Synthesis and properties of unsymmetrical porphyrins possessing an isonicotinic acid moiety and phenyl, methoxyphenyl, or chlorophenyl groups

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Abstract
The isonicotinic acid containing porphyrin compounds 5-{4-[3-(4-pyridylcarbonyloxy)propoxy]phenyl}-10,15,20-triphenylporphyrin, 5-{4-[3-(4-pyridylcarbonyloxy)propoxy]phenyl}-10,15,20-tri(4-methoxyphenyl)porphyrin, and 5-{4-[3-(4-pyridylcarbonyloxy)propoxy]phenyl}-10,15,20-tri(4-chlorophenyl)porphyrin are prepared and characterized by ¹H NMR, ¹³C NMR, MS, elemental analysis, IR, and UV-Vis. In addition, their spectroscopic properties are investigated through using the Raman spectroscopy, fluorescence, and surface photovoltage measurements. The influence of different substituents on Raman spectra is small, but their impact on the fluorescence spectra and surface photovoltage measurements is significant. Molecular dynamic simulations and UV-Vis diffuse-reflectance spectra show that these porphyrin compounds are potential semiconductor materials.

Keywords
isonicotinic acid, porphyrins, spectroscopic properties, substituents, synthesis

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Introduction
In recent years, porphyrins have received considerable attention because of their significant chemical stability and important properties in many fields such as optoelectronic devices,¹–³ molecular logic devices,¹⁴–⁷ optical sensors,⁸–¹⁰ photodynamic therapy,¹¹–¹⁴ supramolecular self-assembly,¹⁵–¹⁸ solar energy harvesting, and in storage devices.¹⁹–²¹ The extended π-conjugation system in the porphyrin skeleton²²–²⁴ leads to a wide range of visible light absorption and p-type properties as an electronic system. Some porphyrins have been tested for the photosensitization of wide-bandgap semiconductors,²⁵ and these p-type organic semiconductors are investigated because of their potential applications in electronic devices such as organic solar cells²⁶–²⁹ and organic field effect transistors.³⁰ Isonicotinic acid is an important drug intermediate with wide application prospects and has been used in the treatment of tuberculosis.³¹ The synthesis of porphyrins combined with isonicotinic acid is expected to be beneficial in realizing the dual activity of porphyrins and isonicotinic acid.

It is important to study the electronic structure of porphyrins in the context of various applications such as photoluminescence and photoelectric conversion. The Raman spectroscopy, fluorescence spectra, surface photovoltage measurements, and UV-Vis absorption spectra are used widely to study the electronic structure of porphyrins.³²–³⁵ In addition, molecular dynamics simulations and UV-Vis diffuse-reflectance spectra are powerful tools for studying the chemical compositions and sample structures. All these techniques provide useful information for investigating the semiconductor properties of materials.³⁶–³⁸

In this work, we have synthesized asymmetric porphyrins possessing an isonicotinic acid moiety and phenyl, methoxyphenyl, or chlorophenyl groups. These porphyrins are characterized by ¹H NMR, ¹³C NMR, MS, elemental...
Results and discussion

The synthetic procedure for the preparation of the porphyrin derivatives and their yields are illustrated in Scheme 1.

From the \(^1\)H NMR spectral data of 3b, it can be seen that the singlet peaks at 4.10 and 4.30 ppm can be ascribed to the methoxy groups of 3b. The signals of the benzene ring for 3b and 3c are shifted downfield relative to those of 3a. The imino protons of 3c occur as resonances at ~2.84 ppm, which are upfield compared to those of 3a (~2.79 ppm), which is probably due to enhanced deshielding effect of the chlorine (electron-withdrawing) groups.

The UV–Vis absorption bands of porphyrins are determined by the electronic transitions from the ground state (S\(_0\)) to the two lowest excited singlet states (S\(_2\) and S\(_1\)). The S\(_0\) to S\(_1\) transition causes weak Q bands in the visible region, 1081–1084 cm\(^{-1}\) are assigned to the skeletal vibrations of the porphyrin. The bands around 1508–1514 and 1471–1472 cm\(^{-1}\) are assigned to the skeletal vibrations of benzene and pyrrole, respectively. The C–O–C stretching vibrations appear in the range of 1222–1248 cm\(^{-1}\). In addition, the medium to strong band at 1089 cm\(^{-1}\) in the IR spectrum of 3c is assigned as overlapping bands due to the C=O stretching vibrations of the porphyrin core. The C–H stretching vibrations appear in the range of 2931–3031 and 1720–1730 cm\(^{-1}\), respectively. The bands around 1508–1514 and 1471–1472 cm\(^{-1}\) are assigned to the skeletal vibrations of benzene and pyrrole, respectively. The C–O–C stretching vibrations appear in the range of 1222–1248 cm\(^{-1}\). In addition, the medium to strong band at 1089 cm\(^{-1}\) in the IR spectrum of 3c is assigned as overlapping bands due to the C=O stretching vibrations of the porphyrin core. The C–H stretching vibrations appear in the range of 2931–3031 and 1720–1730 cm\(^{-1}\), respectively.

The Raman bands at 327–335 cm\(^{-1}\) are assigned to the v\(_\text{s}\) mode.\(^{42,43}\) Comparing the Raman spectra of 3a–c, we find that the nature of the substituent has almost no influence on the Raman spectra of the isonicotinic acid porphyrin compounds.

The fluorescence spectra of 3a–c in chloroform solution (1 × 10\(^{-5}\) mol L\(^{-1}\)) at an excitation wavelength of 420 nm were recorded at room temperature. The emission spectra and associated data of 3a–c are shown in Figure 2 and Table 2, respectively. Both S\(_2\)-S\(_0\) and S\(_1\)-S\(_0\) fluorescence exist in porphyrin compounds.\(^44\) The S\(_2\)-S\(_0\) fluorescence can be attributed to the transition from the second excited singlet state S\(_2\) (or S\(_2^*\)) to the ground state S\(_0\). In addition, the S\(_2\)-S\(_0\) band can be attributed to the transition from the lowest excited singlet state S\(_1\) to S\(_0\). The S\(_2\)-S\(_0\) fluorescence is much stronger than S\(_1\)-S\(_0\) owing to the scattered incident light, the re-absorption by the intense Soret band, and internal conversion. In this work, the S\(_2\)-S\(_0\) fluorescence is too weak to be observed and the S\(_1\)-S\(_0\) fluorescence consists of Q(0, 0) and Q(0, 1) two bands. Q(0, 0) fluorescence bands of 3a–c are observed at 650, 656, and 651 nm, while the Q(0, 1) fluorescence bands occur at 713, 721, and 715 nm. Compared with fluorescence bands of 3a, the emission peaks of 3b and 3c shift to the red by ~2–8 nm, which shows that different substituents have an influence on the fluorescence.

The room-temperature fluorescence quantum yields of 3a–c in chloroform solution (1 × 10\(^{-5}\) mol L\(^{-1}\)) have been confirmed by comparing with the known fluorescence yield from mesotetraphenylporphyrin (TPP, \(\Phi_{\text{TPP}} = 0.11\)).\(^45\) The following equation is used to calculate the quantum yield

\[
\Phi_{\text{sample}} = \frac{F_{\text{sample}}}{F_{\text{TPP}}} \times \frac{A_{\text{TPP}}}{A_{\text{sample}}} \Phi_{\text{TPP}} \tag{1}
\]

where F\(_i\) is the integral areas of fluorescence, A\(_i\) represents the absorbance, and \(\Phi\) represents the quantum yield at the same excitation wavelength. The fluorescence quantum yields of 3a–c are 0.057, 0.082, and 0.025, which show that the fluorescence intensity and quantum yield of the porphyrin increase on substituting with methoxy groups and decrease in the presence of chlorine substituents. A possible reason is that methoxy groups enhance the conjugated ability of the porphyrin macrocycle, while chlorine groups weaken it. Furthermore, the difference in the quantum yields of 3a, 3b, and 3c indicates that the fluorescence intensities and quantum yields are influenced by different substituents connected to the porphyrin ring. The fluorescence intensities and quantum yields of the porphyrin increase by substituting with methoxy groups, and decreased with chloro substituents.

Photogenerated electron transitions on the surface of the solid result in surface photovoltage. As shown in Figure 3, the surface photovoltage spectra of the 3a–c are in the range of 300–800 nm. The surface photovoltage values of 3a–c are 7.5, 3.9, and 15.5 μV without an external field. Contrary to the results of the fluorescence intensity of 3a–c, the photovoltage response signal of 3c is stronger than that of 3b.
Scheme 1. Synthesis route of 3a–c.

![Scheme 1. Synthesis route of 3a–c.](image)

Figure 1. Raman spectra of 3a–c.

![Figure 1. Raman spectra of 3a–c.](image)

Table 1. Raman frequencies and assignments of 3a–c.

|    | 3a       | 3b       | 3c       | Assignment                      |
|----|----------|----------|----------|---------------------------------|
| 1552 vs | 1551 vs  | 1548 vs  | ν_2, ν(C–C_β) |
| 1498 m  | 1494 m   | 1499 m   | ν_2, ν(C–C_β) |
| 1455 m  | 1458 m   | 1457 m   | ν_5, ν(C–N) |
| 1360 w  | 1359 w   | 1361 w   | ν(C–N)/ν(C–C_β) |
| 1329 w  | 1329 w   | 1326 w   | δ(CH_3(Ph/Py)) |
| 1239 m  | 1241 m   | 1240 w   | ν(C–N) |
| 1135 w  | 1136 w   | 1133 w   | ν(C=C) |
| 1081 w  | 1084 w   | 1083 w   | δ(CCN) |
| 1002 w  | 1001 w   | 1001 w   | ν(CH_2) |
| 963 w   | 966 w    | 962 w    | β_3(π)(pyrrole) |
| 335 w   | 329 w    | 327 w    | ν_(N–M)/Ring def. |

vs: very strong; s: strong; m: medium; w: weak.
under the same experimental conditions, which indicates that the electron-withdrawing group (Cl) increases the photovoltage response, but that the electron-donating group (CH3O) decreases it, which makes 3c possess a lower recombination loss of photogenerated electron and photogenerated holes. Moreover, the photovoltage spectra of 3a–c correlated with their UV–Vis spectra. There is a π-conjugated macrocycle system in the molecular structure of porphyrins. The bonding π orbital and the antibonding π orbital are similar to the valence band and the conduction band. Photogenerated holes and electrons transfer to the valence band and the conduction band, respectively. In this system, the Soret band produced by band–band (π → π*) transitions presents a strong positive photovoltage response, which means that 3a–c can be characterized as p-type semiconductors.

The geometric structures of the 3a–c were optimized using the B3LYP functional with the 6–31G(d, p) basis set. All of the simulations are performed using the GAUSSIAN 09 program packages.46,47 Schematic drawings showing the stable conformations of 3a–c are given in Figure 4. The substituted benzene ring and porphyrin ring are almost vertical in the space structure. The configuration energy of the conjugated system is minimized. Figure 5 shows the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) profiles of 3b. The HOMO is distributed on the nitrogen atom of the porphyrin ring causing the nitrogen atom to be the negative charge center of the porphyrin ring. Nevertheless, the LUMO is distributed on the side of the benzene ring, producing a configuration effect on the conjugated system surface average and increasing the floating electron cloud density. As discussed above, the benzene and aromatic ring have a significant role on the electronics. Table 3 shows the total energies (E_{total}), the molecular orbital energies (E_{HOMO} and E_{LUMO}), and the energy level gaps (ΔE) of 3a–c. A lower total energy indicates the stability of the compound. Compared with the E_{total} values of 3b and 3c, compared 3a shows excellent stability, probably due to its better symmetry. As the minimum energy of the electronic transitions from the ground state to the excited state, ΔE is an important parameter reflecting the optical and electrical properties. As shown in Table 3, the ΔE values of 3a–c are 1.742–1.780 eV, indicating that 3a–c are potential semiconductor materials.48

UV-Vis diffuse-reflectance spectra reflect the sample structure and composition through the interactions of light between the molecules such interactions include diffraction, reflection, refraction, and absorption. Quantitative analysis can be achieved by after UV-Vis diffuse-reflectance and correction via the Kubelka–Munk equation correction. At room temperature, and employing a scanning range of 200–800 nm, the UV-Vis diffuse-reflectance spectra of 3a–c are obtained. The UV-Vis diffuse-reflectance spectra and optical absorption spectra of 3a–c are shown in Figure 6. The UV–Vis diffuse-reflectance spectra of the porphyrins solids are similar to those of the porphyrins in chloroform solution, indicating that the porphyrins keep their photochemical properties unchanged. The optical absorption spectra of 3a–c are derived from the Kubelka–Munk equation, on the basis of the diffuse-reflectance data, with the energy level gap (E_g) obtained by the direct method49

\[ X = \frac{1240}{x}, \quad Y = y^2 \]  

where x and y are the λ and FR (Reflectance Function) in the UV-Vis diffuse-reflectance spectrum, respectively. X and Y are the E_g and FR^2 in the optical absorption spectrum, respectively. The E_g values are in the range of 1.74–1.82 eV. The experimental data are similar to that in the quantum chemistry theory, confirming our theoretical inference that 3a–c are potential semiconductor materials.

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**Table 2. Emission spectral data of 3a–c.**

| Compound | Q(0, 0) (nm) | Q(0, 1) (nm) | Φf |
|----------|--------------|--------------|----|
| 3a       | 650          | 713          | 0.057 |
| 3b       | 656          | 721          | 0.082 |
| 3c       | 651          | 715          | 0.025 |

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**Figure 2. Fluorescence spectra of 3a–c.**

**Figure 3. Surface photovoltage of 3a–c.**
Conclusion

In summary, three isonicotinic acid porphyrin compounds have been successfully synthesized and systematically characterized. Their spectroscopic properties have been investigated using Raman, fluorescence, and surface photovoltage spectra. These studies indicate that the fluorescence intensities and quantum yields are influenced by different substituents on the porphyrin ring. The fluorescence intensity and quantum yield of the porphyrin are increased by substituting with methoxy groups, while being decreased by the presence of chloro substituents. However, a competitive process is shown between fluorescence intensity and surface photovoltage intensity. The surface photovoltage intensity of the porphyrin is increased by connecting the chlorine groups, while it is decreased by incorporating methoxy groups. The chlorine (electron-withdrawing) groups have a stronger influence on the fluorescence intensity than methoxy (electron-donating) groups. The nature of the substituent has little influence on the Raman spectra of the isonicotinic acid porphyrin compounds. Furthermore, molecular dynamics simulations and UV-Vis diffuse-reflectance spectra indicate that these porphyrin compounds are potential semiconductor materials. In this paper, our research has focused on the synthesis and properties of three differently substituted isonicotinic acid porphyrin compounds, and the properties of the isonicotinic acid porphyrin metal complexes warrant further exploration in our future work.

Experimental

Apparatus and measurements

$^1$H NMR spectra were recorded on a Varian Unity 500 (MHz) NMR spectrometer in CDCl$_3$. Chemical shifts are expressed in ppm with tetramethylsilane as the internal reference and reported as position ($\delta$), relative integral. $^{13}$C NMR spectra were recorded on a Varian Unity 100 (MHz) NMR spectrometer in CDCl$_3$. Mass spectra (fast atom bombardment (FAB)) were obtained using a VG-Quattro mass spectrometer. Infrared spectra were measured using a Nicolet-360 Fourier transform infrared (FTIR) spectrometer in the region 4000–400 cm$^{-1}$ by incorporating the samples in KBr disks. The UV-Vis absorption spectra in the region 350–700 nm were obtained using a Shimadzu
UV-3000 spectrometer using chloroform as the solvent. Resonance Raman spectra were recorded with a Renishaw RM1000 Raman spectrophotometer equipped with an integral microscopy and radiation of 514.5 nm was obtained from an Ar⁺ laser. Fluorescence spectra were recorded at room temperature with a Shimadzu RF-5301PC spectrofluorometer using chloroform as the solvent in the region of 500–800 nm. The excitation wavelength is 420 nm. Surface photovoltage spectra were recorded at room temperature with a 500-W Xe lamp, an SBP500 monochromator (30 nm/min), an FZ-A radiometer (<80 mW/cm²), a Stanford SR830-DSP lock-in amplifier (23 Hz), and a DSi200 Ultraviolet silicon detector (30 ms). Molecular dynamics simulations were achieved using the Material Studio 4.3. The UV-Vis diffuse-reflectance spectra in the region 200–800 nm were obtained using a Maypro 2000 spectrometer.

Materials

All the reagents and solvents were of analytical reagent grade. Pyrrole and N,N-dimethylformamide (DMF) were freshly distilled before using. Chloroform was dried using 4 Å molecular sieves (>12 h). Sodium isonicotinate was synthesized in our laboratory.

Synthetic procedures

5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin (1a), 5-(4-hydroxyphenyl)-10,15,20-tri(4-methoxyphenyl) porphyrin (1b), and 5-(4-hydroxyphenyl)-10,15,20-tri(4-chlorophenyl)porphyrin (1c) were prepared by Adler’s method.50

5-(4-Hydroxyphenyl)-10,15,20-tri(4-chlorophenyl)porphyrin (1c). Porphyrin 1c was prepared by the same procedure as that used for 1a. Purple solid; yield: 13%. ¹H NMR (500 MHz, CDCl₃): δ −2.80 (s, 2H, inner NH), 7.60-7.64 (d, 2H, ArO-3, 5-H), 7.86-7.90 (m, 6H, Ar-3, 5-H), 8.02-8.10 (m, 8H, Ar-2, 6-H), 8.80-8.84 (d, 8H, pyrrole, β-H), 9.99 (s, 1H, OH) in agreement with literature values.50

5-(4-Hydroxyphenyl)-10,15,20-tri(4-methoxyphenyl)porphyrin (1b). Porphyrin 1b was prepared by the same procedure as that used for 1a. Purple solid; yield: 12%. ¹H NMR (500 MHz, CDCl₃): δ −2.76 (s, 2H, inner NH), 4.10 (s, 9H, OCH₃), 7.62-7.66 (d, 2H, ArO-3, 5-H), 7.92-7.96 (m, 6H, Ar-3, 5-H), 8.08-8.12 (m, 8H, Ar-2, 6-H), 8.80-8.87 (m, 8H, pyrrole, β-H), 9.98 (s, 1H, OH) in agreement with literature values.50

5-(4-Hydroxyphenyl)-10,15,20-tri(4-methyl)porphyrin (1a). A mixture of 4-hydroxybenzaldehyde (2.4 g, 0.021 mol), benzaldehyde (6.4 mL, 0.064 mol), and pyrrole (5.6 mL, 0.078 mol) was added dropwise to boiling propionic acid (250 mL). The reaction solution was refluxed for 0.5 h and then cooled to room temperature and placed in a refrigerator at −18 °C overnight. The mixture was then filtered and the obtained purple solid was washed with absolute ethanol. The crude product was dissolved in chloroform (50 mL) and chromatographed on a column of neutral alumina. The first band containing mesotetraphenylporphyrin was eluted by chloroform. The second band was eluted by chloroform containing 10% absolute ethanol and contained the desired porphyrin. The second fraction was concentrated and cooled. The precipitated product was dried in vacuo. Yield: 14%. ¹H NMR (500 MHz, CDCl₃): δ −2.79 (s, 2H, inner NH), 7.65-7.80 (m, 9H, Ar-3,4,5-H), 7.91-7.96 (d, 2H, ArO-3, 5-H), 8.09-8.20 (m, 8H, pyrrole, β-H), 9.99 (s, 1H, OH) in agreement with literature values.50

5-(4-Hydroxyphenyl)-10,15,20-tri(4-chlorophenyl)porphyrin (1c). Porphyrin 1c was prepared by the same procedure as that used for 1a. Purple solid; yield: 13%. ¹H NMR (500 MHz, CDCl₃): δ −2.76 (s, 2H, inner NH), 7.60-7.64 (d, 2H, ArO-3, 5-H), 7.86-7.90 (m, 6H, Ar-3, 5-H), 8.02-8.10 (m, 8H, Ar-2, 6-H), 8.80-8.84 (d, 8H, pyrrole, β-H), 9.99 (s, 1H, OH) in agreement with literature values.50

5-(4-Bromopropoxy)phenyl-10,15,20-triphenylporphyrin (2a), 5-(4-bromopropoxy)phenyl-10,15,20-tri(4-methoxyphenyl)porphyrin (2b), and 5-(4-bromopropoxy)phenyl-10,15,20-tri(4-chlorophenyl)porphyrin (2c) were synthesized according to the literature method by nucleophilic substitution reactions of 1a–c with 1,3-dibromopropane.51

Figure 6. (a) UV-Vis diffuse-reflectance spectra of 3a–c and (b) optical absorption spectra of 3a–c: 3a, Eg = 1.82 eV; 3b, Eg = 1.74 eV; 3c, Eg = 1.80 eV.
of saturated NaCl solution was added so that the product precipitated. The crude product was filtered and washed with water and methanol. Next, the crude product was dissolved in chloroform (50 mL) and chromatographed on a column of neutral alumina. The first band was eluted by chloroform and contained the desired porphyrin. Purple solid; yield: 60%. 1H NMR (500 MHz, CDCl3): δ = 2.79 (s, 2H, inner NH), 2.45-2.55 (m, 2H, CH2), 4.30-4.36 (t, J = 6.0 Hz, 2H, BrCH2), 4.70-4.78 (t, J = 6.0 Hz, 2H, OCH3), 7.68-7.80 (m, 9H, Ar-3,4,5-H), 7.92-7.98 (m, 2H, Ar-O-3, -5-H), 8.10-8.24 (m, 8H, Ar-2, -6-H), 8.78-8.86 (m, 8H, pyrrole, -H) in agreement with literature values.51

5-[(4-Bromopropoxy)phenyl]-10,15,20-tri(4-methoxyphenyl)porphyrin (2b). Compound 2b was prepared by the same procedure as that used for 2a. Purple solid; yield: 61%. 1H NMR (500 MHz, CDCl3): δ = 2.82 (s, 2H, inner NH), 2.48-2.58 (m, 2H, CH2), 4.36-4.42 (t, J = 5.0 Hz, 2H, BrCH2), 4.70-4.75 (t, J = 5.0 Hz, 2H, OCH3), 7.60-7.64 (d, J = 7.5 Hz, 2H, Ar-O3, -5-H), 7.83-7.89 (m, 6H, Ar-3, -5-H), 8.06-8.12 (m, 8H, Ar-2, -6-H), 8.78-8.84 (d, J = 8.0 Hz, 8H, pyrrole, -H) in agreement with literature values.51

5-[(4-Bromopropoxy)phenyl]-10,15,20-tri(4-chlorophenyl)porphyrin (2c). Compound 2c was prepared by the same procedure as that used for 2a. Purple solid; yield: 61%. 1H NMR (500 MHz, CDCl3): δ = 2.82 (s, 2H, inner NH), 2.41-2.55 (m, 2H, CH2), 4.40-4.46 (t, J = 5.0 Hz, 2H, BrCH2), 4.70-4.78 (t, J = 7.5 Hz, 2H, OCH3), 7.60-7.70 (m, 9H, Ar-3,4,5-H), 7.92-7.98 (m, 2H, Ar-O-3, -5-H), 8.10-8.24 (m, 8H, Ar-2, -6-H), 8.52-8.62 (m, 2H, Py-3, -5-H), 8.78-8.86 (m, 8H, pyrrole, -H) in agreement with literature values.51

5-[(4-(3-(4-Pyridylcarbonyloxy)propoxy)phenyl]-10,15,20-tri(4-methoxyphenyl)porphyrin (3a). A mixture of sodium isonicotinate (57 mg, 0.39 mmol) and compound 2a (100 mg, 0.13 mmol) was added to DMF (15 mL) and the mixture stirred at 80 °C. The process of the reaction was monitored by TLC. After completion of the reaction, the solution was cooled and saturated NaCl (60 mL) solution was added so that the product precipitated. The crude product was filtered and washed with water and methanol. Next, the crude product was dissolved in chloroform (50 mL) and chromatographed on a column of neutral alumina. The second band was eluted by chloroform and contained the desired porphyrin. Purple-red solid; yield: 80%. m.p. > 300 °C. 1H NMR (500 MHz, CDCl3): δ = 2.79 (s, 2H, inner NH), 2.41-2.51 (m, 2H, CH2), 4.40-4.46 (t, J = 5.0 Hz, 2H, BrCH2), 4.72-4.78 (t, J = 6.0 Hz, 2H, OCH3), 7.42-7.48 (t, J = 6.0 Hz, 2H, COOCH3), 7.68-7.80 (m, 9H, Ar-3,4,5-H), 7.92-7.98 (m, 2H, Ar-O-3, -5-H), 8.10-8.24 (m, 8H, Ar-2, -6-H), 8.52-8.62 (m, 2H, Py-3, -5-H), 8.78-8.86 (m, 8H, pyrrole, -H) in agreement with literature values.51

5-[(4-(3-(4-Pyridylcarbonyloxy)propoxy)phenyl]-10,15,20-tri(4-chlorophenyl)porphyrin (3b). Compound 3b was prepared by the same procedure as that used for 3a. Purple-red solid; yield: 79%. m.p. > 300 °C. 1H NMR (500 MHz, CDCl3): δ = 2.76 (s, 2H, inner NH), 2.46-2.52 (m, 2H, CH2), 4.10 (s, 6H, OCH3), 4.30 (s, 3H, OCH3), 4.40-4.46 (t, J = 5.0 Hz, 2H, COOCH3), 4.73-4.78 (t, J = 5.0 Hz, 2H, OCH3), 7.62-7.66 (d, J = 7.5 Hz, 2H, Ar-O3, -5-H), 7.92-7.96 (m, 6H, Ar-3, -5-H), 8.08-8.12 (m, 8H, Ar-2, -6-H), 8.46-8.52 (m, 2H, Py-3, -5-H), 8.80-8.87 (m, 8H, pyrrole, -H), 8.88 (m, 2H, Py-2, -6-H). 13C NMR (100 MHz, CDCl3): δ = 28.4, 55.9, 61.2, 65.1, 111.8, 114.3, 114.8, 119.8, 119.9, 122.9, 124.2, 124.6, 127.0, 128.0, 128.7, 130.7, 131.0, 133.5, 135.4, 137.3, 138.1, 146.6, 146.7, 146.9, 146.9, 150.4, 156.7, 166.0. MS (EIMS) m/z (%) 883.8 [M+]. Elemental analysis for C53H36Cl3N5O3: calcd (%): C, 70.66; H, 4.07; N, 7.81; found (%): C, 70.66; H, 4.04; N, 7.89. IR (KBr, cm−1): 3322 ν(C–H) (benzene), 1724 ν(C=O), 1564 ν(C–N) (pyrrole), 1441 ν(C=N) (pyrrole), 1472 δ(C–C–N) + ν(C≡N) (pyrrole), 1411 δ(C–H), 1385 ν(C≡N) + δ(C≡N), 1358 ν(C≡N) + δ(C≡N), 1286 δ(C≡N), 1246 ν(C=O–C), 1174 δ(C≡N), 966 δ(N–H), 804 ν(C=H) (benzene). UV-Vis (chloroform, λmax/nm, molar extinction coefficients are in parentheses, cm2 mol−1): 420 (5.764 × 104), 515 (3.159 × 104), 550 (1.984 × 104), 590 (1.401 × 104), 645 (1.317 × 104).
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Supplemental material

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