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# A noncovalently assembled porphyrinic catenane consisting of two interlocking [43]-membered rings<sup>†</sup>

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A new macrocycle and the corresponding [2]catenane were prepared quantitatively from relatively large organic fragments using coordination chemistry bonds only (Zn–N bonds for the ring and Cu–N bonds for the catenane). The two constitutive macrorings of the [2]catenane are 43-membered rings. The organic components consist of a bis-Zn porphyrin and a 1,10-phenanthroline derivative, both fragments being significantly larger than those previously used for making related compounds. The catenane was assembled in two steps from a bis-Zn porphyrin and a 2,9-di(4''-pyridyl-4'-phenyl)-1,10-phenanthroline. In a first step the entwined copper(1) complex of the phenanthroline derivative was formed *via* Cu(1)–N interactions. Subsequently, a double ring closing reaction was performed by coordination of two equivalents of bis-Zn porphyrin to the entwined copper(1) complex. The tetraporphyrinic [2]catenane was thus obtained thanks to the formation of four Zn(1)–pyridine bonds. It has a high association constant,  $4 \times 10^{10}$  M<sup>-2</sup>, due to the good geometrical fit between the constituents.

## Introduction

Since the early work of Schill and co-workers, the field of catenanes, rotaxanes and knots has undergone a real revolution.<sup>2</sup> The introduction of templated strategies has profoundly modified the way molecular chemists look at catenanes, mostly due to the accessibility of these compounds after the templated approaches were described. Since these species could be made at a real preparative scale, their use as components of "molecular machines"<sup>3</sup> or in relation to novel materials<sup>4</sup> and energy or electron transfer processes<sup>5</sup> has experienced a spectacular development. The preparation of such compounds under thermodynamic control based on labile covalent bonds<sup>6</sup> or non-covalent bonds such as hydrogen or coordination bonds is particularly promising.<sup>7</sup> The synthesis of transition metalincorporating catenanes for which the ring-forming step involves the formation of a coordination bond has been pioneered by Fujita and his co-workers.<sup>8</sup> By combining copper(I)-1, 10-phenanthroline interactions and palladium(II)-pyridine interactions, several catenanes assembled via coordination chemistry have also been made in collaborative work with Fujita and his team.9 Porphyrin-incorporating catenanes represent a promising

family of molecules and it is particularly interesting to construct such compounds under thermodynamic control using coordination bonds. A few such molecules have recently been reported, which consist of rather short fragments and thus leading to relatively small rings, unable to undergo further copper-directed threading reactions.<sup>1</sup> We would now like to report the synthesis of a new catenane containing larger cycles than those of the previous compounds as well as the data of an equilibrium study in solution. The thermodynamic parameters obtained show that the coordination chemistry-assembled catenane and its constitutive rings are slightly less stable than their smaller homologues, in agreement with entropy considerations.

# **Results and discussion**

## Synthesis of the ligands

The bis-zinc(II)porphyrin **4** was obtained in two steps from the bis-triflate naphthalene derivative  $\mathbf{1}^1$  and the zinc(II) *meso*-iodophenyl porphyrin  $\mathbf{3}^{10}$  as depicted in Scheme 1.

The first step was the conversion of the two triflate functions of **1** into boronic ester functions. **2** was obtained by using the approach of Miyaura with bis(pinacolato)diboron as the transmetalating reagent.<sup>11</sup> In addition to  $PdCl_2(dppf)$  as a catalyst and KOAc as a base, free dppf was required. In fact, its addition allowed the re-activation of the catalyst that was poisoned by the liberation of triflate. After purification of the crude product by chromatography, **2** was isolated as a white solid in 30–40% yield. Pd-catalysed cross-coupling reaction of

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Scheme 1 Synthesis of the bis-Zn porphyrin 4. (i) PdCl<sub>2</sub>(dppf), dppf, KOAc, dioxane, 85 °C, 30–40%; (ii) Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, toluene/EtOH/ H<sub>2</sub>O, 90 °C, 50%.



**Scheme 2** Synthesis of the bis(pyridine)phenanthroline derivative 7. (i) Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, toluene/EtOH/H<sub>2</sub>O, 90 °C, 51%.

**2** with **3** (2 equiv.) gave the desired purple bis-Zn porphyrin **4** in 50% yield by using conditions analogous to those previously described by Sanders and co-workers.<sup>12</sup>

The bis(pyridine) **7** was obtained thanks to a double Suzuki coupling reaction between the 2,9-bis(*para*-bromophenyl)-1,10-phenanthroline  $5^{9c}$  and the commercially available pyridine-4-boronic acid **6** (Scheme 2).

This reaction was performed under classical conditions to afford 7 in 51% yield after purification by column chromatography.

#### Noncovalently assembled ring and [2]catenane

Macrocycle 8 was obtained in one step from 4 and 7 thanks to two non-covalent Zn(II)-N interactions. The reaction is depicted in Scheme 3.

**4** and **7** in stoichiometric proportions ( $c = 1 \times 10^{-3}$  M) were dissolved in chloroform. The solution was stirred at room temperature under argon. Macrocycle **8** was obtained quantitatively and characterized by <sup>1</sup>H NMR (Fig. 1) including COSY (Fig. S1 and S2, ESI<sup>†</sup>) and ROESY (Fig. S3–S5, ESI<sup>†</sup>).

As shown in Fig. 1, the protons of the bis-Zn porphyrin **4** are only slightly affected by formation of ring **8**, contrary to the protons of the bis(pyridine) ligand **7**. In fact, these protons are strongly upfield shifted upon coordination with **4**,



Scheme 3 Formation of the noncovalently assembled macrocycle 8.

particularly the signals  $o_{py}$  and  $m_{py}$  of the pyridine moieties  $(\Delta \delta: -1.51 \text{ and } -4.92 \text{ ppm}, \text{ respectively})$  that lie in the shielding field of a porphyrin. Moreover these signals are broad because of the dissociation equilibrium in which 7 is involved.<sup>1,13</sup>

The constituents **4** and **7** of the macrocycle are perfectly complementary in terms of angles (see Scheme 3). In fact, the sum of the four angles in an hypothetical quadrangle whose 4 edges are co-linear to the two Zn–N coordination axes and the two C–C bonds connecting the porphyrins to the di(4'-phenyl)-2,7-naphthalene fragments is 360°. This should lead to a high association constant.

In order to evaluate the stability of the ring, UV-vis titrations were carried out. To a solution of bis-Zn porphyrin **4** in toluene ( $c = 1.09 \times 10^{-6}$  M), constant aliquots of a solution of bis(pyridine) **7** in toluene ( $c = 3.26 \times 10^{-5}$  M) were gradually added, and UV-vis spectra were recorded after each addition. As expected, upon axial coordination of the pyridyl ligands to the zinc(II) porphyrins, the absorption bands of zinc(II) porphyrins displayed a small bathochromic shift<sup>13,14</sup> and the presence of an isosbestic point indicated that only one species was formed. The UV-vis absorption spectra obtained during the titration of **4** with increasing amounts of **7** are reported in Fig. 2.



Fig. 1 Partial <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>, 298 K) of (a) 4, (b) 7 and (c) 8.



Fig. 2 Absorption spectra (Soret band) in toluene containing 4 ( $c = 1.09 \times 10^{-6}$  M, 3 mL) after additions of constant aliquots (10 µL) of 7 ( $c = 3.26 \times 10^{-5}$  M).

The association constant of the following equilibrium was calculated:

$$4 + 7 \rightleftharpoons 8$$
$$K_{\text{ass}} = \frac{[8]}{[4] \times [7]}$$

The data were analysed (Fig. S6, ESI<sup>†</sup>) and a stability constant of  $K_{ass} = 2 \times 10^5 \pm 0.2 \text{ M}^{-1}$  was obtained.

A higher value was obtained for a related non-covalent porphyrinic macrocycle.<sup>1b</sup> In this previously reported macrocycle, represented in Scheme 4, the number of internal atoms was smaller and equal to 38 compared to 43 for 8.

The Zn–N bond strength being of the same order for each macrocycle, it is expected that formation of a smaller macrocycle is favoured in terms of entropy. Nevertheless, a large ring



**Scheme 4** Chemical structures and number of internal atoms of (a) a related non-covalent macrocycle,  $^{1b}$  (b) macrocycle **8**.

size is needed to be able to construct a [2]catenane with four bulky porphyrins surrounding the central copper bis-phenanthroline core. Previous attempts to synthesize a [2]catenane from a central copper(1) complex coordinated to two di-2,9di(4'-pyridyl)-1,10-phenanthroline chelate failed.<sup>1</sup> In these experiments, the small distances between the pyridyl groups belonging to two chelates prevented the coordination to the porphyrins perpendicularly to their planes, mostly owing to the presence of very bulky groups attached at the periphery of the porphyrin backbones.

From the new ligands **4** and **7**, a [2]catenane was formed in two steps as described in Scheme 5.

In a first step, the entwined precursor complex  $9 \cdot PF_6$  was formed. A solution of  $[Cu(CH_3CN)_4] \cdot PF_6$  (1 equiv.) in acetonitrile was added to a solution of 7 (2 equiv.) in chloroform. After 3 h, the solvents were pumped off to lead quantitatively to



Scheme 5 Synthesis of noncovalently assembled catenane  $10^+$ . (i) [Cu(CH<sub>3</sub>CN)<sub>4</sub>]·PF<sub>6</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>CN, rt, 100%; (ii) 4 (2 equiv.), CHCl<sub>3</sub>, CH<sub>3</sub>CN, rt, 100%.

the desired complex  $9 \cdot PF_6$ , obtained as a red solid.  $9 \cdot PF_6$  was characterized by <sup>1</sup>H NMR and by mass spectrometry ES-MS.

Then,  $9 \cdot PF_6$  (1 equiv.,  $c = 1 \times 10^{-3}$  M) was dissolved in acetonitrile and reacted with 4 (2 equiv.,  $c = 5 \times 10^{-4}$  M) in CHCl<sub>3</sub>. After 3 h, the solvents were removed and <sup>1</sup>H NMR showed the formation of catenane 10  $\cdot PF_6$  as the only product of the reaction (Fig. 3). The different signals could be assigned thanks to COSY (Fig. S7 and S8, ESI<sup>†</sup>) and ROESY (Fig. S9 and S10, ESI<sup>†</sup>) experiments.

The <sup>1</sup>H NMR spectra of the macrocycle 8 and of the [2]catenane  $10 \cdot PF_6$  are compared with one another in Fig. 3.

The protons of ligand 7 are very upfield shifted in 10 PF<sub>6</sub> compared to the same protons in 8 because 7 is involved in the copper(1) entwined complex. The signals of the protons o' and m' are remarkably upfield shifted ( $\Delta\delta$ : -1.51 and -1.27 ppm respectively) proving that an intertwined complex is formed. In fact the entwining places the phenyl of one chelate above the shielding cone of the 1,10-phenanthroline unit of the second chelate.

The association constant of the [2]catenane  $10 \cdot PF_6$  was also determined by absorption titrations. The same protocol as previously was used. To a solution of bis-Zn porphyrin 4 in



toluene ( $c = 1.09 \times 10^{-6}$  M), constant aliquots of  $9 \cdot \mathbf{PF_6}$ in toluene ( $c = 3.26 \times 10^{-5}$  M) were gradually added, and UV-vis spectra were recorded after each addition. The association constant  $K_{ass}$  of the following equilibrium was calculated:

$$2(4) + 9^+ \rightleftharpoons 10^+$$
$$K_{\text{ass}} = \frac{[10^+]}{[4] \times [7]^2}$$

The data were analysed (Fig. S11, ESI<sup>†</sup>) and an association constant of  $K_{ass} = 4 \times 10^{10} \pm 0.1 \text{ M}^{-2}$  was obtained. This corresponds to the square value of the one found for macrocycle 8. There is thus no cooperative effect upon coordination of a second bis(porphyrin) 4 to 9<sup>+</sup>.

## Conclusions

A macrocycle and a [2]catenane were obtained quantitatively under thermodynamic control *via* the formation of zinc(II)– pyridine interactions. These assemblies are stable as attested by the high association constants determined by UV-Vis spectroscopy experiments. The optimized geometrical fit between the constituents and the relatively strong zinc(II)–pyridine interaction enables to obtain in a two step reaction, a tetraporphyrinic [2]catenane.

The large size of the two constitutive rings of the [2]catenane provides the system with empty cavities which will be utilised in the future for coordinating additional species to the free 1,10-phenanthroline fragments so as to lead to more complex threaded species. The present systems pave the way to the stepwise synthesis of large sophisticated assemblies like [2]polycatenanes. Since the cavity of ring **8** appears to be large enough to undergo threading reactions, it could thus be imagined that successive threading steps and coordinationdirected ring closing reactions could progressively lead to the construction of a [2]polycatenane.

# **Experimental section**

#### General methods

Dry solvents were distilled from suitable drying agents (toluene from sodium/benzophenone, dichloromethane from calcium hydride and chloroform from potassium carbonate). Thin layer chromatography was carried out using pre-coated polymeric sheets of silica gel (Macheray-Nagel, POLYGRAM, SIL  $G/UV_{254}$ ). Preparative column chromatography was carried out using silica gel (Merck Kieselgel, silica gel 60, 0.063-0.200 mm). Nuclear Magnetic Resonance (NMR) spectra for <sup>1</sup>H were acquired on Bruker AVANCE 400 or 300 spectrometers. The spectra were referenced to residual proton-solvent references (<sup>1</sup>H: CD<sub>3</sub>CN at 1.94 ppm, CD<sub>2</sub>Cl<sub>2</sub> at 5.32 ppm, CDCl<sub>3</sub> at 7.26 ppm; <sup>13</sup>C: CDCl<sub>3</sub> at 77.36 ppm). In the assignments, the chemical shift (in ppm) is given first, followed, in brackets, by the multiplicity of the signal (s: singlet, d: doublet, t: triplet, m: multiplet, bd: broad doublet), the number of protons implied, the value of the coupling constants in Hertz if applicable, and finally the assignment. Mass spectra were obtained by using a Bruker MicroTOF spectrometer (ES-MS).

#### Starting materials

All chemicals were of best commercially available grade and used without further purification (unless mentioned).

#### Spectral and equilibrium constant measurements

UV-visible spectra were recorded with a Kontron Instruments UVIKON 860 spectrometer at 25 °C with a 1 cm path cell. All measurements were made in toluene solutions,  $c \approx 10^{-6}$  M in bis-zinc(II)porphyrin 4. Dipyridyl derivatives 7 or 9.PF<sub>6</sub> toluene solutions ( $c \approx 10^{-5}$  M) were added to the biszinc(II)porphyrin 4 sample in 10 µL aliquots *via* a 100 µL Hamilton syringe. UV-visible spectrophotometric titrations were analyzed by fitting the series of spectra at 1 nm intervals by using the SPECFIT/32 3.0 (Spectrum Software Associates), which takes into account the changes in volume during the titration.

### Compound 2

A round-bottom flask was charged with methanesulfonic acid 1,1,1-trifluoro-1,1'-(2,7-naphtalenedidyl) ester 1 (278 mg, 0.94 mmol), bis(pinacolato)diboron (665 mg, 3.78 mmol), KOAc (384 mg, 5.64 mmol), 1,1'-bis(diphenylphosphino)-ferrocene (52 mg, 0.094 mmol), Pd(dppf)Cl<sub>2</sub> (53.2 mg, 0.094 mmol) and 5 mL of commercial anhydrous dioxane. The mixture was degassed by three vacuum–argon cycles, and stirred at 80 °C under an atmosphere of argon overnight. The solvent was removed under reduced pressure; the crude product was taken up in CH<sub>2</sub>Cl<sub>2</sub> and washed with water (3 × 10 mL). The crude product was then purified by a fast column chromatography on silica eluted with CH<sub>2</sub>Cl<sub>2</sub>/pentane (90/10), to yield 30–40% of a white solid **2**.

<sup>1</sup>*H NMR* (300 *MHz*, *CDCl*<sub>3</sub>, 298 *K*):  $\delta$  (ppm) 8.41 (s, 2H, 1), 7.87 (dd, 2H, <sup>3</sup>*J* = 8.2 Hz, <sup>4</sup>*J* = 1.0 Hz, 3), 7.80 (d, 2H, <sup>3</sup>*J* = 8.2 Hz, 4), 1.39 (s, 24H, OMe).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 298 K): δ (ppm) 179.54, 137.12, 131.54, 126.79, 83.88, 24.94.

#### **Compound 4**

A round-bottom flask containing *meso* iodophenyl porphyrin **3** (105 mg, 0.046 mmol), Na<sub>2</sub>CO<sub>3</sub> (9.8 mg, 0.092 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (10.6 mg, 10 mol%) was degassed by three vacuum–

argon cycles. The mixture was dissolved in a degassed biphasic mixture of freshly distilled toluene (2 mL), ethanol (0.8 mL) and deionised water (0.6 mL). The reaction mixture was heated at 90 °C overnight under argon. The solvents were evaporated under reduced pressure and the crude product was taken up in CH<sub>2</sub>Cl<sub>2</sub> and washed with water (3 × 30 mL). The resulting material was purified by column chromatographies on silica eluted with pentane/CH<sub>2</sub>Cl<sub>2</sub> (100/0 to 50/50) to yield a purple solid **4** (50 mg, 50%).

<sup>*I*</sup>*H NMR* (300 *MHz*, *CD*<sub>2</sub>*Cl*<sub>2</sub>, 298 *K*):  $\delta$  (ppm) 9.16 (d, 4H, <sup>3</sup>*J* = 4.6 Hz, py<sub>1</sub>), 9.09 (d, 4H, <sup>3</sup>*J* = 4.6 Hz, py<sub>2</sub>), 9.05 (bs, 8H, py<sub>3</sub> + py<sub>4</sub>), 8.68 (s, 2H, 1), 8.46 (d, 4H, <sup>3</sup>*J* = 8.1 Hz, *m*), 8.30 (d, 4H, <sup>3</sup>*J* = 8.1 Hz, *o*), 8.25 (bs, 4H, 3 + 4), 8.17 (d, 8H, <sup>4</sup>*J* = 1.8 Hz, op<sub>x</sub>), 8.15 (d, 4H, <sup>4</sup>*J* = 1.8 Hz, op<sub>z</sub>), 7.90 (m, 6H, <sup>4</sup>*J* = 1.6 Hz, pp<sub>x</sub> + pp<sub>z</sub>), 1.59 (s, 108H, *t*Bu<sub>x</sub> + *t*Bu<sub>z</sub>).

*ES/MS*: m/z 2154.36 [4 + H<sup>+</sup>], calcd 2154.68 for  $C_{146}H_{156}N_8Zn_2H$ .

#### **Compound 7**

A round-bottom flask was charged with 2,9-bis(*para*bromophenyl)-1,10-phenanthroline **5** (200 mg, 0.41 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (28.6 mg, 6 mol%), and degassed by three vacuum–argon cycles. The mixture was dissolved in 8 mL of freshly distilled and degassed toluene. Then were added, respectively, a degassed solution of pyridine-4-boronic acid (152 mg, 1.24 mmol) in EtOH (10 mL) and a degassed solution of Na<sub>2</sub>CO<sub>3</sub> (219 mg, 2 mmol) in deionised water (1.5 mL). The mixture was heated at 90 °C overnight under argon. The solvents were evaporated under reduced pressure and the crude product taken up in CH<sub>2</sub>Cl<sub>2</sub> and washed with water (3 × 30 mL). The organic layers were combined and dried with MgSO<sub>4</sub>. The resulting material was purified by column chromatography on silica eluted with CHCl<sub>3</sub>/MeOH (100/0 to 98/2) to afford a white solid **7** (102 mg, 51%).

<sup>1</sup>*H* NMR (300 MHz, CDCl<sub>3</sub>, 298 K): δ (ppm) 8.66 (d, 4H, <sup>3</sup>*J* = 6.2 Hz,  $m_{py}$ ), 8.59 (d, 4H, <sup>3</sup>*J* = 8.5 Hz, o), 8.37 (d, 2H, <sup>3</sup>*J* = 8.5 Hz, 4, 7), 8.22 (d, 2H, <sup>3</sup>*J* = 8.5 Hz, 3, 8), 7.90 (d, 4H, <sup>3</sup>*J* = 8.5 Hz, m), 7.84 (s, 2H, 5, 6), 7.64 (d, 4H, <sup>3</sup>*J* = 6.3 Hz,  $o_{py}$ ). *ES/MS*: m/z 487.19 [7 + H<sup>+</sup>], calcd 487.19 for C<sub>34</sub>H<sub>22</sub>N<sub>4</sub>H.

#### Compound 8

In a round-bottom flask, 4 (8.8 mg, 0.004 mmol) was dissolved in 1 mL of freshly distilled and degassed CHCl<sub>3</sub>. In another round-bottom flask, 7 (6.7 mg) was dissolved in 15 mL of freshly distilled and degassed CHCl<sub>3</sub>. 4.5 mL (0.004 mmol) of this solution were added dropwise to the solution of 4 in CHCl<sub>3</sub>. The solution turned immediately purple-green. The mixture was allowed to react overnight at room temperature under argon. The solvent was removed under reduced pressure to give quantitatively complex 8 as a purple greenish solid (7.4 mg).

<sup>1</sup>*H* NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ (ppm) 9.04 (d, 4H, <sup>3</sup>*J* = 4.7 Hz, py<sub>1</sub>), 9.01 (bs, 8H, py<sub>3</sub> + py<sub>4</sub>), 9.01 (d, 4H, <sup>3</sup>*J* = 4.7 Hz, py<sub>2</sub>), 8.55 (s, 2H, 1), 8.30 (bs, 2H, 4), 8.13 (d, 8H, <sup>4</sup>*J* = 1.8 Hz, op<sub>x</sub>), 8.11 (d, 4H, <sup>4</sup>*J* = 1.6 Hz, op<sub>z</sub>), 8.09 (m, 10H, o' + 4', 7' + m + 3 + o), 7.87 (d, 6H, <sup>3</sup>*J* = 8.5 Hz, 3', 8'), 7.80 (t, <sup>4</sup>*J* = 1.6 Hz, pp<sub>x</sub> + pp<sub>z</sub>), 7.61 (s, 2H, 5', 6'), 7.01 (d, 4H, <sup>3</sup>*J* = 8.4 Hz, m'), 6.12 (d, 4H, <sup>3</sup>*J* = 5.5 Hz, m<sub>py</sub>), 3.70 (bs, 4H, o<sub>py</sub>), 1.54 (s, 72H, tBu<sub>x</sub>), 1.53 (s, 36H, tBu<sub>z</sub>).

*UV-vis* (toluene):  $\lambda_{max}$  (log  $\varepsilon$ ) = 428 (5.85), 551 (4.52), 591 (3.29) nm.

#### Compound 9.PF<sub>6</sub>

In a round-bottom flask, 7 (10.0 mg, 0.02 mmol) was dissolved in 20 mL of freshly distilled CHCl<sub>3</sub>. The solution was degassed by three vacuum–argon cycles. In a Schlenk, Cu(CH<sub>3</sub>CN)<sub>4</sub>. PF<sub>6</sub> (7.7 mg, 0.02 mmol) was dissolved in 3 mL of degassed CH<sub>3</sub>CN. 1.5 mL (0.01 mmol) of this solution was added dropwise to the solution of 7 in CHCl<sub>3</sub>. The solution turned immediately red. The mixture was allowed to react for 5 hours at room temperature under argon. The solvents were removed under reduced pressure to give quantitatively the desired complex 9.PF<sub>6</sub> as a brown solid (10.4 mg). <sup>1</sup>*H* NMR (400 MHz, CD<sub>3</sub>CN, 298 K: δ (ppm) 8.64 (d, 8H, <sup>3</sup>*J* = 5.7 Hz,  $m_{py}$ ), 8.56 (d, 4H, <sup>3</sup>*J* = 8.4 Hz, 4, 7), 8.02 (d, 4H, <sup>3</sup>*J* = 8.4 Hz, 3, 8), 7.94 (s, 4H, 5, 6), 7.70 (d, 8H, <sup>3</sup>*J* = 8.4 Hz, *o*), 7.21 (d, 8H, <sup>3</sup>*J* = 6.0 Hz,  $o_{py}$ ), 6.96 (d, 8H, <sup>3</sup>*J* = 8.4 Hz, m). *ES/MS*: *m/z* 1035.277 [**9**<sup>+</sup>], calcd 1035.298 for C<sub>68</sub>H<sub>44</sub>N<sub>8</sub>Cu.

#### Compound 10-PF<sub>6</sub>

In a round-bottom flask,  $9 \cdot PF_6$  (3.2 mg, 0.0027 mmol) was dissolved in 1 mL of degassed CH<sub>3</sub>CN. In a round-bottom flask, 4 (11.7 mg, 0.0054 mmol) was dissolved in 5 mL of freshly distilled and degassed CHCl<sub>3</sub>. This solution was added dropwise *via* canula to the solution of  $9 \cdot PF_6$  in CH<sub>3</sub>CN. The solution turned immediately purple-green. The mixture was allowed to react for four hours at room temperature under argon. The solvents were removed under reduced pressure to yield quantitatively the desired complex  $10 \cdot PF_6$  as a purple greenish solid (14.9 mg).

<sup>1</sup>*H* NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ (ppm) 9.02 (d, 8H, <sup>3</sup>*J* = 4.5 Hz, py<sub>1</sub>), 8.97 (s, 16H, py<sub>3</sub> + py<sub>4</sub>), 8.96 (d, 8H, <sup>3</sup>*J* = 4.5 Hz, py<sub>2</sub>), 8.55 (bs, 4H, 1), 8.34 (d, 4H, <sup>3</sup>*J* = 7.5 Hz, 4), 8.17 (d, 4H, <sup>3</sup>*J* = 7.9 Hz, 3), 8.14 (d, 8H, <sup>3</sup>*J* = 7.6 Hz, *o*), 8.07 (*m*, 24H, <sup>4</sup>*J* = 1.7 Hz, op<sub>*Z*</sub>), 7.79 (t, 4H, <sup>4</sup>*J* = 1.7 Hz, op<sub>*x*</sub>), 7.77 (m, 20H, <sup>4</sup>*J* = 1.7 Hz, pp<sub>*x*</sub> + pp<sub>*z*</sub> + *m*), 7.72 (bd, 4H, <sup>3</sup>*J* = 8.7 Hz, 4', 7'), 7.14 (bd, 4H, <sup>3</sup>*J* = 7.5 Hz, 3', 8'), 6.81 (bs, 4H, 5', 6'), 6.58 (bd, 8H, <sup>3</sup>*J* = 6.3 Hz, *o'*), 5.74 (bd, 8H, <sup>3</sup>*J* = 6.7 Hz, *m'*), 5.45 (bs, 8H, *m*<sub>py</sub>), 3.56 (vbs, 8H, *o*<sub>py</sub>). *ES/MS*: *m/z* 5346.7 [10<sup>+</sup>], calcd for 5346.5 C<sub>360</sub>H<sub>356</sub>N<sub>24</sub>CuZn<sub>4</sub>.

*UV-vis* (toluene):  $\lambda_{\text{max}} (\log \varepsilon) = 428$  (5.85), 552 (4.52), 592 (3.29) nm.

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