O}_2\text{Mn}_2\text{Cl}_2$  [ $M$ ] $^+$ : 1669.56; found: 1669.75.

**Data for 17:** UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} (\epsilon) = 1059$  (9600), 889 (9400), 789 (9300), 602 (67000), 377 nm ( $34000 \text{ M}^{-1} \text{ cm}^{-1}$ ); MALDI-TOF-MS (positive mode):  $m/z$ : 1663.92 [ $M$ ] $^+$ , 1629.04 [ $M-\text{Cl}$ ] $^+$ , 1594.21 [ $M-\text{Cl}_2$ ] $^+$ .

**Data for 18:** Yield: 1.7%;  $^1\text{H}$  NMR spectrum was not successfully obtained because of its poor solubility; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} (\epsilon) = 1060$  (9200), 916 (4900), 802 (19000), 730 (16000), 600 (sh, 140000), 575 (230000), 383 nm ( $22000 \text{ M}^{-1} \text{ cm}^{-1}$ ); HR-ESI-TOF-MS (positive mode):  $m/z$  (%) calcd for  $\text{C}_{66}\text{H}_{33}\text{Cl}_{12}\text{N}_6\text{O}_2$  [ $M+H$ ] $^+$ : 1366.8853; found: 1366.8715 (100).

**Data for 19:** Yield: 13%;  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = -0.92$  (s, 1H; NH),  $-0.90$  (s, 1H; NH),  $-0.52$  (s, 2H; NH), 7.38 (t,  $J=7.8$  Hz, 2H; phenyl), 7.47 (t,  $J=7.8$  Hz, 2H; phenyl), 7.53 (t,  $J=7.6$  Hz, 2H; phenyl), 9.22 (d,  $J=4.6$  Hz, 1H; outer  $\beta$ -H), 9.25 (d,  $J=4.6$  Hz, 1H; outer  $\beta$ -H), 9.30 (d,  $J=4.6$  Hz, 1H; outer  $\beta$ -H), 9.34 (d,  $J=4.6$  Hz, 1H; outer  $\beta$ -H), 9.46 (d,  $J=3.7$  Hz, 1H; outer  $\beta$ -H), 9.54 (s, 2H; outer  $\beta$ -H), 9.64 (d,  $J=5.0$  Hz, 1H; outer  $\beta$ -H), 10.90 (s, 1H; outer  $\beta$ -H), 10.93 ppm (s, 1H; outer  $\beta$ -H);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ):  $\delta = -161.97$  (br, 4F; *meta*-F),  $-161.67$  (br, 4F; *meta*-F),  $-160.48$  (br, 4F; *meta*-F),  $-151.79$  (br, 2F; *para*-F),  $-150.01$  (br, 4F; *para*-F),  $-137.02$  (br, 4F; *ortho*-F),  $-136.36$  (br, 4F; *ortho*-F),  $-136.24$  ppm (br, 4F; *ortho*-F); UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} (\epsilon) = 1049$  (8800), 906 (6500), 792 (27000), 721 (18000), 589 (sh, 150000), 566 (310000), 382 nm ( $33000 \text{ M}^{-1} \text{ cm}^{-1}$ ); HR-ESI-TOF-MS (negative mode):  $m/z$  (%) calcd for  $\text{C}_{66}\text{H}_{10}\text{F}_{24}\text{N}_6\text{O}_2$  [ $M-H$ ] $^-$ : 1383.1192; found: 1383.1183 (100).

**Data for 20:** Yield: 13%;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta = -0.71$  (s, 2H; NH),  $-0.24$  (s, 2H; NH), 1.29–1.34 (54H; *tert*-butyl), 4.35 (s, 2H;  $\text{OCH}_2$ ), 4.39 (s, 2H;  $\text{OCH}_2$ ), 4.40 (s, 2H;  $\text{OCH}_2$ ), 9.20 (d,  $J=4.1$  Hz, 2H; outer  $\beta$ -H), 9.27 (d,  $J=4.6$  Hz, 2H; outer  $\beta$ -H), 9.44 (d,  $J=4.6$  Hz, 2H; outer  $\beta$ -H), 9.53 (d,  $J=4.6$  Hz, 2H; outer  $\beta$ -H), 10.81 ppm (s, 2H; outer  $\beta$ -H);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ):  $\delta = -157.37$  (d,  $J=17.4$  Hz, 4F; *meta*-F),  $-156.98$  (d,  $J=17.4$  Hz, 4F; *meta*-F),  $-155.90$  (d,  $J=17.4$  Hz, 4F; *meta*-F),  $-138.86$  (d,  $J=17.3$  Hz, 4H; *ortho*-F),  $-138.50$  (d,  $J=26.0$  Hz, 4F; *ortho*-F),  $-138.20$  ppm (d,  $J=17.3$  Hz, 4F; *ortho*-F); UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} (\epsilon) = 1050$  (9300), 907 (6200), 795 (30000), 724 (20000), 587 (sh, 190000), 569 (370000), 384 nm ( $33000 \text{ M}^{-1} \text{ cm}^{-1}$ ); HR-ESI-TOF-MS (positive mode):  $m/z$  (%) calcd for  $\text{C}_{90}\text{H}_{81}\text{F}_{24}\text{N}_6\text{O}_8$  [ $M+H$ ] $^+$ : 1902.5760; found: 1902.5743 (100).

**Crystal data for 3:**  $\text{C}_{66}\text{H}_{10}\text{F}_{30}\text{N}_6\text{O}_2\text{Cu}_2 \cdot 2(\text{C}_8\text{H}_{18}) \cdot 2(\text{C}_6) = 1728$ , triclinic, space group  $P\bar{1}$  (No. 2),  $a = 7.92(1)$ ,  $b = 15.04(2)$ ,  $c = 17.50(2)$  Å,  $\alpha = 80.8(1)$ ,  $\beta = 79.2(1)$ ,  $\gamma = 79.5(1)^\circ$ ,  $V = 1996$  (5) Å $^3$ ,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.594 \text{ g cm}^{-3}$ ,  $T = -150^\circ\text{C}$ ,  $R_1 = 0.097$  [ $I > 2\sigma(I)$ ],  $R_w = 0.245$  (all data), GOF = 1.396.

**Crystal data of 15:**  $\text{C}_{66}\text{H}_{10}\text{F}_{30}\text{N}_6\text{O}_2\text{Co}_2 \cdot 6(\text{C}_4\text{H}_8\text{O}) \cdot 2\text{O} = 2071$ , monoclinic, space group  $P2_1/n$  (No. 14),  $a = 20.43(1)$ ,  $b = 8.927(7)$ ,  $c = 25.14(2)$  Å,  $\beta = 97.94(4)^\circ$ ,  $V = 4541(6)$  Å $^3$ ,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.515 \text{ g cm}^{-3}$ ,  $T = -150^\circ\text{C}$ ,  $R_1 = 0.071$  [ $I > 2\sigma(I)$ ],  $R_w = 0.227$  (all data), GOF = 1.239.

CCDC-280247 (3) and CCDC-280248 (15) contain 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](http://www.ccdc.cam.ac.uk/data_request/cif).

**Near-IR fluorescence spectra:** The fluorescence emission was detected by using a near-IR photomultiplier (Hamamatsu, H9170–75), a lock-in am-

plifier (EG&G, 5210) combined with a chopper after laser excitation at 442 nm from a CW He-Cd laser (Melles Griot, Omnicrome 74).

**Femtosecond transient absorption measurements:** The dual-beam femtosecond time-resolved transient absorption spectrometer consisted of a self-mode-locked femtosecond Ti:sapphire laser (Coherent, MIRA), a Ti:sapphire regenerative amplifier (Clark MXR, CPA-1000) pumped by a Q-switched Nd:YAG laser (ORC-1000), a pulse stretcher/compressor, OPG-OPA system, and an optical detection system. A femtosecond Ti:sapphire oscillator pumped by a cw Nd:YVO4 laser (Coherent, Verdi) produced a train of 60 fs mode-locked pulses with an averaged power of 600 mW at 800 nm. The seed pulses from the oscillator were stretched (~250 ps) and sent to a Ti:sapphire regenerative amplifier pumped by a Q-switched Nd:YAG laser operating at 1 kHz. The femtosecond seed pulses and Nd:YAG laser pulses were synchronized by adjusting an electronic delay between Ti:sapphire oscillator and Nd:YAG laser. Then, the amplified pulse train inside the Ti:sapphire regenerative amplifier cavity was cavity-dumped by using Q-switching technique, and about 30000-fold amplification at 1 kHz was obtained. After recompression, the amplified pulses were color-tuned by optical parametric generation and optical parametric amplification (OPG-OPA) technique. The resulting laser pulses had a pulse width of ~150 fs and an average power of 5–30 mW at 1 kHz repetition rate in the range 550–700 nm. The pump beam was focused to a 1 mm diameter spot, and laser fluence was adjusted less than ~1.0 mJ cm $^{-2}$  by using a variable neutral-density filter. The fundamental beam remaining in the OPG-OPA system was focused onto a flowing water cell to generate a white-light continuum, which was again split into two parts. The one part of the white-light continuum was overlapped with the pump beam at the sample to probe the transient, while the other part of the beam was passed through the sample without overlapping the pump beam. The time delay between pump and probe beams was controlled by making the pump beam travel along a variable optical delay. The white continuum beams after sample were sent to a 15 cm focal length spectrograph (Acton Research) through each optical fiber and then detected by the dual 512 channel photodiode arrays (Princeton Instruments). The intensity of the white light of each 512 channel photodiode array was processed to calculate the absorption difference spectrum at the desired time delay between pump and probe pulses. To obtain the time-resolved transient absorption difference signal at the specific wavelength, the monitoring wavelength was selected by using an interference filter. By chopping the pump pulses at 43 Hz, the modulated probe pulses as well as the reference pulses were detected by two separate photodiodes. The output current was amplified with a homemade fast preamplifier, and then the resultant voltage signals of the probe pulses were gated and processed by a boxcar averager. The resultant modulated signal was measured by a lock-in amplifier and then fed into a personal computer for further signal processing.

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