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Programmable Arrangement of Metal Ions in a Cofacially Stacked Assembly of Porphyrinoids toward Molecular Tags

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Cofacial assemblies of metalloporphyrinoids represent a fascinating platform for the fabrication of novel functional molecular assemblies based on π-π, d-d, and d-π interactions between components. In this paper, we present a novel synthetic strategy for the programmable arrangement of different metal ions inside a cofacially stacked trimer of porphyrinoids. A combination of two different assemblies was utilized for our purpose: a tetracationic fourfold rotaxane heterodimer between a porphyrin with four alkylammonium chains and a phthalocyanine bearing four peripheral crown ethers, and a stacked assembly between the fourfold rotaxane heterodimer and an additional tetraanionic porphyrin. Three metal ions, namely Cu(II), Ag(II), and Au(III), were arranged inside the cofacially stacked assembly of three porphyrinoids. Moreover, paramagnetic Cu(II) ions were arranged inside a cofacially stacked heterotrimer of porphyrinoids and were precisely programmed, affording the desired spin-spin communications as readable information. These results indicated that the developed strategy is effective for arranging various metal ions in cofacially stacked assemblies of porphyrinoids toward the creation of molecular tags or bar codes.

Introduction

Precise control of the sequential arrangement of molecular components is important for designing novel functional molecular assemblies. In biomacromolecules, such as DNA and proteins, controlled sequential arrangement of a limited number of components provides a large variety of unique functions including selective molecular recognition, efficient catalytic reactions, directional electron transfer, and storage of genetic information.[1] Inspired by these sophisticated functional biomacromolecules, various artificial supramolecular architectures have been constructed *via* self-assembly of functional components. Since self-assembly is a powerful methodology to construct symmetric nanostructures, it has significantly contributed to the development of molecular assembly chemistry.[2] However, self-assembly is not necessarily suitable for controlling the sequential arrangements of several components. Therefore, the development of novel methodologies for arranging components in a programmable manner is essential for fabricating sophisticated artificial supramolecular architectures similar to functional biomacromolecules.

Metalloporphyrins and metallophthalocyanines are versatile building blocks that can be used in supramolecular assemblies because they can form stable metal complexes with a large variety of metal ions. Their chemical and physical properties, including redox properties[3], catalytic activities[4-6], photo activities[7-9], and spin properties[10], can be tuned by changing the central metal ion or chemically modifying the tetrapyrrole cores. Among porphyrinoids supramolecular assemblies, cofacial stacked assemblies are a promising platform because direct electronic communication between the π-planes and metal ions can be achieved.[11-17] Moreover, cofacial arrangements of different metalloporphyrinoids in a pre-programmable fashion may lead to novel intermolecular electronic communication.[18-21] However, it is difficult to design the cofacial assembly of several different types of metalloporphyrinoids. These porphyrinoids are intrinsically prone to self-assemble to form 1D polymeric cofacial stacked assemblies due to their π-planar structures.[22] Therefore, it is necessary to develop an appropriate method to control the sequential arrangement of metalloporphyrinoids for the programmable construction of cofacially stacked assemblies.[23]

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Electronic Supplementary Information (ESI) available: Synthetic scheme of [H_2**Pc**-Cu(II)**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$ and [Cu(II)**Pc**-H_2**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$, MS of stacked assemblies ([H_2**Pc**-Cu(II)**Por**]$^{4+}$·4Cl$^-$, [Cu(II)**Pc**-H_2**Por**]$^{4+}$·4Cl$^-$, [Cu(II)**Pc**-Ag(II) **Por**]$^{4+}$·4Cl$^-$, [H_2**Pc**-Cu(II)**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$ and [Cu(II)**Pc**-H_2**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$. See DOI: 10.1039/x0xx00000x

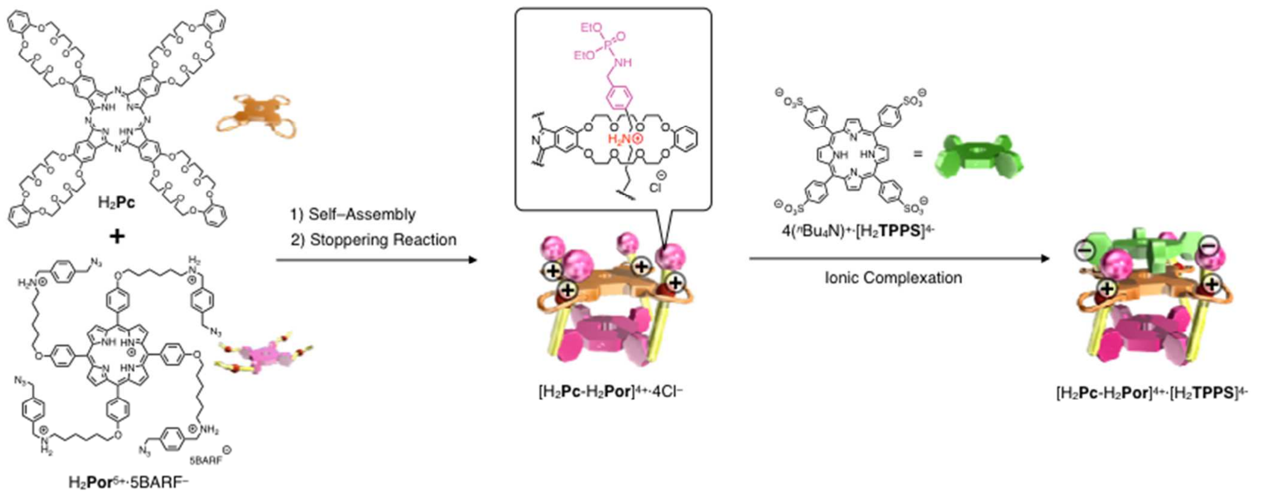
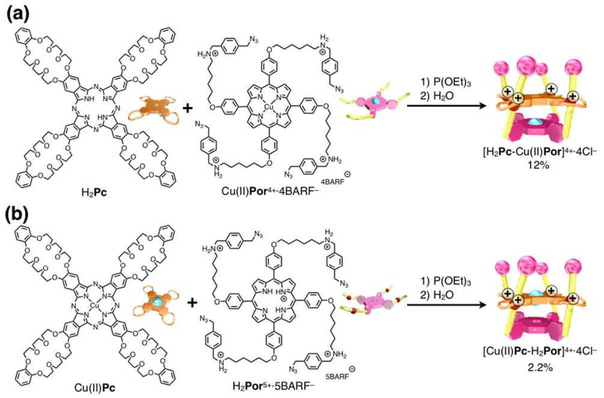


Fig. 1 Fourfold rotaxane formation of a porphyrin with a phthalocyanine to afford a fourfold rotaxane heterodimer [H_2**Pc**-H_2**Por**]$^{4+}$·4Cl$^-$, followed by ionic complexation with a tetraanionic porphyrin [H_2**TPPS**]$^{4-}$ to give a stacked assembly [H_2**Pc**-H_2**Por**]$^{4+}$·[H_2**TPPS**]$^{4-}$.

Recently, we reported the synthesis of a cofacial heterodimer consisting of a porphyrin and phthalocyanine connected through a four-fold rotaxane structure (Fig. 1).[24, 25] Furthermore, it was determined that the cofacial dimer was expanded to a triply stacked ionic trimer *via* quadruple ionic interactions between the tetracationic cofacial dimer and tetraphenylporphyrin tetrasulfonate (**TPPS**$^{4-}$).[26] It is likely that the appropriate combination of these assemblies will enable the arrangement of different metal ions inside a cofacially stacked assembly with tunable properties. To assess the effectiveness of this strategy, the heterogeneous assembly of three metal ions (Au(III), Ag(II), Cu(II)) inside a trimeric cofacial metalloporphyrinoid assembly was developed. Moreover, homogeneous assembly of two or three Cu(II) ions inside a triply stacked array was also demonstrated allowing for the pre-programming of the spin-spin interaction between Cu^{2+} ions to demonstrate to be spinic molecular tags.



Scheme 1 Fourfold rotaxane formation for the synthesis of (a) [H_2**Pc**-Cu(II)**Por**]$^{4+}$·4Cl$^-$ and (b) [Cu(II)**Pc**-H_2**Por**]$^{4+}$·4Cl$^-$.

Results and discussion

Programmable Arrangement of Cu(II) Ions in Cofacial Assemblies of Porphyrinoids

For the preparation of homogeneous and heterogeneous metal ion assemblies, a mononuclear Cu(II) ion complex of a four-fold rotaxane heterodimer of a porphyrin and phthalocyanine was synthesized. We recently reported the site-selective metalation of the four-fold rotaxane heterodimer with Fe(III), Ni(II), and Mn(II).[27] However, site-selective metalation with Cu(II) of a four-fold rotaxane heterodimer proved difficult because the Cu(II) ions were easily introduced into both the porphyrin and phthalocyanine. Therefore, stepwise construction of the cofacial trimer was chosen for the arrangement of Cu(II) ions, as shown in Scheme 1.

A mononuclear Cu(II) heterodimer, [H_2**Pc**-Cu(II)**Por**]$^{4+}$·4Cl$^-$, was obtained through the formation of a pseudo-rotaxane between Cu(II)**Por**$^{4+}$·4BARF$^-$ (BARF = tetrakis[(3,5-bis-trifluoromethyl)phenyl]borate) and H_2**Pc** in 4:1 ratio of chloroform and acetone. This was followed by locking through the Staudinger-phosphite reaction to converts azide groups to phosphoramidate units. Similarly, [Cu(II)**Pc**-H_2**Por**]$^{4+}$·4Cl$^-$ was obtained by mixing H_2**Por**$^{5+}$·5BARF$^-$ and Cu(II)**Pc**. Although the identification of mononuclear Cu(II) heterodimers by ^{1}H-NMR spectroscopy was difficult due to the paramagnetism of Cu(II), a combination of MALDI-TOF MS (Fig. S1, S2 in the Supplementary Information) and TLC analyses facilitated the isolation of the desired complexes. Importantly, disproportionation of Cu(II) between the porphyrin- and the phthalocyanine-centers of the heterodimer was not observed at room temperature. Considering that the metal-free fourfold rotaxane heterodimer was previously obtained in 41% yield, the yields for both mono-Cu(II) complexes are comparatively low (12% for [H_2**Pc**-Cu(II)**Por**]$^{4+}$·4Cl$^-$ and 2.2% for [Cu(II)**Pc**-

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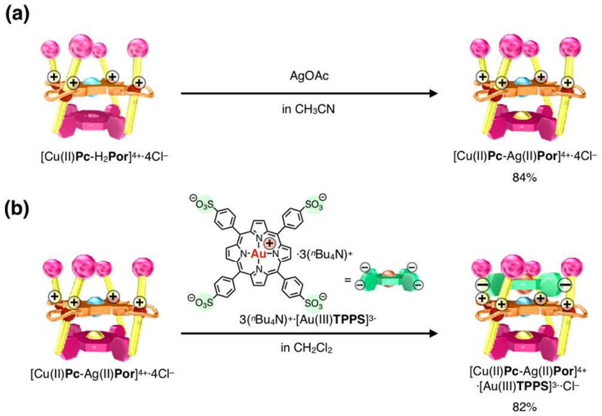

Scheme 2 (a) Synthesis of [Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·4Cl^{-}. (b) Ionic complexation to obtain [Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·[Au(III)**TPPS**]$^{3-}$·Cl^{-}.

H$_2$**Por**]$^{4+}$·4Cl^{-}). These low yields can be attributed to the inefficient purification process.

Arrangement of Three Different Metal Ions into Cofacially Stacked Arrays.

The mononuclear Cu(II) complex [Cu(II)**Pc**-H$_2$**Por**]$^{4+}$·4Cl was converted into a heteronuclear metal array by stepwise metalation and ionic complexation. [Cu(II)**Pc**-H$_2$**Por**]$^{4+}$·4Cl^{-} was condensed with AgOAc at 70 °C in CH$_3$CN (Scheme 2(a)). Although identification of the product by ^{1}H-NMR was difficult due to the paramagnetism of Cu(II) and Ag(II), the desired complex [Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·4Cl^{-} was successfully isolated in 84% isolated yield by recrystallization, as determined by mass and TLC analyses. The sets of signals corresponding to [Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·4Cl^{-} were observed in their respective MALDI-TOF mass spectra (Fig. S3 in the Supplementary Information). The heterotrinuclear complex [Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·[Au(III)**TPPS**]$^{3-}$·Cl^{-} was successfully obtained by mixing [Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·4Cl^{-} with 3(^{n}Bu$_4$N$^+$)·[Au(III)**TPPS**]$^{3-}$ (1 equiv.) in CH$_2$Cl$_2$ at room temperature, followed by reprecipitation with 82% yield (Scheme 2(b)).[26, 28] Signals arising from [Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·[Au(III)**TPPS**]$^{3-}$ were observed at *m/z* = 1811.9 and the isotopic distribution pattern corresponded with the calculated value for [[Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·[Au(III)**TPPS**]$^{3-}$ + 2Na]$^{3+}$ ($C_{264}H_{296}CuAuAgN_{24}O_{60}P_4S_4Na_2$, Fig. 2). Thus, the combination of four-fold rotaxane formation and ionic complexation is a useful method for the construction of heterotrinuclear metal complexes.

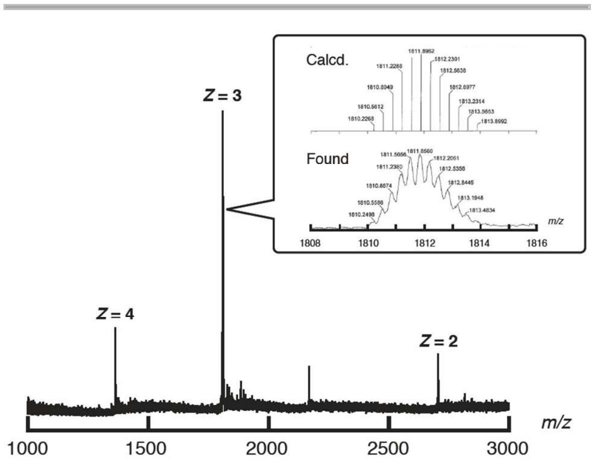

Fig. 2 ESI-TOF mass spectrum of [Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·[Au(III)**TPPS**]$^{3-}$·Cl^{-}. Inset: Calculated (top) and observed isotopic distribution patterns for [[Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·[Au(III)**TPPS**]$^{3-}$ + 2Na]$^{3+}$ ($C_{264}H_{296}CuAuAgN_{24}O_{60}P_4S_4Na_2$).

Programmable Arrangement of Paramagnetic Cu(II) Ions Inside a Cofacially Stacked Trimer.

It is possible to encode molecular information into a cofacially stacked assembly using the heterogeneous metal ion assembly in a cofacially stacked trimer. We attempted to demonstrate the pre-programmed arrangement of paramagnetic Cu(II) ions inside the trimer, such that the sequentially arranged Cu^{2+} ions can be read as patterns of spin-spin interaction between the *S* = 1/2 spins of Cu^{2+}. The triply stacked arrays [H$_2$**Pc**-Cu(II)**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$ and [Cu(II)**Pc**-H$_2$**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$ were obtained by mixing [H$_2$**Pc**-Cu(II)**Por**]$^{4+}$·4Cl^{-} or [Cu(II)**Pc**-H$_2$**Por**]$^{4+}$·4Cl^{-}, respectively, with 4(^{n}Bu$_4$N$^+$)·[Cu(II)**TPPS**]$^{4-}$ in CH$_2$Cl$_2$, followed by purification by gel permeation chromatography with CHCl$_3$ as the eluent (Scheme S1(a) and (b)). The sets of signals corresponding to [H$_2$**Pc**-Cu(II)**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$ and [Cu(II)**Pc**-H$_2$**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$ were observed in their respective ESI-TOF mass spectra (Figs. S4 and S5 in the Supplementary Information).

The EPR spectra of the prepared Cu(II) complexes were recorded at 5 K in a frozen CH$_2$Cl$_2$ solution and the results are summarized in Fig. 3 (parameters for the simulation were shown on Supplementary Information). We previously reported a dinuclear Cu(II) complex of a fourfold rotaxane

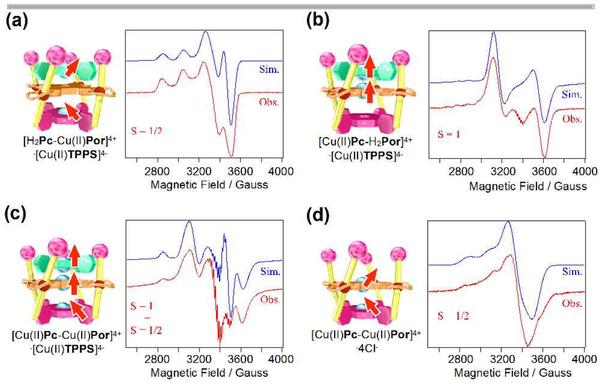

Fig. 3 EPR spectra of Cu(II) complexes (a) [H$_2$**Pc**-Cu(II)**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$, (b) [Cu(II)**Pc**-H$_2$**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$, (c) [Cu(II)**Pc**-Cu(II)**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$, and (d) [Cu(II)**Pc**-Cu(II)**Por**]$^{4+}$·4Cl^{-} in CH$_2$Cl$_2$ at 5 K with their simulations.

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heterodimer exhibited a typical doublet (Fig. 3(d)). This indicated that the distance between Cu(II) ions in the phthalocyanine and porphyrin units was large (at least 6 Å) due to the long C_6 sidechains (~ 8 Å) of the fourfold rotaxane structure. The distance was large enough so that the two Cu(II) *S* = 1/2 spins did not interact with each other.[24] Considering the EPR spectrum of [Cu(II)**Pc**-Cu(II)**Por**]$^{4+}$, the spectra of the Cu(II) stacked trimer complexes could easily be elucidated. The spectrum of [H_2**Pc**-Cu(II)**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$ exhibited a sum of two isolated doublet (*S* = 1/2) spins, indicating the absence of interaction between the two Cu(II) ions due to the large distance between Cu(II)**Por** and [Cu(II)**TPPS**]$^{4-}$ (Fig. 3(a)). In contrast, the *S* = 1 signal was observed in the [Cu(II)**Pc**-H_2**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$ spectrum (Fig. 3(b)). This is likely due to the direct interaction between the Cu(II) ions of [Cu(II)**TPPS**]$^{4-}$ units and adjacent Cu(II)-phthalocyanine units. For [Cu(II)**Pc**-Cu(II)**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$, the spectrum exhibited a sum of *S* = 1 and *S* = 1/2 signals (Fig. 3(c)). Thus, it was demonstrated that various spin-spin communications could be created *via* programmed arrangement of paramagnetic Cu(II) ions inside the prepared triply stacked arrays. Considering that the spin information contained in the arrays is readable molecular information, the arrays where Cu(II) spin numbers and positions are precisely controlled could be used for molecular tags or bar codes.

Conclusions

In this study, a novel synthetic strategy was developed for programmable arrangement of metal ions inside a cofacially stacked porphyrinoid trimer. For this purpose, we used a tetracationic heterodimer of a porphyrin and phthalocyanine linked through a fourfold rotaxane structure. This fourfold rotaxane heterodimer formed a well-defined cofacially stacked trimer with an additional tetraanionic porphyrin through tetraionic and π-π stacking interactions. Stepwise construction of this cofacially stacked trimer allowed the fabrication of various assemblies where metal ions were arranged with precisely controlled numbers and positions inside the trimer. Three different metal ions, namely Au(III), Ag(II), and Cu(II), were arranged in the cofacially stacked trimer using this method. We also demonstrated that paramagnetic Cu(II) ions were arranged in the assembly so that their spin-spin communication could be observed in a preprogrammed fashion. Since porphyrins and phthalocyanines can form stable metal complexes with various metal ions, this cofacially stacked porphyrinoid trimer, where desired metal ions are arranged with precisely controlled numbers, positions, and sequences, could be used as an information carrier in molecular tags or bar codes.

Experimental

Materials

All reagents and solvents were purchased at the highest commercial quality available and used without further purification. H_2**Por**$^{5+}$·5BARF$^-$, Cu(II)**Por**$^{4+}$·4BARF$^-$, H_2**Pc** and Cu(II)**Pc** were prepared according to our previous reports.[24, 26]

Instrumentation and Methods

Elemental analysis were performed on a Yanaco MT-6 analyzer. ESI (electrospray ionization) mass spectrometry was performed with a Waters LCT-Premier XE Spectrometer controlled using Masslynx software. Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) MS was performed with a Bruker Ultraflex III. CW EPR measurements were performed using a Bruker model ELEXES E500 X-band spectrometer equipped with an Oxford 900 cryostat. All samples were deaerated by freeze-and-thaw cycles before the EPR measurements.

Synthetic procedures

Synthesis of [H_2Pc-Cu(II)Por]$^{4+}$·4Cl$^-$

To an acetone solution (5.7 mL) of Cu(II)**Por**$^{4+}$·4BARF$^-$ (178 mg, 34.4 μmol) was added a $CHCl_3$ solution (28.7 mL) of H_2**Pc** (68.7 mg, 34.4 μmol). The resulting mixture was stirred at ambient temperature for 21 hrs, and then $P(OEt)_3$ (1.4 mL, 18.9 mmol) was added. After 86 hrs, water (1 mL) was added to the reaction mixture. It was stirred for 12 hrs. The resulting solution was evaporated. The residual oil was poured into a 1:1 mixture of hexane and Et_2O (100 mL). The blackish green precipitate was collected by centrifugation and dissolved in MeOH (100 mL). Ion-exchange resin (IRA 400CJ (Cl$^-$ form), 50 mL) was added to the solution to remove BARF$^-$. The resin was removed after 1 hr. This ion exchange procedure was repeated twice. After the resulting solution was evaporated, the crude product was purified by silica gel column chromatography (4 cmϕ⍰× 21 cm, $CHCl_3$: MeOH = 4:1 – 1:1 – $CHCl_3$: MeOH : H_2O : brine = 20 : 20 : 2 : 1) and pTLC ($CHCl_3$: MeOH = 4:1) to obtain black green solid. Finally, recrystallization from $CHCl_3$: MeOH = 4:1 / Et_2O yielded [H_2**Pc**-Cu(II)**Por**]$^{4+}$·4Cl$^-$ as blackish green solid (17.8 mg, 4.1 μmol, 12%). MALDI-TOF, positive) *m/z*: calcd for 4155.2: $C_{220}H_{275}N_{20}O_{48}P_4Cu$ ([[H_2**Pc**-Cu(II)**Por**]$^{4+}$ – 3H]$^+$), found: 4155.9.

Synthesis of [Cu(II)Pc-H_2Por]$^{4+}$·4Cl$^-$

To an acetone solution (7.7 mL) of H_2**Por**$^{5+}$·5BARF$^-$ (307 mg, 46.4 μmol) was added a $CHCl_3$ solution (38.7 mL) of Cu(II)**Pc** (95.4 mg, 46.4 μmol). The resulting mixture was stirred at ambient temperature for 15 hrs, and then $P(OEt)_3$ (0.90 mL, 11.8 mmol) was added. After 86 hrs, water (1 mL) was added to the reaction mixture. It was stirred for 12 hrs. The resulting solution was evaporated. The residual oil was poured into a 1:1 mixture of hexane and Et_2O (100 mL). The blackish green precipitate was collected by centrifugation and dissolved in MeOH (100 mL). Ion-exchange resin (IRA 400CJ (Cl$^-$ form), 50 mL) was added to the solution to remove BARF$^-$. The resin was removed after 1 hr. This ion exchange procedure was repeated twice. After the resulting solution was evaporated,

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the crude product was purified by silica gel column chromatography (4 cmϕ × 21 cm, $CHCl_3$: MeOH = 4:1 – 1:1 – $CHCl_3$: MeOH : H_2O : brine = 20:20:2:1) and pTLC ($CHCl_3$: MeOH = 4:1) to obtain black green solid. Finally, recrystallization from $CHCl_3$: MeOH = 4:1 / Et_2O yielded [Cu(II)**Pc**-H_2**Por**]$^{4+}$·4Cl$^-$ as blackish green solid (4.3 mg, 1.0 μmol, 2.2%). MS (MALDI-TOF, positive) *m/z*: calcd for 4155.2: $C_{220}H_{275}N_{20}O_{48}P_4Cu$ ([[Cu(II)**Pc**-H_2**Por**]$^{4+}$ –3H]$^+$), found: 4155.6.

Synthesis of [Cu(II)Pc-Ag(II)Por]$^{4+}$·4Cl$^-$

[Cu(II)**Pc**-H_2**Por**]$^{4+}$·4Cl$^-$ (7.16 mg, 1.67 μmol), AgOAc (1.57 g, 9.42 μmol), and dry CH_3CN (2.1 mL) were added to a 50 mL Schlenk flask. Oxygen was removed by freezing–thaw method by three times. The mixture was stirred at 70 ºC under dark for 17 hrs, and then diluted with $CHCl_3$ (100 mL), washed with brine (50 mL × 3), dried with anhydrous Na_2SO_4, filtered, and evaporated. The reaction was monitored by MALDI-TOF MS. Since the complexation was not completed, the crude product was condensed with AgOAc (1.73 mg, 10.4 μmol) in dry CH_3CN (2.1 mL) for 8 hrs. The resulting mixture was diluted with $CHCl_3$ (100 mL), washed with brine (50 mL × 3), dried with anhydrous Na_2SO_4, filtered, and evaporated. The crude product was purified by recrystallization from $CHCl_3$: MeOH = 4 : 1 / Et_2O to obtain the title compound as a green needle crystals (6.23 mg, 1.41 μmol, 84%, TLC). MS (MALDI-TOF) *m/z*: calcd for 4261.8: $C_{220}H_{273}AgCuN_{20}O_{48}P_4$ ([[Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$ – 3H$^+$]$^+$), found: 4263.8. Anal. calcd for [Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·4Cl$^-$ + 3$CHCl_3$ + Et_2O, [$C_{220}H_{276}AgCl_4CuN_{20}O_{48}P_4$ + 3$CHCl_3$ + Et_2O]: C, 56.35; H, 6.02; N, 5.79. Found: C, 56.69; H, 6.23; N, 5.91 (0.34% error).

Synthesis of [Cu(II)Pc-Ag(II)Por]$^{4+}$·[Au(III)TPPS]$^{3-}$·Cl$^-$

3(^{n}Bu$_4$N$^+$)·[Au(III)**TPPS**]$^{3-}$ (0.95 mg, 0.50 μmol) was added to a solution of [Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·4Cl$^-$ (2.15 mg, 0.49 μmol) in CH_2Cl_2 (0.4 mL). The resulting mixture was stirred, and then the solvent was evaporated (3.13 mg). The residual brown solid was dissolved in a mixture of $CHCl_3$ and MeOH (5 mL, 4 : 1(*v/v*)) and the solution was filtered through cellulose powder. After the solution was concentrated, the crude product was purified by reprecipitation from $CHCl_3$ / Et_2O by vapor diffusion at room temperature to obtain title compound as a brown solid (2.19 mg, 0.401 μmol, 82%). MS (ESI-TOF) *m/z*: calcd for 1811.9: $C_{264}H_{296}CuAuAgN_{24}O_{60}P_4S_4Na_2$ ([[Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·[Au(III)**TPPS**]$^{3-}$ + 2Na]$^{3+}$), found: 1811.9. Anal. calcd for [Cu(II)**Pc**-Ag(II)**Por**]$^{4+}$·[Au(III)**TPPS**]$^{3-}$·Cl$^-$ + 3$CHCl_3$, [$C_{220}H_{276}AgCl_4CuN_{20}O_{48}P_4$ + 3$CHCl_3$]: C, 55.45; H, 5.28; N, 5.81. Found: C, 55.32; H, 5.50; N, 5.75 (0.34% error).

Synthesis of [H$_2$Pc-Cu(II)Por]$^{4+}$·[Cu(II)TPPS]$^{4-}$

A solution containing [H_2**Pc**-Cu(II)**Por**]$^{4+}$·4Cl$^-$ (20.4 mg, 4.75 μmol) and 4(^{n}Bu$_4$N$^+$)·[Cu(II)**TPPS**]$^{4-}$ (9.92 mg, 4.99 μmol) in MeOH (5.0 mL) was stirred for 10 min. After the solvent was evaporated off, the residual solid was dissolved in a mixture of $CHCl_3$ and MeOH (5 mL, 4 : 1 (*v/v*)). The mixture was filtered through a short column of fine cellulose powder (3cmϕ×3 cm, eluent : $CHCl_3$: MeOH = 1 : 1). The filtrate was subjected to recycling GPC (JAIGEL, 20cmϕ, 3H-2.5H, $CHCl_3$) to obtain brown solid. Finally, reprecipitation from $CHCl_3$: MeOH = 4:1 / Et_2O yielded the title compound as a brown solid (9.96 mg, 1.93 μmol, 41%). MS (ESI-TOF, positive) *m/z*: calcd for 1739.6: $C_{264}H_{302}N_{24}O_{60}P_4S_4Cu_2Na_3$ ([[H_2**Pc**-Cu(II)**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$ + 3Na]$^{3+}$), found: 1739.6. Anal. calcd. for $C_{275}H_{323}Cl_9Cu_3N_{24}O_{62}P_4S_4$ ([H_2**Pc**-Cu(II)**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$ + 5$CHCl_3$ + 3Et_2O): C, 56.53; H, 5.69; N, 5.63. Found. C, 56.89; H, 5.83 N, 5.29. (0.36% Error).

Synthesis of [Cu(II)Pc-H$_2$Por]$^{4+}$·[Cu(II)TPPS]$^{4-}$

A solution containing [Cu(II)**Pc**-H_2**Por**]$^{4+}$·4Cl$^-$ (4.3 mg, 1.0 μmol) and 4(^{n}Bu$_4$N$^+$)·[Cu(II)**TPPS**]$^{4-}$ (2.1 mg, 1.1 μmol) in MeOH (5.0 mL) was stirred for 10 min. After the solvent was evaporated off, the residual solid was dissolved in a mixture of $CHCl_3$ and MeOH (5 mL, 4 : 1 (*v/v*)). The mixture was filtered through a short column of fine cellulose powder (3cmϕ×3 cm, eluent : $CHCl_3$: MeOH = 1 : 1). The filtrate was subjected to recycling GPC (JAIGEL, 20cmϕ, 3H-2.5H, $CHCl_3$) to obtain brown solid. Finally, reprecipitation from $CHCl_3$: MeOH = 4:1 / Et_2O yielded the title compound as a brown solid (1.18 mg, 0.229 μmol, 23%). MS (ESI-TOF, positive) *m/z*: calcd for 1739.6: $C_{264}H_{302}N_{24}O_{60}P_4S_4Cu_2Na_3$ ([[Cu(II)**Pc**-H_2**Por**]$^{4+}$·[Cu(II)**TPPS**]$^{4-}$ + 3Na]$^{3+}$), found: 1739.5.

Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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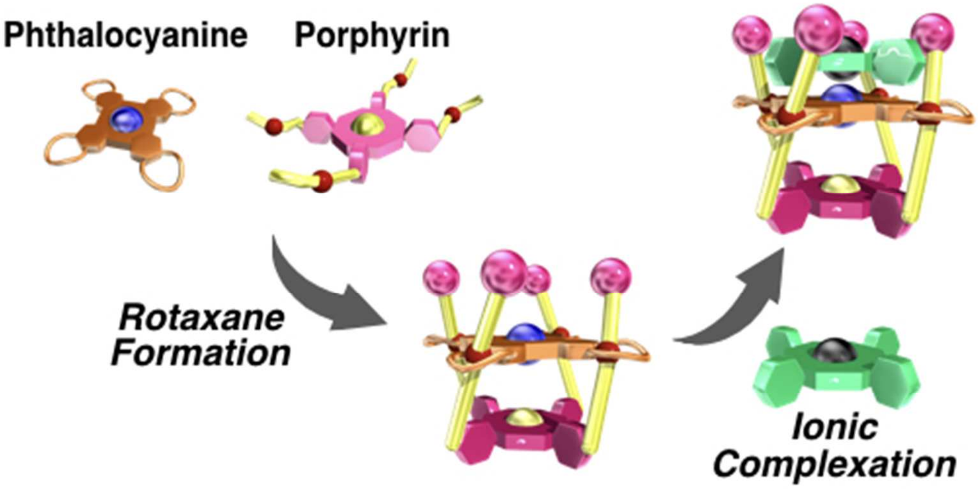

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