

Change in Supramolecular Networks through In Situ Esterification of Porphyrins

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A series of porphyrins, M[TCPP-Et₄] [M = Zn (**1**), Cu (**2**), and Ni (**3**); Et = CH₂CH₃; TCPP = *meso*-tetra(4-carboxyphenyl)porphyrin], M[TCPP-Me₄] [M = Zn (**4**), Cu (**5**), and Co (**6**); Me = CH₃], and two nonmetalated compounds, TCPP-Et₄ (**7**) and TCPP-Me₄·H₂O (**8**), were synthesized by solvothermal reactions and characterized by single-crystal X-ray diffraction. Compounds **1–3** feature an isolated structure with a planar macrocycle and an embedded metal-ion coordinating to four pyrrole nitrogen atoms. Compound **4** is characterized as a two-dimensional coordination polymer, and the zinc ion coordinates to four nitrogen atoms and two oxygen atoms. Compound **4** possesses a large void space (361 Å³), which corresponds to 14 % of the unit-cell volume. Compounds **5** and **6** are characteristic of an isolated motif with a four-coordinate metal ion and a saddle-distorted nonplanar porphyrin macrocycle. Nonmetalated compounds **7** and **8** also show an

isolated structure with a planar macrocycle. For compounds **1–3** and **7**, the TCPP is esterified with ethanol, while for compounds **4–6** and **8**, the TCPP is esterified with methanol. The molecules in **1** and **6–8** are interconnected by hydrogen bonds and π - π interactions to yield 3D supramolecular networks, while in **2–5**, 2D supramolecular motifs are formed. The reaction mechanism was explored. Esterification plays an important role in changing the properties of the compounds as well as in the formation of different structural motifs and supramolecular networks. The UV/Vis, FTIR, fluorescence, phosphorescence, and MALDI-TOF MS spectra, quantum yields, luminescence lifetimes, and cyclic voltammograms were also studied in detail.

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Introduction

Porphyrins are among the most widely studied chemical systems with abundant properties, and the vital roles played by porphyrins in nature have been known for decades, as well as their applications in catalysis, medicine, solar energy conversion, amongst others.^[1–12] The aggregation and self-assembly of porphyrins are an area of intense research, and so far, many porphyrin supramolecular assemblies, which can be used as molecular-level electronics, sensors, photonic materials, and for molecular recognition, have been prepared through noncovalent interactions such as π - π stacking interactions and hydrogen-bonding interactions.^[13–24] The coordination of metal ions at the center of the porphyrin ring, as well as the substitution at the periphery of the porphyrin rings by suitable organic groups, provide various programming elements for the design of porphyrin supramolecular assemblies. The modification through peripheral substitutions can change the chemical, electronic absorp-

tion and emission spectral, and redox properties of porphyrins. Thus, extensive efforts have been devoted to the preparation and chemical transformation of porphyrins into new porphyrin derivatives bearing reformative characteristics that may enable them to be used in practical applications.^[25–29]

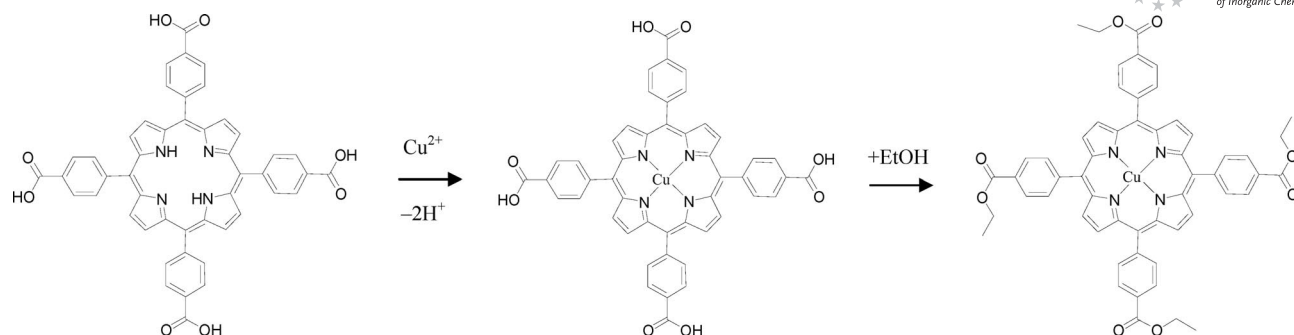
Multifarious substituent groups in numerous organic reactions have been utilized to decorate the periphery of porphyrins. However, esterification of porphyrins has scarcely been reported. The large, rigid and square-planar symmetrical *meso*-tetra(4-carboxyphenyl)porphyrin (TCPP) molecule with divergent carboxylic groups is an extraordinary building block for supramolecular self-assemblies. Metalation of the TCPP core usually serves to strengthen the structural rigidity and it is accompanied with deprotonation of the TCPP molecule during the reaction to account for charge equilibrium, without the requirement of incorporation of other counteranions. Besides metalation and deprotonation, esterification is the third most important characteristic of TCPP because of its carboxylic groups that can possibly be esterified. However, the structures and functions of TCPP supramolecules have yet to be explored.

We report herein the synthesis, X-ray crystal structures, and properties of a series of esterified porphyrin compounds, M[TCPP-Et₄] [M = Zn (**1**), Cu (**2**), and Ni (**3**)], M[TCPP-Me₄] [M = Zn (**4**), Cu (**5**) and Co (**6**)], and two nonmetalated compounds TCPP-Et₄ (**7**) and TCPP-

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Scheme 1. Schematic diagram of the reaction mechanism (taking compound **2** as an example).

$\text{Me}_4\cdot\text{H}_2\text{O}$ (**8**), which were obtained by solvothermal reactions. It should be noted that the title compounds cannot be prepared by the traditional solution method because the high temperatures and pressures necessary for esterification cannot be achieved. The title compounds were characterized in detail by using single-crystal X-ray diffraction, UV/Vis, FTIR, fluorescence and phosphorescence spectroscopy, quantum yields, luminescence lifetimes, cyclic voltammetry, and MALDI-TOF MS spectrometry. It should be pointed out that the title compounds were synthesized by using in situ esterification construction methods.

To the best of our knowledge, only several compounds containing both TCPP and ester groups have been documented thus far, and for most of these compounds, the ester groups were introduced from the starting materials.^[30,31] As for the reaction mechanism of preparing the title compounds, we propose the following logical process: TCPP undergoes a deprotonation and metalation procedure, followed by esterification (Scheme 1). The vital role, played by the esterification in tuning the properties and supramolecular networks, was explored for the first time.

We found that supramolecular networks were controllable, namely, supramolecular networks can be easily adjusted by the esterification under solvothermal conditions. To the best of our knowledge, although many porphyrins have so far been reported, investigations on the ability of esterification to tune the supramolecular networks have yet to be performed. Moreover, this work provides a convenient synthetic method for the esterification of porphyrins.

Results and Discussion

General Characterization

For all the title compounds, the MALDI-TOF MS spectra in CHCl_3 (matrix: CHCA; negative mode) exhibit molecular peak values that are consistent with the corresponding calculated exact mass numbers (see Supporting Information, Figure S1). This indicates that all the compounds maintain their structures in solution as in the solid state. As for the solubility, it has a dramatic change before and after the peripheral modification of the porphyrins. Before peripheral esterification, TCPP dissolves well in ethanol and methanol, but is insoluble in CHCl_3 . In contrast, after pe-

ripheral esterification, the porphyrins dissolve well in CHCl_3 but are insoluble in ethanol and methanol.

The IR spectra of **1–8** display similar features, and the bands mainly appear in the range $700\text{--}1750\text{ cm}^{-1}$, as shown in Figure S2 (see Supporting Information). From the IR spectra of free-base TCPP, there are two bands observed at ca. 3319 and ca. 967 cm^{-1} , which correspond to the $\nu_{\text{N-H}}$ and $\delta_{\text{N-H}}$ vibrations of the pyrrole rings. These two bands can also be found in the IR spectra of the nonmetalated compounds TCPP- Et_4 (**7**) and TCPP- $\text{Me}_4\cdot\text{H}_2\text{O}$ (**8**), in good agreement with the fact that the N-H bonds of the pyrrole rings are still intact in **7** and **8**. However, in the IR spectra of **1–6**, these two bands disappear as result of the deprotonation and the metalation of the pyrrole rings. This result proves that the free-base porphyrin is converted into a metalloporphyrin.

Crystal Structures

$M[\text{TCPP-Et}_4]$ [$M = \text{Zn}$ (**1**), Cu (**2**), Ni (**3**), and H_2 (**7**)] and $\text{TCPP-Me}_4\cdot\text{H}_2\text{O}$ (**8**)

The selected bond lengths and angles are presented in Table 1, and a summary of the crystallographic data and structure analyses is listed in Table 5.

X-ray diffraction analysis reveals that the structures of compounds **1–3**, **7**, and **8** have a common feature despite different cells (but, incidentally, the same space group), and herein compound **1** is presented as an example and discussed in detail.

The molecular structure of **1** is depicted as an ORTEP drawing in Figure 1. Compound **1** consists of neutral $\text{Zn}[\text{TCPP-Et}_4]$ molecules and crystallizes in the space group $P2_1/c$. The Zn^{2+} ion resides in a crystallographic inversion center and has an approximately ideal square-planar geometry without axial ligation. The bond lengths from the zinc ion (at the center of the almost perfectly planar porphyrin macrocycle) to the pyrrole nitrogen atoms are in the range $2.040(2)\text{--}2.051(2)\text{ \AA}$ in **1**, which is comparable to that found in the literature.^[32–42] Bond valence calculations indicate that the zinc ion is in a +2 oxidation state [$\text{Zn1: } 1.90$].^[43] The distortion angles of the phenyl rings with respect to the macrocycle plane are $52.37(6)^\circ$ and $85.79(8)^\circ$. All four carboxylic groups are esterified with ethanol molecules.

Table 1. Selected bond lengths [Å] and bond angles [°].

1			
Zn1–N1 × 2	2.051(2)	N2–Zn1–N1 × 2	90.62(7)
Zn1–N2 × 2	2.040(2)	N2#1–Zn1–N1 × 2 ^[a]	89.38(7)
N2–Zn1–N2#1 ^[a]	180.00(6)	N1#1–Zn1–N1 ^[a]	180.00(9)
2			
Cu1–N1 × 2	1.994(2)	N2–Cu1–N1 × 2	89.99(7)
Cu1–N2 × 2	1.997(1)	N2#1–Cu1–N1 × 2 ^[b]	90.01(7)
N2–Cu1–N2#1 ^[b]	180.0(1)	N1#1–Cu1–N1 ^[b]	180.0(1)
3			
Ni1–N1 × 2	1.957(1)	N2–Ni1–N1 × 2	89.82(6)
Ni1–N2 × 2	1.954(2)	N2#1–Ni1–N1 × 2 ^[c]	90.18(6)
N2–Ni1–N2#1 ^[c]	180.00(5)	N1#1–Ni1–N1 ^[c]	180.00(5)
4			
Zn1–N1 × 2	2.030(2)	N2–Zn1–N1 × 2	90.27(9)
Zn1–N2 × 2	2.046(2)	N2#2–Zn1–N1 × 2 ^[e]	89.73(9)
Zn1–O3#1 × 2 ^[d]	2.543(2)	N1#2–Zn1–N1 ^[e]	180.000(1)
N2–Zn1–N2#2 ^[e]	180.00(0)		
5			
Cu1–N1	1.974(2)	N1–Cu1–N3	173.94(9)
Cu1–N2	1.983(2)	N1–Cu1–N4	89.63(8)
Cu1–N3	1.981(2)	N2–Cu1–N3	90.07(8)
Cu1–N4	1.994(2)	N2–Cu1–N4	175.26(9)
N1–Cu1–N2	90.35(8)	N3–Cu1–N4	90.45(8)
6			
Co1–N1	1.953(2)	N1–Co1–N3	172.25(7)
Co1–N2	1.956(2)	N1–Co1–N4	90.25(7)
Co1–N3	1.955(2)	N2–Co1–N3	90.55(7)
Co1–N4	1.956(2)	N2–Co1–N4	172.83(8)
N1–Co1–N2	89.93(7)	N3–Co1–N4	90.24(7)

[a] Symmetry codes #1: $-x, -y, -z$. [b] Symmetry codes #1: $-x + 1, -y, -z$. [c] Symmetry codes #1: $-x, -y, -z$. [d] Symmetry codes #1: $x, 1.5 - y, 0.5 + z$. [e] Symmetry codes #2: $-x + 1, -y + 2, -z + 1$.

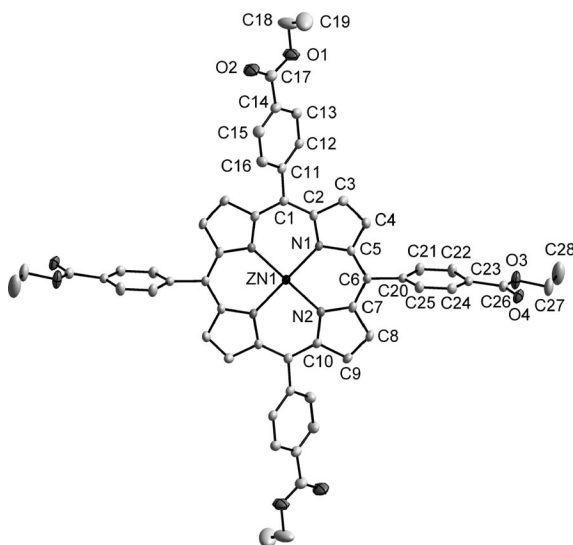


Figure 1. ORTEP drawing of **1** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

There is no solvent molecule in the crystal structure, and the closest Zn–porphyrin plane distance inside one unit cell is 8.417(3) Å with a plane dihedral angle of 0°. In **1**, the abundant C–H $\cdots\pi$ interactions bridge the molecules to construct a 3D supramolecular network (Figure 2). It is noteworthy that the C19–H $\cdots\pi$ interaction between one of the ester groups (shown enclosed in a circle in Figure 2) and a neighboring phenyl ring plays an important role in the formation of the 3D supramolecular network. If this C19–H $\cdots\pi$ interaction were absent, a 2D supramolecular structure would form rather than a 3D supramolecular network.

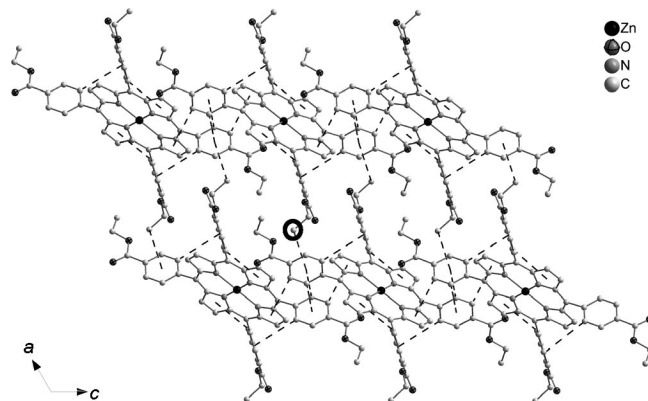


Figure 2. Packing diagram of **1** with the dashed lines representing C–H $\cdots\pi$ interactions [the circle highlights the ester carbon atom involved in the formation of a C19–H $\cdots\pi$ interaction]. Represented hydrogen-bonding interactions: C12–H12A $\cdots$ C_g1 with $d_{C\cdots C_g} = 3.943(3)$ Å and $\angle(\text{DHA}) = 144.11^\circ$; C24–H24A $\cdots$ C_g2 with $d_{C\cdots C_g} = 3.318(3)$ Å and $\angle(\text{DHA}) = 118.43^\circ$; C21–H21A $\cdots$ C_g3 with $d_{C\cdots C_g} = 3.788(3)$ Å and $\angle(\text{DHA}) = 171.32^\circ$; C19–H19A $\cdots$ C_g4 with $d_{C\cdots C_g} = 3.788(5)$ Å and $\angle(\text{DHA}) = 174.26^\circ$; C25–H25A $\cdots$ C_g4 with $d_{C\cdots C_g} = 3.922(3)$ Å and $\angle(\text{DHA}) = 153.74^\circ$ [C_g1, C_g2, C_g3, and C_g4 stand for the centers of gravity of the rings N1(C2–C5), N2(C7–C10), C11–C16, and C20–C25, respectively].

Zn[TCPP-Me₄] (**4**)

In contrast to the case described above, the X-ray diffraction analysis reveals that the structure of **4** comprises neutral 2D polymer layers, as shown in Figures 3 and 4. Compound **4** crystallizes in the space group $P2_1/c$ of the monoclinic system with two formula units in a cell. All crystallographically independent atoms are in general positions with the exception of the Zn1 atom which lies on the crystallographic center of inversion. The 24-membered macrocyclic core of the porphyrin is coplanar, and the displacement of each atom in the equatorial mean plane is within ± 0.059 Å. The six-coordinate zinc atom is located at the center of this almost perfectly planar porphyrin macrocycle and is bonded to four nitrogen and two oxygen atoms to construct an octahedron (Figure 3). The Zn–N bond lengths range from 2.030(2) to 2.046(2) Å with an average value of 2.038(2) Å, which is similar to that of **1** and comparable to that found in the literature.^[32–42] The Zn–O bond length is 2.543(2) Å, which is comparable to those found for related species in the Cambridge Structural Database.^[44–48] The bond valence calculations show that the zinc ion has a +2

oxidation state [Zn1: 2.14]. The four phenyl groups are approximately perpendicular to the macrocycle core; the dihedral angles between the macrocycle and their mean planes are $64.63(9)^\circ$ and $88.0(1)^\circ$, respectively. Each Zn[TCPP-Me₄] unit links to four neighboring molecules through Zn–O bonds, which gives a condensed 2D coordination polymer assembly with a herring-bone pattern (Figure 4).

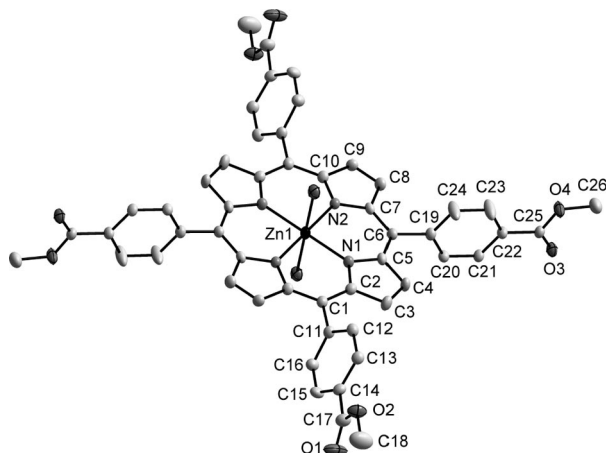


Figure 3. ORTEP drawing of **4** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

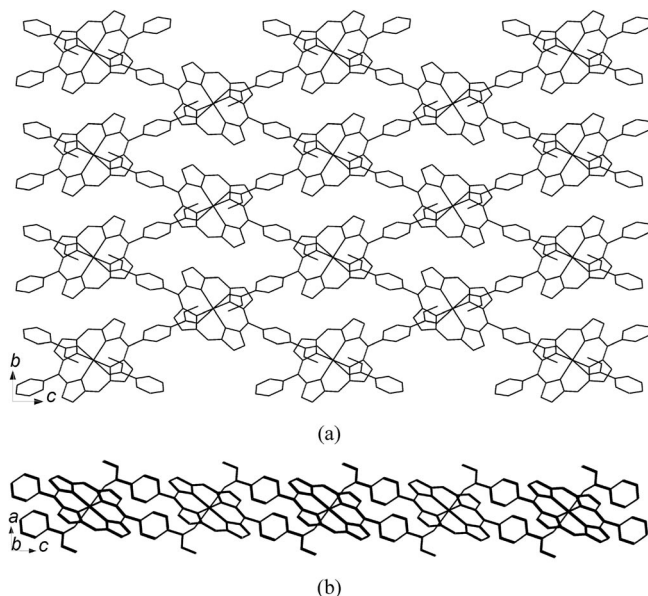


Figure 4. (a) Top view and (b) side view of the 2D slab of **4** (wire representation).

There are only one hydrogen-bonding and two C–H $\cdots\pi$ interactions among the molecules of **4**. It should be pointed out that no C–H $\cdots\pi$ interactions exist between the ester groups (shown enclosed in a circle in Figure 5a) and the neighboring phenyl rings, and, as a result, a 3D supramolecular network cannot be constructed (Figure 5a). This is quite different from **1**. Such a difference is probably related to the fact that both compounds have different ester groups (ethyl and methyl for **1** and **4**, respectively), and the ethyl group is larger and therefore is able to reach a neigh-

boring phenyl ring to form a C–H $\cdots\pi$ interaction. Therefore, supramolecular structures can be modified through different ester groups.

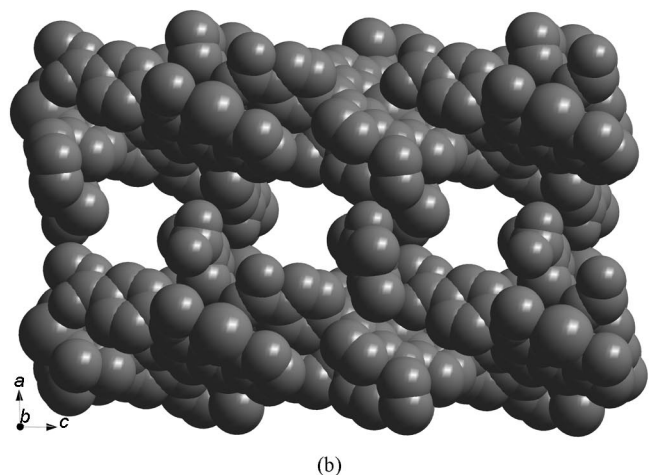
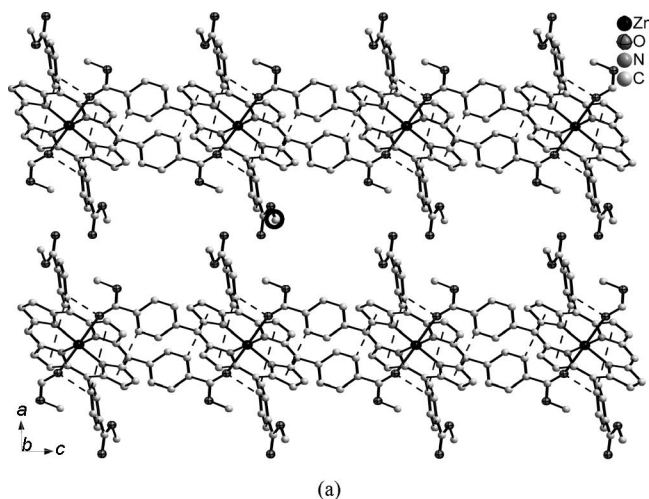


Figure 5. (a) Packing diagram of **4** with the dashed lines representing hydrogen-bonding and C–H $\cdots\pi$ interactions (the circle highlights the ester carbon atom that is not involved in the formation of a C–H $\cdots\pi$ interaction). Represented interactions: C12–H12A $\cdots$ C_g1 with $d_{C\cdots C_g} = 3.597(3)$ Å and $\angle(\text{DHA}) = 146.81^\circ$; C21–H21A $\cdots$ C_g2 with $d_{C\cdots C_g} = 3.319(3)$ Å and $\angle(\text{DHA}) = 124.14^\circ$; O3 $\cdots$ C13 ($1 - x, 0.5 + y, 0.5 - z$) = $3.225(4)$ Å [C_g1 and C_g2 stand for the centers of gravity of the rings N1(C2–C5) and N2(C7–C10), respectively]. (b) Space-filling illustration of the porous crystalline architecture of **4**.

As shown in Figure 5b, it is noteworthy that compound **4** exhibits a large void space of 361 Å^3 , that is 14% of the unit-cell volume. There is no need to incorporate other counteranions into compound **4**, as the charges are already balanced during the metalation and deprotonation of the TCPP core. Therefore, no counteranions exist in the large voids.

M[TCPP-Me₄] [*M* = Cu (**5**) and Co (**6**)]

The X-ray structural determination reveals that compounds **5** and **6** feature an isolated structural motif in which a four-coordinate metal ion resides at the center of a saddle-distorted nonplanar porphyrin macrocycle. X-ray diffrac-

tion analyses show that the structures of **5** and **6** consist of neutral $M[\text{TCPP-Me}_4]$ moieties, as shown in Figures 6 and S7 (Supporting Information). The four-coordinate copper or cobalt atom is located at the center of the porphyrin macrocycle and is bonded to four nitrogen atoms. The Cu–N bond lengths range from 1.974(2) to 1.994(2) Å with an average value of 1.983(2) Å in **5**, which is comparable to that reported.^[49–59] For compound **6**, the Co–N distances are in the narrow range 1.953(2)–1.956(2) Å, which is comparable to those previously documented.^[60–63] The porphyrin macrocycles in **5** and **6** display a four-saddle conformation, and the four pyrrole rings appreciably distort in an alternant fashion, either upward and downward with respect to the mean plane of the saddlelike porphyrin core. The displacement of the four pyrrole N atoms is within ± 0.11 Å (in **5**) and ± 0.15 Å (in **6**) from their mean N4 plane. For compound **5**, the dihedral angles between the planes of the four pyrrole rings distorted in the same direction with respect to the N4 plane are 25.7(2)° and 22.4(2)°, while these angles are 20.2(1)° and 28.8(1)° for **6**. The dihedral angles between the neighboring pyrrole rings are 19.7(2)°, 17.2(2)°, 14.9(1)°, and 16.6(2)° in **5** and 18.7(1)°, 22.4(1)°, 19.9(1)°, and 17.0(1)° in **6**. With respect to the N4 plane, which may represent the mean plane of the porphyrin core, the twist angles of the aryl rings are 52.04(8)°, 49.81(7)°, 69.48(8)°, and 83.90(7)° in **5** and 48.85(6)°, 80.44(6)°, 89.24(8)°, and 58.07(8)° in **6**.

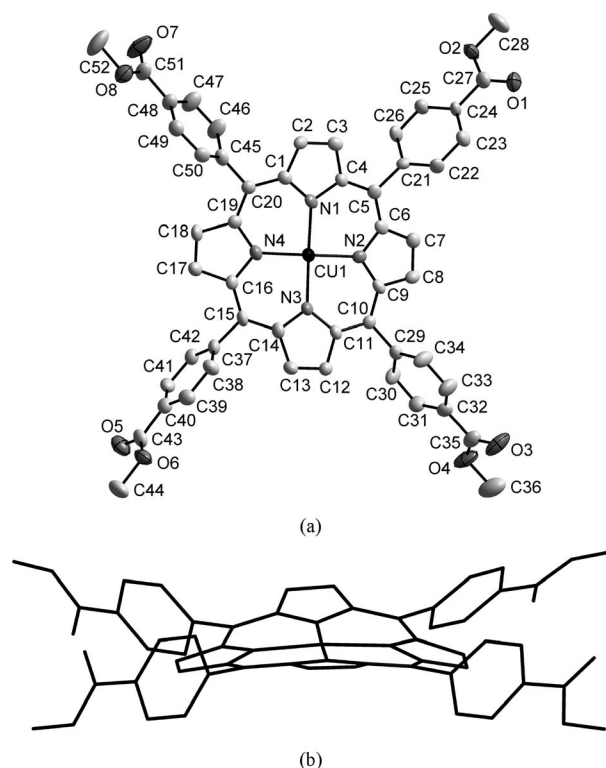


Figure 6. (a) Face-on view (ORTEP drawing with 30% thermal ellipsoids) and (b) edge-on view (wire representation) of **5**.

In contrast to **4**, there are plenty C–H $\cdots\pi$, π – π , and hydrogen-bonding interactions between the molecules of **5** and **6**, as shown in Figures 7 and S8 (Supporting Infor-

mation). However, no C–H $\cdots\pi$ interactions exist between the ester groups and the neighboring aryl rings, in contrast to that in **4**. This is probably because the methyl group is not large enough to interact with an adjacent aryl ring to yield a C–H $\cdots\pi$ interaction. For compound **5**, the $\text{Cu}[\text{TCPP-Me}_4]$ moieties are interconnected together by C–H $\cdots\pi$ and hydrogen-bonding interactions to form a 2D supramolecular network (Figure 7). For compound **6**, the $\text{Co}[\text{TCPP-Me}_4]$ molecules link to each other through more abundant C–H $\cdots\pi$, π – π , and hydrogen-bonding interactions to construct a 3D supramolecular structure (see Supporting Information, Figure S8). The different packing motifs between **5** and **6** may result from the different metal centers in **5** and **6**, because different metal ions would lead to different sizes of the molecules and different distances between the molecules.

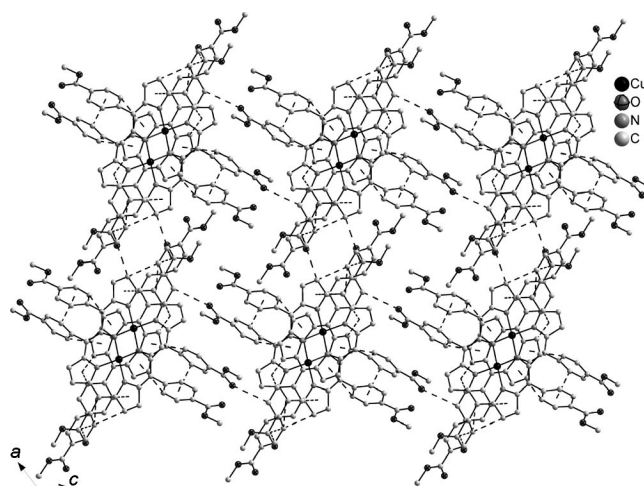


Figure 7. Packing diagram of **5** with the dashed lines representing hydrogen-bonding and C–H $\cdots\pi$ interactions. Represented hydrogen-bonding interactions: C30–H30A $\cdots$ C_g1 with $d_{\text{C}\cdots\text{C}_g}$ = 3.566(3) Å and $\angle(\text{DHA})$ = 134.42°; C50–H50A $\cdots$ C_g2 with $d_{\text{C}\cdots\text{C}_g}$ = 3.622(4) Å and $\angle(\text{DHA})$ = 119.85°; C3–H3A $\cdots$ C_g3 with $d_{\text{C}\cdots\text{C}_g}$ = 3.825(3) Å and $\angle(\text{DHA})$ = 115.77°; C26–H26A $\cdots$ C_g3 with $d_{\text{C}\cdots\text{C}_g}$ = 3.430(3) Å and $\angle(\text{DHA})$ = 110.17°; C22–H22A $\cdots$ C_g4 with $d_{\text{C}\cdots\text{C}_g}$ = 3.344(3) Å and $\angle(\text{DHA})$ = 108.76°; C42–H42A $\cdots$ C_g5 with $d_{\text{C}\cdots\text{C}_g}$ = 3.926(3) Å and $\angle(\text{DHA})$ = 119.72°; C17–H17A $\cdots$ C_g6 with $d_{\text{C}\cdots\text{C}_g}$ = 4.020(4) Å and $\angle(\text{DHA})$ = 131.99°; C34–H34A $\cdots$ C_g7 with $d_{\text{C}\cdots\text{C}_g}$ = 3.734(4) Å and $\angle(\text{DHA})$ = 149.89°; O3 $\cdots$ C25 ($x, -y, 0.5 + z$) = 3.202(4) Å [_Cg1, _Cg2, _Cg3, _Cg4, _Cg5, _Cg6, and _Cg7 stand for the centers of gravity of the rings N1(C1–C4), N2(C6–C9), N3(C11–C14), N4(C16–C19), C21–C26, C37–C42, and C45–C50, respectively].

For the zinc-containing compounds **1** and **4**, compound **1** exhibits an isolated structural feature and a 3D supramolecular network with the zinc ion in a four-coordination sphere, while compound **4** is characteristic of a 2D coordination polymer and a 2D supramolecular network with the zinc metal in a six-coordination environment. The different coordination environments of the zinc ions, the different structural motifs, and the different supramolecular networks result from different ester groups that were generated by using different esterification materials. For compound **1**, the ester groups come from the esterification of TCPP with ethanol; while for compound **4**, TCPP is esterified with

methanol. Similarly, for the copper-containing compounds **2** and **5**, compound **2** features a nearly perfectly planar porphyrin macrocycle, while compound **5** shows a four-saddle distorted conformation. This difference is also caused by the different ester groups, as the cases of **1** and **4**. Thus, esterification plays an important role in constructing different structural motifs and different supramolecular networks.

UV/Vis Absorption Spectroscopy

According to Gouterman's four orbitals model,^[64] metalloporphyrins usually exhibit two types of intense absorption bands, i.e. the intense B band (Soret band) around 400 nm with an absorption coefficient (ϵ) of ca. $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ and the less intense Q bands between 500 and 650 nm with an ϵ value of ca. $10^3\text{--}10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Figure 8a displays the UV/Vis absorption spectra for compounds **1–3**, **7**, and free-base TCPP. The B band and four Q bands for free-base TCPP are observed at 416, 512, 546, 590, and 645 nm. The B band of compounds **1–3** and **7** appears at 422 nm ($\epsilon = 4.18 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), 418 nm ($\epsilon = 3.84 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), 417 nm ($\epsilon = 3.58 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), and 421 nm ($\epsilon = 1.48 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. They are shifted to the red by one to several nanometers relative to that of TCPP. Compounds **1–3** only have one Q band in the range 530–

7 and free-base TCPP (Table 2). This difference is attributed to an increase in the molecular symmetry, which results from the metalation of the free-base TCPP. By the same token, compounds **4–6** also exhibit only one Q band around 540 nm (Figure 8b). The absorption coefficients of the B bands for metalloporphyrins **1–6** are about $10^5 \text{ M}^{-1} \text{ cm}^{-1}$, which is in good agreement with that found by Gouterman.^[64] The B band of free-base TCPP displays a large molar absorption coefficient (magnitude of a million), which is over one magnitude larger than that of the esterified compounds **1–8**. This clearly indicates that the esterification results in a decrease in the absorption coefficient. Thus, modification through peripheral esterification can change the electronic absorption properties of porphyrins. This enables porphyrins to be potentially useful sensors of their surrounding environments.

Table 2. UV/Vis absorption data (CHCl_3 and EtOH for **1–8** and TCPP, respectively, 298 K).

	$\lambda(\text{B band}) [\text{nm}]$ ($\epsilon, \text{M}^{-1} \text{cm}^{-1}$)	$\lambda(\text{Q band}) [\text{nm}]$
Zn[TCPP-Et ₄] (1)	422 (4.18×10^5)	548
Cu[TCPP-Et ₄] (2)	418 (3.84×10^5)	540
Ni[TCPP-Et ₄] (3)	417 (3.58×10^5)	530
Zn[TCPP-Me ₄] (4)	422 (4.88×10^5)	549
Cu[TCPP-Me ₄] (5)	418 (2.22×10^5)	540
Co[TCPP-Me ₄] (6)	410 (1.12×10^5)	542
TCPP-Et ₄ (7)	421 (1.48×10^5)	516, 550, 595, 633
TCPP-Me ₄ (8)	421 (2.37×10^5)	516, 550, 591, 654
TCPP	416 (7.27×10^6)	512, 546, 590, 645

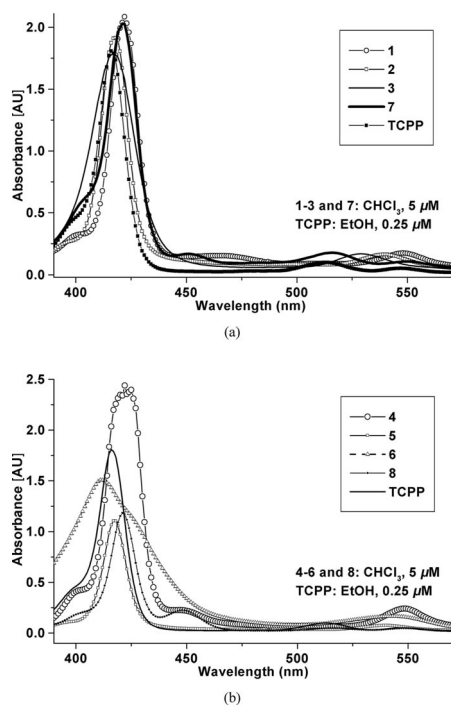


Figure 8. UV/Vis absorption spectra measured at room temperature (CHCl_3 and EtOH for **1–8** and TCPP, respectively): (a) **1–3**, **7**, and TCPP; (b) **4–6**, **8**, and TCPP. Molar absorption coefficients: $\epsilon_{422\text{nm}} = 4.18 \times 10^5$ (**1**), $\epsilon_{418\text{nm}} = 3.84 \times 10^5$ (**2**), $\epsilon_{417\text{nm}} = 3.58 \times 10^5$ (**3**), $\epsilon_{422\text{nm}} = 4.88 \times 10^5$ (**4**), $\epsilon_{418\text{nm}} = 2.22 \times 10^5$ (**5**), $\epsilon_{410\text{nm}} = 1.12 \times 10^5$ (**6**), $\epsilon_{421\text{nm}} = 1.48 \times 10^5$ (**7**), $\epsilon_{421\text{nm}} = 2.37 \times 10^5$ (**8**), and $\epsilon_{416\text{nm}} = 7.27 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$ (TCPP).

Photoluminescence

For solid-state porphyrins and their derivatives, it is well known that they cannot display emission bands because of concentration quenching. If, however, they were dissolved in solution, they would usually exhibit bright emission bands that occur in the red region of the spectrum. For this reason, photoluminescence investigations have been carried out in CHCl_3 and ethanol solutions for **1–8** and TCPP, respectively.

The low-temperature (77 K) phosphorescence spectra of **1–8** were measured, and the results are shown in Figures S13–S20 (Supporting Information). For compound **1**, the maximum phosphorescence emission band appears at 605 nm with a shoulder at 658 nm, upon excitation at 561 nm (Supporting Information, Figure S13). For compounds **2** and **3**, the maximum phosphorescence emission bands appear at 722 nm ($\lambda_{\text{ex}} = 531 \text{ nm}$) and 701 nm ($\lambda_{\text{ex}} = 568 \text{ nm}$), respectively. These bands are shifted to the red relative to that of **1** (Supporting Information, Figures S14 and S15). This is probably as a result of the different metal centers between compound **1** (zinc) and compound **2** (copper) or **3** (nickel). Compound **4** has a maximum phosphorescence emission band at 614 nm with a shoulder at 657 nm ($\lambda_{\text{ex}} = 566 \text{ nm}$; Supporting Information, Figure S16), which is similar to that in **1** as could be expected as both compounds contain zinc centers. Although both

compounds **2** and **5** have the same metal center (copper), they show largely different phosphorescence emission bands. Compound **5** exhibits a maximum phosphorescence emission band at 840 nm ($\lambda_{\text{ex}} = 558$ nm; Supporting Information, Figure S17), which is redshifted by 118 nm relative to that of **2**. Such a large redshift should be attributed to the different structural motifs between **2** and **5**. In comparison with the almost perfectly planar porphyrin macrocycle of **2**, the saddle-distorted nonplanar porphyrin macrocycle of **5** exhibits a phosphorescence emission band with lower energy. Since different structural motifs result from different esterification processes, esterification processes also play an important role in changing the phosphorescence properties. Similarly to **5**, compound **6** also displays a lower-energy phosphorescence emission band at 855 nm ($\lambda_{\text{ex}} = 568$ nm), as shown in Figure S18 (Supporting Information). For the nonmetalated compounds **7** and **8**, they show maximum phosphorescence emission bands at 661 nm and 692 nm by excitation at 559 nm and 460 nm, respectively (Supporting Information, Figures S19 and S20).

The fluorescence emission spectra of **1–3** measured at room temperature are shown in Figure 9. The fluorescence spectrum of **1** shows two emission bands at 600 nm and 643 nm by excitation at 549 nm. Similarly, compound **2** displays a main emission band at 651 nm and a weaker band at 700 nm, upon excitation at 589 nm. When excited at 374 nm, compound **3** exhibits two split emission bands at 443 nm and 461 nm, which are largely blueshifted relative to those of **1** and **2**. This difference clearly results from the different metalation in **1–3**. As for compound **4**, upon excitation at 558 nm, the emission spectrum also displays two emission bands at 604 and 648 nm, which is similar to that in the other zinc-containing compound **1** (Figure 10). Both compounds **5** and **6** show one main band located at 676 nm and 474 nm upon excitation at 451 nm and 367 nm, respectively (Figure 10). For the two nonmetalated compounds **7** and **8**, their fluorescence emission spectra show similar features with a dominant band and a shoulder at 662 and 713 nm ($\lambda_{\text{ex}} = 543$ nm) for **7** and at 650 and 706 nm ($\lambda_{\text{ex}} = 589$ nm) for **8** (Figure 11). It should be pointed out that the emission spectra of free-base TCPP features a main band at 650 nm and a shoulder at 710 nm upon excitation at 589 nm, which is similar to that observed in nonmetalated **7** and **8** (Figure 11).

By using a time-correlated single photon counting technique, the fluorescence lifetimes in solution were measured upon excitation at 421 nm, where light can be absorbed by the porphyrin molecules. The time-resolved fluorescence decay profiles for **1**, **3**, **4**, **6–8**, and TCPP are shown in Figure 12. The time decay curves were fitted as single exponentials, and the results are summarized in Table 3. The fluorescence lifetimes of the metalated compounds **1–6** are less than 3.5 ns, which is much shorter than those of the nonmetalated compounds **7** and **8** (11.21 ns and 11.51 ns, respectively). This is ascribed to the heavy metal effect, i.e. metalation of the porphyrin quenches the fluorescence. Comparison with the lifetime of the free-base TCPP (15.65 ns) shows that the fluorescence lifetimes of com-

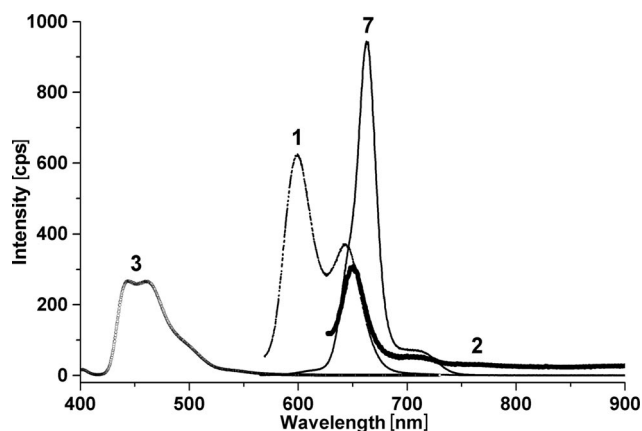


Figure 9. Emission spectra of **1–3** and **7** at room temperature.

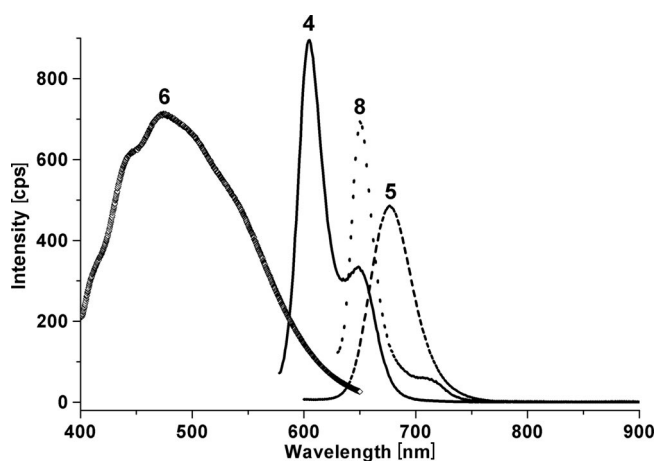


Figure 10. Emission spectra of **4–6** and **8** at room temperature.

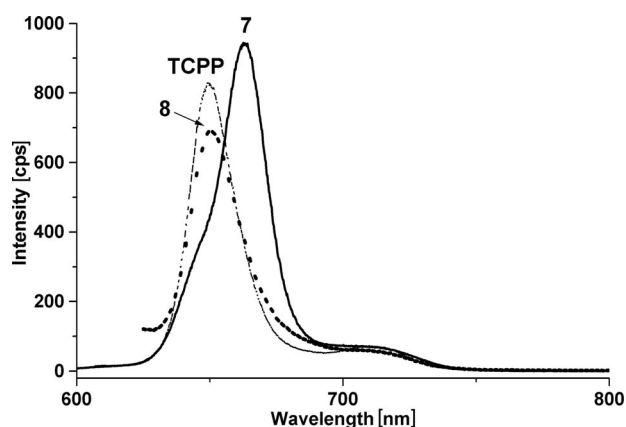


Figure 11. Emission spectra of **7**, **8**, and TCPP at room temperature.

pounds **7** and **8** are about 4 ns shorter. This decrease in the fluorescence lifetime may be caused by the esterification of the peripheral groups of porphyrins. The emission quantum yields for the solution samples were determined, and the results are also presented in Table 3. The emission quantum yields of the metalated compounds **1–6** are obviously lower

than those of the nonmetalated compounds **7** and **8** and the free-base TCPP, and this decrease is also ascribed to the heavy metal effect.

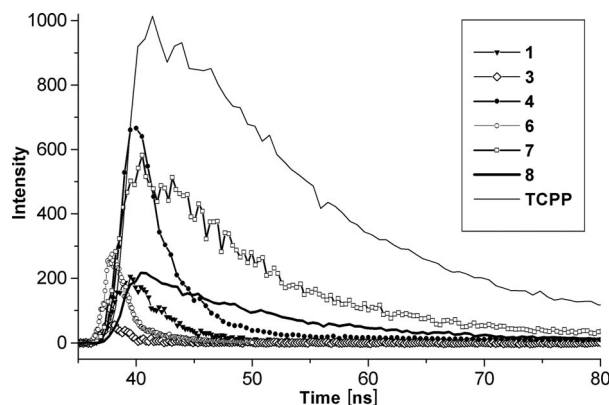


Figure 12. Time-resolved fluorescence decay profiles for **1**, **3**, **4**, **6**, **7**, **8**, and TCPP.

Table 3. Emission quantum yields Φ and fluorescence lifetimes τ .

	Φ	τ [ns]		Φ	τ [ns]
1	0.012	3.15	6	0	1.54
2	0	0	7	0.056	11.21
3	0.014	2.06	8	0.046	11.51
4	0.027	0.553	TCPP	0.044	15.65
5	0	0			

Electrochemical Studies

According to Kadish et al.,^[65] the vital factors that mostly affect metalloporphyrin redox potentials can be grouped into (a) the properties of the supporting electrolyte and solvent and (b) the properties of porphyrin itself. The latter set includes the type and number of axial ligands, the type and oxidation state of the metal center, and the type and planarity of the macroring. Depending on different substituents, the redox potentials can be varied up to 1.0 V or more.

Cyclic voltammograms of **1–8** were recorded in benzonitrile at room temperature in the presence of TBAPF₆ (0.1 M) to investigate their redox properties (Supporting Information, Figure S21 and Table 4). As shown in Figure S21, slow sweep cyclic voltammetry on **1** exhibits three quasi-reversible waves with $E_{1/2} = 0.87, 0.50$, and -1.69 V, and the electrochemical HOMO–LUMO gap is 2.19 V, which is close to the value for ZnTPP (2.15 V).^[65] The cyclic voltammogram of **2** features two quasi-reversible waves with $E_{1/2} = 0.70$ V and -1.60 V, and the accompanying electrochemical HOMO–LUMO gap is 2.30 V, which is comparable to that found for CuTPP (2.27 V).^[65] The slow scan cyclic voltammogram of **3** displays two reversible redox couples with $E_{1/2}$ values of 0.79 V and -1.62 V. Compound **3** has the largest HOMO–LUMO gap of 2.41 V (2.30 V for NiTPP^[65]) among compounds **1–3** with similar molecular structures. The electrochemical HOMO–LUMO gap increases in the order: **1** (Zn) < **2** (Cu) < **3** (Ni), which is

consistent with that found for TPP compounds.^[65] The obvious difference in the electrochemical properties of **1–3** could be related to their different metal centers, which verifies that metalation could affect the electrochemical properties of porphyrins. For compound **4**, three quasi-reversible waves with $E_{1/2} = 0.35, -1.35$, and -1.85 V are found in the cyclic voltammograms. The HOMO–LUMO gap for **4** is 1.70 V, smaller than that of **1**, which is also a zinc-containing compound. The lower oxidation potential and the higher reduction potential of **4** relative to those of **1** may result from the different structural motifs of **1** and **4**: compound **4** has a 2D coordination polymer structure, whereas compound **1** is monomeric as indicated by an isolated structural feature in the crystal (vide supra). Such a structural difference between **1** and **4** is also caused by their different ester groups as discussed in the crystal structure section. Thus, esterification also plays an important role in changing the electrochemical properties.

Table 4. Half-wave potentials ($E_{1/2}$, [V] vs. Ag/AgNO₃) and the electrochemical HOMO–LUMO gap [V].

	$E_{1/2}$ [V]	HOMO–LUMO gap [V]
1	0.87, 0.50, -1.69	2.19
2	0.70, -1.60	2.30
3	0.79, -1.62	2.41
4	0.35, $-1.35, -1.85$	1.70
5	0.66, -1.64	2.30
6	1.14, 0.86, -1.23	2.09
7	0.73, 0.52, -1.50	2.02
8	0.73, 0.50, -1.46	1.96

The cyclic voltammogram of **5** is characterized by two quasi-reversible redox couples with $E_{1/2} = 0.66$ V and -1.64 V. The first oxidation half-wave potential for **2** and **5** are 0.70 V and 0.66 V, respectively, which suggests that compound **5** can be oxidized more easily than **2**. This ease in oxidation of **5** is in good agreement with the fact that it has a nonplanar conformation, while compound **2** adopts a planar motif; this is in agreement with that found in the literature.^[66] The HOMO–LUMO gap for **5** is 2.30 V, in accordance with that of **2**. For the cobalt-containing compound **6**, the slow sweep cyclic voltammogram exhibits three quasi-reversible waves with $E_{1/2}$ values of 1.14, 0.86, and -1.23 V and a HOMO–LUMO gap of 2.09 V. The cyclic voltammogram of **7** is characteristic of three quasi-reversible redox couples with $E_{1/2} = 0.73, 0.52$, and -1.50 V. The HOMO–LUMO gap for **7** is 2.02 V, obviously smaller than those of **1–3**, which have similar structural motifs to **7**. The difference in the electrochemical properties between the nonmetalated compound **7** and the metalloporphyrins **1–3** is caused by the metalation effect. Similar to that of **7**, the cyclic voltammogram of **8** also features three quasi-reversible redox couples with $E_{1/2} = 0.73, 0.50, -1.46$ V and a HOMO–LUMO gap of 1.96 V.

Conclusions

By using a solvothermal in situ esterification method, we have successfully synthesized eight porphyrin compounds

with the aim of preparing a series of porphyrins with different supramolecular networks and properties. These compounds have been well characterized by X-ray structural analysis, MALDI-TOF MS spectrometry, FTIR, UV/Vis, fluorescence, and phosphorescence spectroscopy, quantum yields, luminescence lifetimes, and cyclic voltammetry. The esterification of porphyrins under solvothermal conditions can easily control the formation of various supramolecular networks. Future research in our laboratory will aim at synthesizing other porphyrin supramolecules, to gain a deeper insight into the synthetic methodology, as well as the relationship between the synthesis and the crystal structures and properties.

Experimental Section

Measurements: Elemental analyses were carried out with an Elementar Vario EL III microanalyzer. The infrared spectra were recorded on a Thermo Nicolet NEXUS 870 FTIR spectrophotometer over the frequency range 4000–400 cm^{-1} by using KBr pellets. The UV/Vis absorption spectra were recorded at room temperature on a computer-controlled Hewlett Packard 89090A UV/Vis spectrometer with a wavelength range of 190–1100 nm. Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectra were measured on a Kratos Compact MALDI I (Shimadzu). The phosphorescence and the fluorescence studies were conducted on a Shimadzu RF-530XPC fluorescence spectroscopy instrument at 77 K and at room temperature, respectively. Measurements of the emission quantum yields of the solution samples were carried out on a Hamamatsu C9920-0X(PMA-12) U6039-05 fluorescence spectrofluorometer with an integrating sphere adapted to a right-angle configuration at room temperature and involve the determination of the diffuse reflectance spectra of the samples. The measured results were corrected for the detector response as a function of wavelength. Fluorescence lifetime measurements were conducted by using a Photon Technology International GL-3300 nitrogen laser with a Photon Technology International GL-302 dye laser and a nitrogen laser/pumped dye laser system equipped with a four-channel digital delay/pulse generator (Standard Research System Inc., model DG535) and a motor driver (Photon Technology International, model MD-5020). The excitation wavelength was set at 421 nm with use of a POPOP chromophore. Cyclic voltammetry was performed at 298 K with a BAS 100 W electrochemical analyzer in deaerated benzonitrile containing 0.1 M TBAPF₆ (tetra-*n*-butylammonium hexafluorophosphate) as a supporting electrolyte. A conventional three-electrode cell was used with a platinum working electrode and a platinum wire as a counter electrode. The measured potentials were recorded with respect to the Ag/AgNO₃ system (1.0×10^{-2} M). All electrochemical measurements were carried out under an atmospheric pressure of argon.

Syntheses: All reactants of A. R. grade were obtained commercially and used without further purification.

Zn[TCPP-Et₄] (1): This compound was prepared by mixing ZnSO₄·H₂O (0.1 mmol, 17.9 mg), TCPP (0.1 mmol, 79 mg), and ethanol (10 mL) in a 23 mL Teflon-lined stainless steel autoclave and by heating the mixture at 453 K for 1 d. After the mixture is slowly cooled to room temperature at 6 K/h, purple crystals suitable for X-ray analysis were obtained. Yield: 76 mg (79%, based on zinc). C₅₆H₄₄N₄O₈Zn (964.25): calcd. C 69.54, H 4.55, N 5.80;

found C 69.25, H 4.65, N 5.87. FTIR (KBr): $\tilde{\nu}$ = 2975 (w), 2935 (w), 2900 (w), 2362 (w), 1933 (w), 1829 (w), 1720 (vs), 1605 (s), 1560 (m), 1460 (w), 1400 (m), 1366 (m), 1271 (vs), 1172 (m), 1097 (s), 1022 (m), 997 (s), 863 (w), 803 (m), 758 (m), 738 (w) and 703 (w) cm^{-1} . MALDI-TOF MS [CHCl₃, matrix CHCA (α -cyano-4-hydroxycinnamic acid)]: m/z calcd. for C₅₆H₄₄N₄O₈Zn 964.25; found 963.97 (Supporting Information, Figure S1).

Cu[TCPP-Et₄] (2): This compound was prepared by the procedure described for **1** by using CuCl₂·2H₂O (0.1 mmol, 17 mg) instead of ZnSO₄·H₂O. Yield: 80 mg (83%, based on copper). C₅₆H₄₄CuN₄O₈ (963.26): calcd. C 69.67, H 4.56, N 5.81; found C 69.98, H 4.77, N 5.89. FTIR (KBr): $\tilde{\nu}$ = 2973 (w), 2938 (w), 2897 (w), 2361 (w), 1829 (w), 1720 (vs), 1655 (w), 1605 (s), 1560 (w), 1510 (w), 1461 (w), 1401 (m), 1366 (w), 1346 (m), 1271 (vs), 1206 (w), 1172 (m), 1095 (s), 1022 (m), 997 (vs), 867 (w), 803 (m), 763 (s), 723 (w) and 669 (m) cm^{-1} . MALDI-TOF MS (CHCl₃, matrix CHCA): m/z calcd. for C₅₆H₄₄CuN₄O₈ 963.26; found 963.45.

Ni[TCPP-Et₄] (3): Compound **3** was prepared by the procedure described for **1** by using NiCl₂ (0.1 mmol, 13 mg) instead of ZnSO₄·H₂O. Yield: 72 mg (75%, based on nickel). C₅₆H₄₄N₄NiO₈ (958.25): calcd. C 70.03, H 4.59, N 5.84; found C 69.82, H 4.72, N 5.89. FTIR (KBr): $\tilde{\nu}$ = 2977 (w), 2938 (w), 2896 (w), 2361 (w), 1829 (w), 1719 (vs), 1655 (w), 1605 (s), 1560 (w), 1505 (w), 1456 (w), 1400 (m), 1351 (m), 1271 (vs), 1207 (w), 1172 (m), 1097 (s), 997 (s), 863 (w), 828 (w), 803 (m), 763 (s), 709 (w) and 669 (m) cm^{-1} . MALDI-TOF MS (CHCl₃, matrix CHCA): m/z calcd. for C₅₆H₄₄N₄NiO₈ 958.25; found 957.66.

Zn[TCPP-Me₄] (4): This compound was prepared by the procedure described for **1** by using methanol instead of ethanol. Yield: 65 mg (72%, based on zinc). C₅₂H₃₆N₄O₈Zn (908.18): calcd. C 68.55, H 3.96, N 6.15; found C 68.30, H 4.22, N 6.21. FTIR (KBr): $\tilde{\nu}$ = 3438 (m), 2970 (m), 2875 (m), 2820 (w), 2661 (m), 2531 (m), 1680 (vs), 1605 (s), 1565 (m), 1505 (w), 1425 (s), 1316 (s), 1291 (s), 1182 (m), 1126 (w), 1072 (w), 1022 (w), 997 (s), 867 (m), 798 (s), 768 (m), 723 (w) and 668 (m) cm^{-1} . MALDI-TOF MS (CHCl₃, matrix CHCA): m/z calcd. for C₅₂H₃₆N₄O₈Zn 908.18; found 907.67.

Cu[TCPP-Me₄] (5): Compound **5** was prepared by the procedure described for **1** by using CuCl₂·2H₂O (0.1 mmol, 17 mg) and methanol instead of ZnSO₄·H₂O and ethanol. Yield: 69 mg (76%, based on copper). C₅₂H₃₆CuN₄O₈ (907.19): calcd. C 68.69, H 3.96, N 6.16; found C 68.90, H 4.08, N 6.15. FTIR (KBr): $\tilde{\nu}$ = 2950 (w), 2840 (w), 2362 (w), 2337 (w), 1929 (w), 1819 (w), 1724 (vs), 1605 (s), 1565 (w), 1435 (s), 1400 (m), 1346 (m), 1271 (vs), 1206 (m), 1176 (w), 1112 (s), 997 (s), 863 (w), 822 (m), 798 (m), 763 (s), 718 (m) cm^{-1} . MALDI-TOF MS (CHCl₃, matrix CHCA): m/z calcd. for C₅₂H₃₆CuN₄O₈ 907.19; found 906.39.

Co[TCPP-Me₄] (6): This compound was prepared by the procedure described for **1** by using CoCl₂·6H₂O (0.1 mmol, 23.8 mg) and methanol instead of ZnSO₄·H₂O and ethanol. Yield: 63 mg (70%, based on cobalt). C₅₂H₃₆CoN₄O₈ (903.19): calcd. C 69.04, H 4.00, N 6.20; found C 68.96, H 4.15, N 6.23. FTIR (KBr): $\tilde{\nu}$ = 3423 (m), 2950 (w), 2840 (w), 2361 (w), 2337 (w), 1719 (vs), 1605 (s), 1565 (w), 1435 (m), 1400 (w), 1351 (m), 1276 (vs), 1177 (w), 1112 (s), 1002 (s), 868 (w), 823 (m), 798 (m), 762 (s), 719 (m) cm^{-1} . MALDI-TOF MS (CHCl₃, matrix CHCA): m/z calcd. for C₅₂H₃₆CoN₄O₈ 903.19; found 903.00.

TCPP-Et₄ (7): This compound was prepared by the procedure described for **1** by using MoCl₃ (0.1 mmol, 20.2 mg) instead of ZnSO₄·H₂O, and the reaction time was only 1 h. Yield: 78 mg (87%). C₅₆H₄₆N₄O₈ (902.33): calcd. C 74.42, H 5.10, N 6.20; found C 74.04, H 5.17, N 6.08. FTIR (KBr): $\tilde{\nu}$ = 3319 (w), 2974 (w), 2935

(w), 2900 (w), 2362 (w), 1717 (vs), 1654 (w), 1607 (s), 1582 (w), 1559 (w), 1538 (w), 1508 (w), 1472 (w), 1403 (m), 1365 (w), 1306 (w), 1271 (vs), 1214 (w), 1173 (w), 1097 (s), 1023 (m), 995 (w), 966 (m), 865 (w), 806 (w), 765 (m), 742 (w), 668 (m) cm^{-1} . MALDI-TOF MS (CHCl_3 , matrix CHCA): m/z calcd. for $\text{C}_{56}\text{H}_{46}\text{N}_4\text{O}_8$ 902.33; found 901.57.

TCPP-Me₄-H₂O (8): Compound **8** was prepared by the procedure described for **1** by using MoCl_3 (0.1 mmol, 20.2 mg) and methanol instead of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ and ethanol, and the reaction time was only 1 h. Yield: 77 mg (91%). $\text{C}_{52}\text{H}_{40}\text{N}_4\text{O}_9$ (846.27): calcd. C 72.21, H 4.62, N 6.47; found C 72.58, H 4.35, N 6.43. FTIR (KBr): $\tilde{\nu}$ = 3428 (m), 3320 (w), 2945 (w), 2841 (w), 2361 (w), 2341 (w), 1929 (w), 1817 (w), 1725 (vs), 1605 (s), 1561 (w), 1435 (m), 1401 (m), 1350 (w), 1275 (vs), 1211 (w), 1191 (w), 1112 (s), 1022 (m), 992 (w), 967 (m), 866 (w), 823 (w), 803 (m), 759 (m), 738 (w) cm^{-1} . MALDI-

TOF MS (CHCl_3 , matrix CHCA): m/z calcd. for TCPP-Me₄ $\text{C}_{52}\text{H}_{38}\text{N}_4\text{O}_8$ 846.27; found 845.87.

X-ray Crystallographic Studies: The intensity data sets were collected on Rigaku AFC-8 X-ray diffractometers with graphite monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption corrections.^[67,68a] The structures were solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software.^[68b] The difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. The hydrogen atom positions were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters. The structures were refined by using a full-matrix least-

Table 5. Crystal parameters of compounds **1–8**.

	1	2	3	4
Formula	$\text{C}_{56}\text{H}_{44}\text{N}_4\text{O}_8\text{Zn}$	$\text{C}_{56}\text{H}_{44}\text{CuN}_4\text{O}_8$	$\text{C}_{56}\text{H}_{44}\text{NiO}_8$	$\text{C}_{52}\text{H}_{36}\text{N}_4\text{O}_8\text{Zn}$
F_w	966.34	964.50	959.64	910.22
Color	purple	dark red	dark red	red
Crystal size [mm]	$0.25 \times 0.20 \times 0.13$	$0.48 \times 0.45 \times 0.44$	$0.48 \times 0.18 \times 0.15$	$0.42 \times 0.22 \times 0.10$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [$\text{\AA}$]	14.434(6)	9.218(4)	9.205(3)	13.716(3)
b [$\text{\AA}$]	8.417(3)	10.792(3)	10.780(4)	9.004(2)
c [$\text{\AA}$]	21.357(6)	23.945(7)	23.792(7)	21.062(2)
β [$^\circ$]	120.34(2)	111.65(1)	111.68(1)	92.590(4)
V [$\text{\AA}^3$]	2239(1)	2214(1)	2194(1)	2598.4(9)
Z	2	2	2	2
$2\theta_{\text{max}}$ [$^\circ$]	50	50	50	50
Reflections collected	14163	14019	13721	16125
Independent, observed reflections (R_{int})	3936, 3449 (0.0420)	3885, 2519 (0.0399)	3751, 3345 (0.0357)	4487, 2105 (0.0486)
$d_{\text{calcd.}}$ [g/cm^3]	1.433	1.447	1.453	1.163
μ [mm^{-1}]	0.614	0.559	0.509	0.525
T [K]	123.15	123.15	123.15	123.15
$F(000)$	1004	1002	1000	940
$R1, wR2$	0.0623, 0.1671	0.0656, 0.1758	0.0578, 0.1530	0.0692, 0.1809
S	1.016	1.047	1.039	1.007
Largest, mean Δ (σ)	0.001, 0	0, 0	0, 0	0, 0
$\Delta\rho(\text{max, min})$ [$\text{e/\AA}^3$]	0.379, −0.506	1.574, −0.681	0.767, −0.746	0.944, −0.309
	5	6	7	8
Formula	$\text{C}_{52}\text{H}_{36}\text{CuN}_4\text{O}_8$	$\text{C}_{52}\text{H}_{36}\text{CoN}_4\text{O}_8$	$\text{C}_{56}\text{H}_{46}\text{N}_4\text{O}_8$	$\text{C}_{52}\text{H}_{40}\text{N}_4\text{O}_9$
F_w	908.40	903.78	902.97	864.88
Color	red	purple	red	red
Crystal size [mm]	$0.25 \times 0.10 \times 0.08$	$0.30 \times 0.22 \times 0.20$	$0.48 \times 0.35 \times 0.32$	$0.12 \times 0.11 \times 0.06$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [$\text{\AA}$]	20.357(3)	20.137(5)	9.040(2)	8.509(3)
b [$\text{\AA}$]	8.900(4)	9.150(2)	10.837(2)	10.786(1)
c [$\text{\AA}$]	30.161(6)	29.857(5)	23.886(5)	22.252(3)
β [$^\circ$]	129.22(1)	129.28(1)	110.678(7)	102.258(9)
V [$\text{\AA}^3$]	4233(2)	4259(2)	2189.3(8)	1995.7(8)
Z	4	4	2	2
$2\theta_{\text{max}}$ [$^\circ$]	50	50	50	50
Reflections collected	25819	25672	13187	12029
Independent, observed reflections (R_{int})	7279, 3448 (0.1234)	7136, 4956 (0.0398)	3813, 3337 (0.0579)	3415, 1378 (0.1416)
$d_{\text{calcd.}}$ [g/cm^3]	1.425	1.410	1.370	1.439
μ [mm^{-1}]	0.580	0.467	0.092	0.100
T [K]	123.15	123.15	123.15	123.15
$F(000)$	1876	1868	948	904
$R1, wR2$	0.0845, 0.1104	0.0699, 0.1756	0.0518, 0.1475	0.1043, 0.2234
S	1.012	1.051	1.036	1.021
Largest, mean Δ (σ)	0.001, 0	0.001, 0	0, 0	0.002, 0
$\Delta\rho(\text{max, min})$ [$\text{e/\AA}^3$]	0.529, −0.399	0.653, −0.414	0.449, −0.347	0.343, −0.460

squares refinement on F^2 . All atoms except for hydrogen atoms were refined anisotropically (Table 5). CCDC-727779, -727780, -727781, -727782, -727783, -727784, -727785, -727786 for compounds 1–8, respectively, 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.

Supporting Information (see footnote on the first page of this article): IR spectra, MALDI-TOF MS spectra, phosphorescence spectra, and some structural figures for this article are presented.

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