

Facile Synthesis and Nonlinear Optical Properties of Push–Pull 5,15-Diphenylporphyrins

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A series of 5,15-diphenylporphyrinatonicel(II) derivatives containing electron-releasing (Me₂-NC₆H₄C≡C-) and -withdrawing groups [-CHO, -CH=C(CN)₂, -CH=C(CO₂Et)₂, -CH=CHCHO] in opposite meso positions has been synthesized through the classical formylation, halogenation, Knoevenagel condensation, and palladium-catalyzed cross-coupling reaction of porphyrins. The molecular first hyperpolarizabilities (β) of two of these push–pull porphyrins, namely 5-(2',2'-dicyanoethenyl)-15-[[4''-(*N,N*-dimethylamino)phenyl]ethynyl]-10,20-diphenylporphyrinatonicel(II) (**7**) and 5-formyl-15-[[4''-(*N,N*-dimethylamino)phenyl]ethynyl]-10,20-diphenylporphyrinatonicel(II) (**8**) have been determined experimentally by electric-field-induced second-harmonic generation (EFISH) at 1907 nm and computationally by semiempirical methods (ZINDO sum-over-states). The values of β_{μ} (124 and 66×10^{-30} cm⁵ esu⁻¹, for **7** and **8**, respectively) are moderate because the acceptor group is significantly tilted with respect to the porphyrin core in these complexes, which decreases the electronic coupling across the system. This nonplanar geometry has been confirmed by X-ray structure analyses and molecular modeling studies.

Introduction

Molecules showing large and fast nonlinear optical (NLO) responses have been studied extensively because of their potential applications for optical communications, information storage, optical switching, and electrooptical signal processing.¹ Through the tremendous effort devoted by experimentalists and theorists, the structural control of β , the molecular first hyperpolarizability, has been elucidated.² Generally, molecules with strong electron-donor and -acceptor groups that are connected by a large conjugated π -system usually exhibit high β values, although a balance among these three components is still important,^{2a,3} and exceptions such as octupolar molecules are well-known that can exhibit nonzero β , despite being nonpolar.⁴ A variety of organic systems such as polyenes, thiophenes, stilbenes, and azo compounds containing terminal donor and acceptor groups have been investi-

gated extensively, and exciting progress has been achieved in recent years.⁵

Among the various classes of NLO chromophores, porphyrins appear to have unique characteristics that render them superior as NLO materials.⁶ These macrocycles with their large polarizable π -conjugated system constitute a two-dimensional framework for electronic communication. Their optical properties can be tailored by changing the metal center, its oxidation state, the axial ligands, or the nature of the substituents at the peripheral sites of the macrocycle. Apart from the architectural flexibility, porphyrins also offer advantages in ease of fabrication and high thermal stability. To date, a substantial number of porphyrin-based NLO chromophores have been reported with particular emphasis on their third-order NLO properties.⁷ Unsymmetrical porphyrins showing second-order NLO effects usually consist of donor and/or acceptor groups attached to the aryl groups of *meso*-tetraarylporphyrins^{8,9} or an acceptor group attached to one of the β -positions.^{9,10} The β values for these porphyrins are not exceptionally high because electronic coupling between the donor and acceptor in the former system is hindered by the torsional barrier to rotation about the C(*meso*)–C(aryl) bond, and electronic

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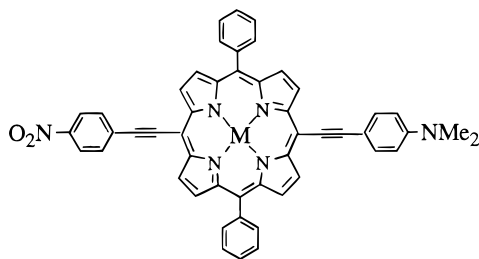
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asymmetry in the latter system is low due to the absence of a donor group. Recently, Therien et al. have reported two push-pull (arylethynyl)porphyrins **1** and **2**,^{11–13} in which the electron donor, acceptor, and linker are essentially coplanar, enabling effective electronic interactions within the molecule. The first hyperpolarizabilities



1 M = Cu
2 M = Zn

of these compounds, as determined by hyper-Rayleigh scattering (HRS)¹¹ and electronic Stark effect,¹³ are extremely high due to resonance enhancement.¹³ The value for the zinc complex ($\beta = 4933 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ at 1064 nm), which is by far the largest β value yet measured for an organic-based chromophore, is 10-fold larger than the theoretical value based on INDO/SCI calculations ($472 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$).¹² In an effort to gain a better understanding of the structure-properties relationship of this novel class of materials, we describe herein the synthesis of a series of closely related push-pull porphyrins in which the acceptor is linked to the porphyrin core by an ethynyl moiety. The NLO properties of two of these compounds have been studied by electric-field-induced second-harmonic generation (EFISH) measurements and by ZINDO sum-over-states calculations.

Results and Discussion

5,15-Diphenylporphyrinatonicel(II) (**3**) is a desirable starting material for push-pull porphyrins as the two

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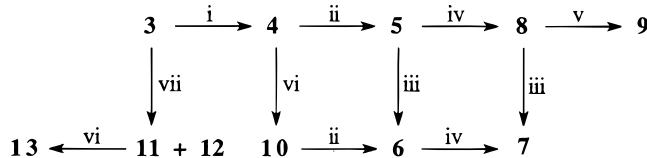
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Scheme 1^a



^a Reagents and conditions: (i) POCl₃, DMF, dichloroethane, rt, 2 h, then aqueous NaOAc, 60 °C, 2 h; (ii) NBS, pyridine, CHCl₃, rt, 2 h; (iii) CH₂(CN)₂, TiCl₄, pyridine, THF, rt, 15 h; (iv) Me₂NC₆H₄C≡CH, CuI, Pd(PPh₃)₂Cl₂, Et₃N, THF, rt, 2 h; (v) CH₂(CO₂Et)₂, TiCl₄, pyridine, THF, rt, 15 h; (vi) CH₂(CN)₂, Et₃N, THF, rt, 2 h; (vii) POCl₃, Me₂NCH=CHCHO, CH₂Cl₂, 50 °C, 7 h, then aqueous NaOAc, 60 °C, 2 h.

unsubstituted meso positions are highly reactive¹⁴ to which electron-donor and -acceptor groups can be introduced readily, and the net dipole moment is well aligned with the charge-transfer axis. Treatment of **3** with the Vilsmeier reagent gave the meso-formylated porphyrin **4** as the major product (Scheme 1, Chart 1), along with small amounts of β -formylated and diformylated products.¹⁵ Bromination of **4** with NBS led to the formation of **5** in good yield. A *meso*, β -dibromo-*meso*-formylporphyrin was also produced in small quantity which was characterized by ¹H NMR and liquid secondary ion (LSI) mass spectrometry, but the position of the β -bromo group could not be unambiguously determined.

Porphyrin **5** is a versatile precursor to a series of push-pull porphyrins via reactions of the bromo and formyl functionalities. Treatment of **5** with malononitrile under the Knoevenagel conditions did not lead to the isolation of **6**, but several unidentified products were obtained instead. However, by using an excess amount of TiCl₄,¹⁶ the coupling proceeded smoothly and porphyrin **6** was obtained in good yield. This compound underwent a palladium-catalyzed coupling reaction with [4-(*N,N*-dimethylamino)phenyl]ethyne to give **7** in which an electron-donating dimethylamino group and electron-withdrawing cyano groups are linked to the porphyrin core.

Transformation could also be performed on the bromo group first with comparable yields. Reaction of **5** with [4-(*N,N*-dimethylamino)phenyl]ethyne in the presence of palladium catalyst resulted in the formation of **8**, which coupled with malononitrile or diethyl malonate, with the aid of TiCl₄, to give **7** or **9**, respectively. A simplified alternative involved the conversion of **4** to **10**. Without the bromo or alkynyl moiety at the opposite meso position, the conversion of aldehyde to a dicyanoethenyl group could be performed readily using triethylamine. Bromination of **10**, again with NBS, produced **6** in excellent yield.

To introduce an extra double bond between the aldehyde and the porphyrin core, a vinylogous Vilsmeier formylation was performed.¹⁷ Reaction of **3** with 3-(dimethylamino)acrolein and phosphorus oxychloride afforded mainly the *meso*-(2'-formylethenyl)porphyrin **11** together with a small amount of the *meso*-diformylated derivative

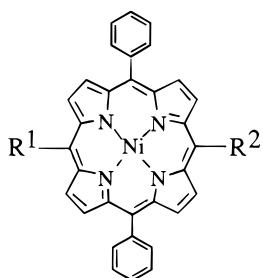
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Chart 1



Compound	R ¹	R ²
3	H	H
4	H	CHO
5	Br	CHO
6	Br	
7		
8		CHO
9		
10	H	
11	H	
12		
13	H	

12. In attempt to brominate **11** with NBS, it appeared that the ethenyl group was also susceptible to bromo attack. The ¹H NMR spectrum of the product showed two singlets at δ 10.00 and 9.91, four doublets between δ 8.66 and 9.40 assignable to the four types of β -pyrrole protons, and multiplets around δ 7.7 and 7.9 due to the phenyl protons. These data along with the accurate mass measurement suggested that the product was probably 5-bromo-15-(2'-bromo-2'-formylethenyl)-10,20-diphenylporphyrinatonicel(II). No further characterization was carried out on this compound. Porphyrin **11** could, however, couple with malononitrile using triethylamine as a base to give **13** in excellent yield.

Scheme 2 shows an alternative route to a push–pull porphyrin containing a formylethenyl acceptor. Bromination of 5,15-diphenylporphyrin (**14**) with 1.4 equiv of NBS gave 50% of *meso*-bromo product **15** after chromatographic separation from the contaminating *meso*-dibromoporphyrin.¹⁸ The iodo analogue **16** was prepared by

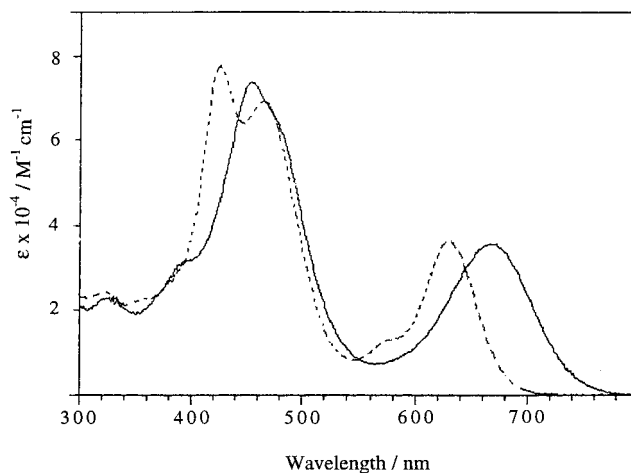


Figure 1. Vis spectra of **7** (—) and **8** (---) in CH₂Cl₂.

the procedure described by Dolphin et al.¹⁹ Metalation of **15** and **16** followed by vinylogous Vilsmeier formylation led to the formation of **19** and **20**, respectively. Since the metalloporphyrins **17** and **18** are only sparingly soluble in organic solvents, halogenation was performed prior to metalation. Actually, the removal of dibromo- and diiodoporphyrins was found to be much more convenient after the formylation step. Coupling of **19** with [4-(*N,N*-dimethylamino)phenyl]ethyne afforded the expected product **21**.

All of the new compounds were characterized with a range of spectroscopic methods and elemental analyses or accurate mass measurements. As displayed in Figure 1, the electronic spectrum of **7** in CH₂Cl₂ shows a broad Soret band at 453 nm and a broad Q-band at 667 nm that resembles the spectra of other bis(ethynyl)metalloporphyrins.^{11,20} Compounds **9** and **21** also give similar spectra, but the absorption bands for the latter are significantly blue-shifted (B band 448 nm, Q-band 635 nm). Interestingly, the B band is clearly split (424 and 464 nm) in the spectrum of **8** as shown in Figure 1.

The molecular structures of **8** and **21** were also determined by X-ray diffraction analyses. The structures are illustrated in Figures 2 and 3, together with the common atomic numbering scheme. Selected bond lengths and angles for the donor and acceptor parts are given in Table 1. It is interesting that the structure of **21** is far more distorted from planarity than is the structure of **8**, as measured by the least squares plane through the central porphyrin skeleton. The root-mean-square deviation of fitted atoms is 0.33 Å for the former and 0.19 Å for the latter. It is no coincidence that C(17) is the greatest distance from this plane in both structures (0.66 Å for **21**, 0.32 Å for **8**). These are in contrast to the structures of 5,15-bis[(4'-fluorophenyl)ethynyl]-10,20-diphenylporphyrinatozinc(II) (**22**) and 5,15-bis[(4'-methoxyphenyl)ethynyl]-10,20-diphenylporphyrin (**23**), which are virtually flat.²⁰ Other interesting features include the following: (i) While the orientation of the C(4*n*) (*n* = 1–6) phenyl ring with respect to the porphyrin macrocycle is almost identical in **8** and **21** (dihedral angle = 70.8° and 69.6°, respectively), the dihedral angle between

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Scheme 2

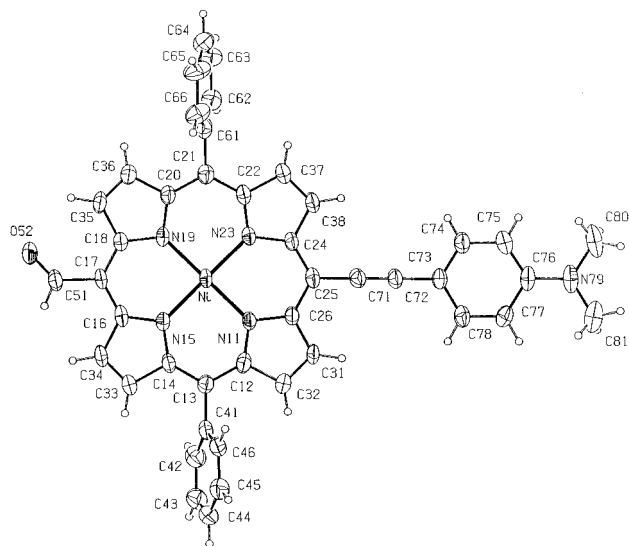
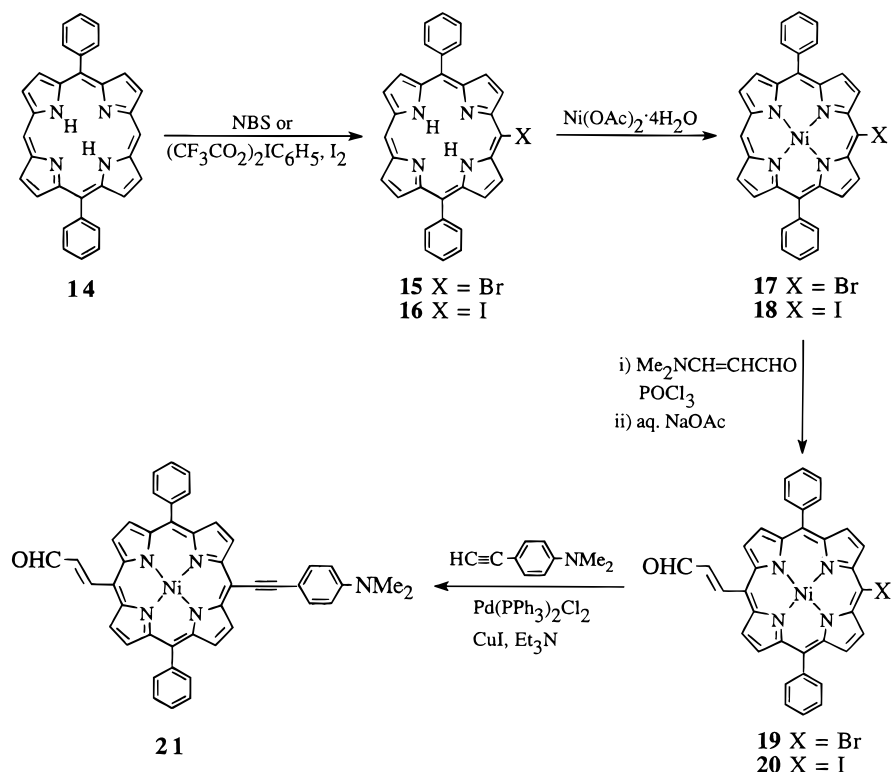


Figure 2. Molecular structure of **8**. Ellipsoids are shown at 30% probability. Hydrogen atoms are shown with small radii of arbitrary size.

the other phenyl group C(6*n*) (*n* = 1–6) and the porphyrin ring is much larger in **8** (80.6°) than in **21** (68.3°), which may derive in large part from crystal packing forces. (ii) The arylethynyl group C(7*n*) (*n* = 1–6) and the porphyrin ring adopt a nearly coplanar arrangement in **8** with a dihedral angle of 3.9°, which is in accord with the structures of **22** and **23**. The corresponding angle for **21**, however, is significantly larger (10.3°). (iii) The plane containing the aldehyde [C(17), C(51), O(52) for **8**], in particular for **21** [C(17), C(5*n*) (*n* = 1–3), O(54)], is also twisted relative to the porphyrin ring (dihedral angle = 15.7° for **8**, 38.7° for **21**). (iv) The C(71)=C(72) triple bond is unexceptional, but the C(25)–C(71) bond is slightly longer than the C(72)–C(73) bond in both

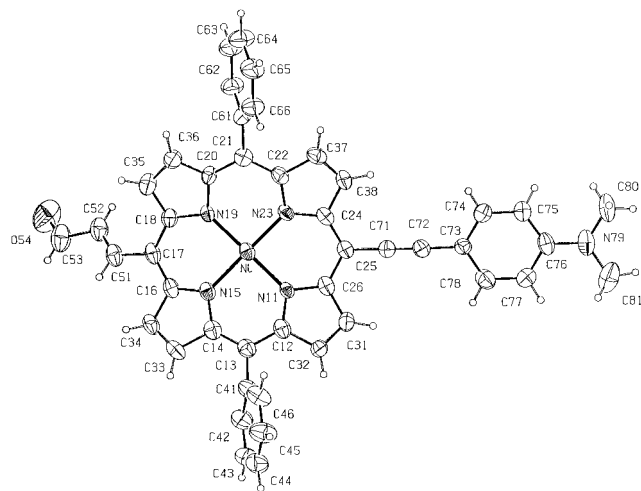


Figure 3. Molecular structure of **21**. Ellipsoids are shown at 30% probability. Hydrogen atoms are shown with small radii of arbitrary size.

structures (Table 1), suggesting that a substantial cumulenenic character is present in these compounds that was not observed in **22** and **23**.²⁰

Measurement of the molecular first hyperpolarizability (β) for **8** was attempted using the HRS method in CHCl_3 solution with an incident irradiation wavelength of 1064 nm.²¹ Although unprecedentedly large β values were reported for the related porphyrins **1** and **2** as determined by this technique, we found that **8** was highly fluorescent and the two-photon absorbance fluorescence photons outweighed the scattering signals, which is a commonly observed phenomenon.²² Because of this, we employed an alternative method to study the second-order NLO properties of these push–pull porphyrins.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for **8 and **21****

	8	21
C(17)–C(51)	1.462 (8)	1.464 (12)
C(51)–O(52)	1.198 (8)	
C(51)–C(52)		1.323 (13)
C(52)–C(53)		1.51 (2)
C(53)–O(54)		1.20 (2)
C(25)–C(71)	1.425 (8)	1.441 (12)
C(71)–C(72)	1.175 (8)	1.198 (12)
C(72)–C(73)	1.411 (8)	1.425 (13)
C(73)–C(74)	1.378 (9)	1.393 (12)
C(73)–C(78)	1.397 (9)	1.373 (12)
C(74)–C(75)	1.355 (8)	1.381 (12)
C(75)–C(76)	1.376 (10)	1.392 (13)
C(76)–C(77)	1.412 (10)	1.407 (13)
C(77)–C(78)	1.347 (9)	1.396 (13)
C(76)–N(79)	1.363 (8)	1.371 (12)
C(17)–C(51)–O(52)	129.0 (7)	
C(17)–C(51)–C(52)		127.2 (10)
C(51)–C(52)–C(53)		119.4 (12)
C(52)–C(53)–O(54)		122 (2)
C(25)–C(71)–C(72)	178.9 (6)	179.5 (10)
C(71)–C(72)–C(73)	175.8 (7)	175.0 (10)

Table 2. Hyperpolarizabilities, Dipole Moments, and Absorption Maxima

compd	$\mu^{\beta a,b}$ (expt)	$\mu^{c,d}$ (calc)	$\lambda_{\max}^{e,f}$ (expt)	$\lambda_{\max}^{d,f}$ (calc)	$\beta_{\mu}^{b,g}$ (expt)	$\beta_{\mu}^{d,g}$ (calc)	ϕ^h (calc)
7	1170	9.5	667	633	124	70	57
8	570	8.7	630	636	66	84	26

^a In units of 10^{-48} cm⁶. ^b In CHCl₃. ^c In units of debye (1 D = 10^{-18} esu cm). ^d Computed from ESFF geometry. ^e In CH₂Cl₂. ^f In units of nm. ^g In units of 10^{-30} cm⁵ esu⁻¹. ^h In units of degrees, dihedral angle between the plane of porphyrin ring and the plane of electron acceptor substituent.

Hyperpolarizabilities for compounds **7** and **8** were determined experimentally by EFISH²³ and computationally using the ZINDO sum-over-states method^{23–25} (Table 2). The values of the dot product $\mu \cdot \beta$ measured experimentally at 1907 nm, along with the computed dipole moments, enable the determination of β_{μ} , the hyperpolarizability in the direction of the dipole moment. The β_{μ} values for **7** ($\beta_{\mu, 1907 \text{ nm}} = 124 \times 10^{-30}$ cm⁵ esu⁻¹) and **8** ($\beta_{\mu, 1907 \text{ nm}} = 66 \times 10^{-30}$ cm⁵ esu⁻¹) are not corrected for resonance enhancement because the second harmonic signal (954 nm) lies far from the electronic absorptions.

The computed values of β_{μ} and λ_{\max} for **7** and **8** display modest agreement with experiment (Table 2). The discrepancies may be rationalized in terms of two factors. First, the conformational populations sampled in the

EFISH experiment are not taken into account by the calculations. Second, the computed magnitudes of β_{μ} and λ_{\max} are extremely sensitive to the dihedral angle, ϕ . Overlap of p-orbitals displays a $\cos^2 \phi$ dependence; in the vicinity of $\phi \approx 55^\circ$ (compound **7**), the $\cos^2 \phi$ function changes rapidly. Small changes in computed geometry translate into large changes in computed absorption maximum and hyperpolarizability.

Direct comparison of the experimental hyperpolarizabilities for **7** and **8** with those for Therien's porphyrin systems is difficult because of differing experimental conditions. The very large hyperpolarizabilities for **1** ($\beta_{1064 \text{ nm}} = 1501 \times 10^{-30}$ cm⁵ esu⁻¹) and **2** ($\beta_{1064 \text{ nm}} = 4933 \times 10^{-30}$ cm⁵ esu⁻¹) measured by HRS are resonance enhanced.^{11,13} The hyperpolarizability for **2** ($\beta_{1907 \text{ nm}} = 540 \times 10^{-30}$ cm⁵ esu⁻¹) measured at longer wavelength by Stark effect spectroscopy reflects a much lesser degree of resonance enhancement. Even though Hupp's Stark measurement and our EFISH measurement were performed at the same wavelength, the methods sample different components of the hyperpolarizability tensor and are thus not directly comparable. Qualitatively, it appears that porphyrins **7** and **8** possess smaller hyperpolarizabilities than **2**. Our ZINDO calculations indicate that the differences between the zinc-containing porphyrin **2** and the nickel-containing analogues **7** and **8** cannot be attributed to the metal center. Hyperpolarizabilities computed for the zinc-containing analogues of **7** and **8** [**7(Zn)** 74, **8(Zn)** 82×10^{-30} cm⁵ esu⁻¹] are very similar to those of their nickel-containing counterparts.

Compounds **1**, **2**, **7**, and **8** contain the same donor substituent, namely the [4-(*N,N*-dimethylamino)phenyl]ethynyl group. The acceptor substituent of **1** and **2** (4-nitrophenylethynyl) differs from those in **7** and **8** (dicyanoethenyl and formyl, respectively). The key distinction involves steric factors. The ethyne moiety of 4-nitrophenylethynyl substituent does not encounter steric repulsions with the β -hydrogens of the porphyrin ring, thereby allowing the acceptor subunit of **1** and **2** to maintain conjugation across the donor–porphyrin–acceptor framework.^{11–13} This extensive delocalization affords a large molecular hyperpolarizability. The acceptor substituents of **7** and **8** are both sp²-hybridized at the point of attachment to the porphyrin ring. Steric repulsions with the β -hydrogens cause the acceptor substituent to twist out of the plane of the porphyrin ring.²⁶ Molecular modeling shows the angle between porphyrin core and acceptor planes for **7** and **8** to be 57° and 26°, respectively (Table 2). This deviation from coplanarity dramatically decreases the electronic coupling across the donor–porphyrin–acceptor framework, resulting in a smaller molecular hyperpolarizability.

In comparing the EFISH results for **7** and **8**, the dicyanoethenyl acceptor affords a larger hyperpolarizability than the formyl acceptor (124 vs 66×10^{-30} cm⁵ esu⁻¹, respectively). This observation can be rationalized in terms of the higher electronic acceptor strength of the dicyanoethenyl substituent relative to the formyl group.²⁷ The experimental absorption spectra reveal that the longest-wavelength Q-band for **7** (667 nm) occurs 37 nm to the red of that for **8** (630 nm). This observation may

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(24) Geometry optimizations for **7**, **8**, **7(Zn)**, and **8(Zn)** were performed with the ESFF molecular mechanics force field, as implemented in the InsightII program (Version 95.0, Biosym/MSI, San Diego CA, 1995). Geometry optimizations for **7(Zn)** and **8(Zn)** were also performed using the AM1 semiempirical method, as implemented in MOPAC [version 6.0, Quantum Chemistry Program Exchange (QCPE # 455), Department of Chemistry, Indiana University, Bloomington, Indiana]. The computed geometries obtained for **7(Zn)** and **8(Zn)** by both methods display good agreement.

(25) Frequency-dependent molecular hyperpolarizabilities were from the ESFF geometries for **7** and **8** using the ZINDO sum-over-states program (1907 nm, summed over the lowest 145 excited states using single pair excitations from the highest 11 occupied orbitals into the lowest 12 unoccupied orbitals) (ZINDO, version 96.0/4.0.0, Biosym/MSI, San Diego CA, 1996).

(26) Calculations using the ESFF force field readily confirmed that acceptor substituents are twisted out of conjugation with the porphyrin ring in the optimized geometries of **7** and **8**. This is in agreement with the molecular structures of **8** and **21** determined by X-ray diffraction analyses.

account for the larger hyperpolarizability of **7** in terms of both a larger intrinsic hyperpolarizability and a slightly higher degree of resonance enhancement.²⁸

Conclusion

By employing several well-established procedures including formylation, halogenation, Knoevenagel condensation, and palladium-catalyzed cross-coupling reactions, we have prepared a series of push–pull porphyrins based on the 5,15-diphenylporphyrinatonicel(II) core. These NLO chromophores having a net dipole moment essentially aligned with the charge transfer axis exhibit relatively high β values compared with the push–pull *meso*-tetraarylporphyrins^{8a,9} and β -acceptor porphyrins.^{10b} Since the acceptor groups of these chromophores that are linked to the porphyrin core through an ethenyl moiety are significantly tilted with respect to the conjugated π -system, the β values, however, are smaller than those of push–pull (arylethynyl)porphyrins such as **1** and **2**.^{11–13} The synthetic routes described in this work are rather general and can be extended to tailor the porphyrin-based chromophores with a view to optimizing their NLO responses.

Experimental Section

General Methods. Air-sensitive reactions were carried out using standard Schlenk-line techniques under an atmosphere of nitrogen. Phosphorus oxychloride and pyrrole were fractionally distilled from sodium and CaH₂, respectively. Triethylamine and CH₂Cl₂ were distilled from CaH₂ prior to use. Dichloroethane and DMF were distilled from BaO. THF was distilled from sodium benzophenone ketyl. All other solvents and reagents were purchased from commercial sources and used without further purification. Chromatographic purifications were performed on silica gel columns (Merck, 70–230 mesh) with the indicated eluents. Hexanes used in chromatography was distilled from anhydrous CaCl₂. [4-(*N,N*-Dimethylamino)phenyl]ethyne²⁹ and compounds **3**,³⁰ **14**,³¹ and **16**¹⁹ were prepared according to literature procedures.

Melting points are uncorrected. ¹H NMR spectra were recorded in CDCl₃ solutions at either 250 or 300 MHz and are reported in ppm downfield from TMS. Visible spectra were measured in CH₂Cl₂ solutions at ambient temperature. IR spectra were obtained on an FT-IR spectrometer as KBr pellets. LSI and FAB mass spectra were taken using a 3-nitrobenzyl alcohol matrix. High-resolution accurate mass measurements using the LSI technique were performed on an FT-ICR mass spectrometer.

NLO Measurements. Measurements of molecular hyperpolarizabilities were performed via the EFISH method at 1907

nm using a series of solutions (10⁻³–10⁻⁴ M) in CHCl₃. Other experimental details of the hyperpolarizability measurements have previously been described.²³ A reference channel was not used due to power limitations at 1907 nm. Ground-state geometries and dipole moments were calculated using the ESFF force field supported in the InsightII computational chemistry package.²⁴ Hyperpolarizabilities and absorption spectra were obtained via ZINDO.²⁵

(10-Formyl-5,15-diphenylporphyrinato)nickel(II) (4). Freshly distilled POCl₃ (1.5 mL, 16 mmol) was mixed with DMF (1.5 mL, 19 mmol) at 0 °C under nitrogen. The pale-red mixture was allowed to stand at room temperature for 30 min and then added dropwise via a syringe to a solution of **3** (200 mg, 0.39 mmol) in dichloroethane (70 mL). After being stirred at room temperature for 2 h, the green solution was mixed with saturated aqueous NaOAc (150 mL), and the mixture was vigorously stirred at 60 °C for 2 h. The organic layer was separated, washed with water (3 × 100 mL), dried over anhydrous Na₂SO₄, and rotary-evaporated. The residue was chromatographed with toluene as eluent. The first greenish red fraction was collected and evaporated to give the formylated product **4** (148 mg, 70%): *R*_f = 0.54; ¹H NMR (300 MHz) δ 12.07 (s, 1 H), 9.82 (d, *J* = 5.1 Hz, 2 H), 9.67 (s, 1 H), 9.00 (d, *J* = 4.8 Hz, 2 H), 8.86 (d, *J* = 5.1 Hz, 2 H), 8.70 (d, *J* = 4.8 Hz, 2 H), 7.93–7.96 (m, 4 H), 7.69–7.72 (m, 6 H); ¹³C{¹H} NMR (75.4 MHz) δ 193.1, 144.2, 141.8, 141.2, 140.0, 135.3, 133.5, 133.2, 132.4, 130.5, 128.1, 127.1, 120.4, 108.6, 106.3; vis [λ _{max} nm (log ϵ)] 416 (5.79), 544 (4.48), 588 (4.67); HRMS (LSI) *m/z* calcd for C₃₃H₂₀N₄⁵⁸NiO (M⁺) 546.0991, found 546.0948. Anal. Calcd for C₃₃H₂₀N₄NiO: C, 72.43; H, 3.68; N, 10.24. Found: C, 72.18; H, 3.54; N, 10.15.

(5-Bromo-15-formyl-10,20-diphenylporphyrinato)nickel(II) (5). To a solution of **4** (60 mg, 0.1 mmol) in CHCl₃ (25 mL) at 0 °C were added pyridine (0.1 mL) and NBS (20 mg, 0.1 mmol). The mixture was gradually warmed to room temperature and then kept stirring at this temperature for 2 h. The volatiles were removed under reduced pressure and the residue was chromatographed with toluene as eluent. The first purple band was collected to give a small amount of *meso*, β -dibromoporphyrin. Further elution developed a dark purple band, which was collected and rotary-evaporated to afford **5** as purple microcrystals (52 mg, 76%): *R*_f = 0.60; ¹H NMR (300 MHz) δ 11.93 (s, 1 H), 9.70 (d, *J* = 5.2 Hz, 2 H), 9.35 (d, *J* = 5.1 Hz, 2 H), 8.76 (d, *J* = 5.1 Hz, 2 H), 8.58 (d, *J* = 4.7 Hz, 2 H), 7.88–7.90 (m, 4 H), 7.67–7.70 (m, 6 H); ¹³C{¹H} NMR (62.9 MHz) δ 192.2, 144.7, 144.4, 141.4, 141.0, 139.4, 135.6, 134.1, 133.4, 132.9, 130.9, 128.2, 127.1, 121.0, 107.0, 106.1; vis [λ _{max} nm (log ϵ)] 424 (5.81), 550 (4.52), 596 (4.72); IR 1659s cm⁻¹ (CO stretching); HRMS (LSI) *m/z* calcd for C₃₃H₁₉⁸¹BrN₄⁵⁸NiO (M⁺) 626.0076, found 626.0052. Anal. Calcd for C₃₃H₁₉BrN₄NiO: C, 63.30; H, 3.06; N, 8.95. Found: C, 63.29; H, 3.06; N, 8.81.

[5-Bromo-15-(2',2'-dicyanoethenyl)-10,20-diphenylporphyrinato]nickel(II) (6). **From 5.** A mixture of TiCl₄ (3.1 mL) and CCl₄ (7 mL) was added through an addition funnel to a 250 mL three-necked round-bottomed flask containing THF (50 mL). A solution of compound **5** (31 mg, 0.05 mmol) and malononitrile (0.88 g, 13.3 mmol) in THF (15 mL) was slowly added to the yellow solution, and then pyridine (4.4 mL) in THF (8 mL) was added dropwise over 3 h. The green mixture was stirred at room temperature for a further 15 h. Water (100 mL) was added, and the dark green solution was stirred at room temperature for 10 min before being extracted with diethyl ether (100 mL). The extract was washed with water (2 × 50 mL), dried over anhydrous MgSO₄, and evaporated. The residue was chromatographed with toluene as eluent. The second band was collected to afford **6** as a green solid (28 mg, 83%). **From 10.** Pyridine (0.2 mL) and NBS (40 mg, 0.22 mmol) were added to a solution of **10** (119 mg, 0.20 mmol) in CHCl₃ (35 mL) at 0 °C. The mixture was stirred at room temperature for 2 h, and then the volatiles were removed in vacuo. The crude product was purified by column chromatography with toluene as eluent (121 mg, 90%): *R*_f = 0.76; ¹H NMR (250 MHz) δ 9.90 (s, 1 H), 9.33 (d, *J* = 4.9 Hz, 2 H), 9.08 (d, *J* = 5.0 Hz, 2 H), 8.75 (d, *J* = 5.2 Hz, 2 H), 8.56

(27) Consider the EFISH values (1907 nm, CHCl₃) measured for a series of simple *N,N*-dimethylaniline derivatives substituted with the electron acceptors of relevance to our study: (4-nitrophenyl)ethynyl ($\beta_u = 46 \times 10^{-30}$ cm⁵ esu⁻¹), dicyanoethenyl ($\beta_u = 32 \times 10^{-30}$ cm⁵ esu⁻¹), and formyl ($\beta_u = 6.3 \times 10^{-30}$ cm⁵ esu⁻¹). (a) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631. (b) Cheng, L.-T.; Tam, W.; Marder, S. R.; Steigman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643.

(28) The computed dipole moments of **7** (9.5 D) vs **8** (8.7 D) reveal that the dicyanoethenyl-substituted compound is more polar than the formyl analogue. Given the fact that the acceptors in both **7** and **8** are twisted out of the plane of the porphyrin ring, the substituent effect on the dipole moment could arise via purely an inductive effect. Only by considering differences in the absorption spectra does one find evidence for a resonance contribution.

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(d, $J = 5.0$ Hz, 2 H), 7.87–7.90 (m, 4 H), 7.67–7.70 (m, 6 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz) δ 159.2, 144.4, 142.0, 141.7, 141.5, 139.0, 135.5, 134.6, 133.5, 133.4, 130.6, 128.4, 127.2, 121.9, 114.4, 112.8, 107.4, 103.2, 89.3; vis [λ_{max} nm (log ϵ)] 391 (5.11), 448 (5.68), 617 (4.83); IR 2205 cm^{-1} (CN stretching); HRMS (LSI) m/z calcd for $\text{C}_{36}\text{H}_{19}\text{BrN}_6\text{Ni}$ (M^+) 674.0189, found 674.0224. Anal. Calcd for $\text{C}_{36}\text{H}_{19}\text{BrN}_6\text{Ni}$: C, 64.14; H, 2.84; N, 12.47; Br, 11.85. Found: C, 64.49; H, 3.15; N, 11.87; Br, 11.97.

[5-(2',2'-Dicyanoethenyl)-15-[[4'-(*N,N*-dimethylamino)phenyl]ethynyl]-10,20-diphenylporphyrinato]nickel(II) (7). From **6**. A mixture of **6** (34 mg, 50 μmol), Pd(PPh₃)₂Cl₂ (3 mg, 4 μmol), CuI (2 mg, 10 μmol), [4-(*N,N*-dimethylamino)phenyl]ethyne (9 mg, 60 μmol), and triethylamine (0.7 mL) in THF (4 mL) was stirred at room temperature for 2 h. The volatiles were removed in vacuo, and the dark green residue was extracted with CH₂Cl₂ (40 mL). The extract was washed with water (2 \times 30 mL), dried over anhydrous MgSO₄, concentrated in reduced pressure, and then chromatographed using toluene as eluent. The second band was collected and rotary-evaporated to give **7** as a dark green solid (30 mg, 81%). **From 8**. By using the procedure described for **6**, compound **8** (69 mg, 0.10 mmol) was treated with TiCl₄ (6.2 mL), CCl₄ (14 mL), malononitrile (1.5 g, 22.6 mmol), and pyridine (8.8 mL) in THF (150 mL) to give **7** (54 mg, 73%): $R_f = 0.46$; ^1H NMR (300 MHz) δ 9.85 (s, 1 H), 9.34 (d, $J = 4.8$ Hz, 2 H), 9.01 (d, $J = 5.1$ Hz, 2 H), 8.67 (d, $J = 5.1$ Hz, 2 H), 8.50 (d, $J = 4.8$ Hz, 2 H), 7.86–7.89 (m, 4 H), 7.75 (d, $J = 8.9$ Hz, 2 H), 7.63–7.71 (m, 6 H), 6.80 (d, $J = 8.9$ Hz, 2 H), 3.09 (s, 6 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz) δ 159.2, 150.8, 143.9, 143.3, 141.6, 141.4, 139.3, 134.9, 133.3, 133.2, 132.8, 132.6, 130.0, 128.2, 127.2, 122.1, 114.7, 113.0, 111.9, 109.4, 106.2, 103.3, 102.5, 88.3, 88.1, 40.2; vis [λ_{max} nm (log ϵ)] 453 (4.82), 667 (4.50); HRMS (LSI) m/z calcd for $\text{C}_{46}\text{H}_{29}\text{N}_7\text{Ni}$ (M^+) 737.1838, found 737.1867. Anal. Calcd for $\text{C}_{46}\text{H}_{29}\text{N}_7\text{Ni}$: C, 74.82; H, 3.96; N, 13.28. Found: C, 74.76; H, 3.97; N, 13.30.

[5-Formyl-15-[[4'-(*N,N*-dimethylamino)phenyl]ethynyl]-10,20-diphenylporphyrinato]nickel(II) (8). A mixture of **5** (63 mg, 0.10 mmol), Pd(PPh₃)₂Cl₂ (10 mg, 14 μmol), CuI (5 mg, 26 μmol), [4-(*N,N*-dimethylamino)phenyl]ethyne (17 mg, 0.12 mmol), and triethylamine (1.4 mL) in THF (8 mL) was stirred at room temperature for 2 h. After the volatiles were removed in vacuo, the dark green residue was extracted with CH₂Cl₂ (50 mL) and then purified by chromatography using toluene as eluent (50 mg, 73%): $R_f = 0.50$; ^1H NMR (300 MHz) δ 11.97 (s, 1 H), 9.70 (d, $J = 5.1$ Hz, 2 H), 9.44 (d, $J = 4.8$ Hz, 2 H), 8.74 (d, $J = 5.1$ Hz, 2 H), 8.59 (d, $J = 4.8$ Hz, 2 H), 7.92–7.95 (m, 4 H), 7.78 (d, $J = 8.7$ Hz, 2 H), 7.68–7.71 (m, 6 H), 6.81 (d, $J = 8.7$ Hz, 2 H), 3.09 (s, 6 H); vis [λ_{max} nm (log ϵ)] 424 (4.89), 464 (4.84), 630 (4.56). Anal. Calcd for $\text{C}_{43}\text{H}_{29}\text{N}_5\text{NiO}$: C, 74.80; H, 4.23; N, 10.14. Found: C, 73.56; H, 4.35; N, 9.65.

[5-[2',2'-Bis(ethoxycarbonyl)ethenyl]-15-[[4'-(*N,N*-dimethylamino)phenyl]ethynyl]-10,20-diphenylporphyrinato]nickel(II) (9). According to the procedure described for **6**, compound **8** (70 mg, 0.10 mmol) was treated with TiCl₄ (6.2 mL), CCl₄ (14 mL), diethyl malonate (2 mL, 13.2 mmol), and pyridine (8.8 mL) in THF (150 mL) to give **9** (44 mg, 53%): $R_f = 0.45$; ^1H NMR (300 MHz) δ 10.02 (s, 1 H), 9.52 (d, $J = 4.8$ Hz, 2 H), 9.12 (d, $J = 5.1$ Hz, 2 H), 8.67–8.69 (two overlapping d, 4 H), 7.93 (br s, 4 H), 7.79 (d, $J = 8.4$ Hz, 2 H), 7.67–7.74 (m, 6 H), 6.81 (d, $J = 8.7$ Hz, 2 H), 4.50 (q, $J = 7.1$ Hz, 2 H), 3.32 (q, $J = 7.1$ Hz, 2 H), 3.08 (s, 6 H), 1.47 (t, $J = 7.1$ Hz, 3 H), –0.10 (t, $J = 7.1$ Hz, 3 H); vis [λ_{max} nm (log ϵ)] 454 (5.34), 658 (4.89); HRMS (LSI) m/z calcd for $\text{C}_{50}\text{H}_{39}\text{N}_5\text{NiO}_4$ (M^+) 831.2355, found 831.2391. Anal. Calcd for $\text{C}_{50}\text{H}_{39}\text{N}_5\text{NiO}_4$: C, 72.13; H, 4.72; N, 8.41. Found: C, 70.78; H, 4.74; N, 8.10.

[10-(2',2'-Dicyanoethenyl)-5,15-diphenylporphyrinato]nickel(II) (10). The formylated porphyrin **4** (97 mg, 0.18 mmol) and malononitrile (40 mg, 0.6 mmol) were dissolved in THF (16 mL). Triethylamine (0.4 mL) was added, and the mixture was stirred at room temperature for 2 h. The volatiles were removed under reduced pressure, and the residue was chromatographed with toluene as eluent. The first green band was collected, which upon evaporation yielded **10** as a greenish purple solid (104 mg, 98%): $R_f = 0.71$; ^1H NMR (250 MHz) δ 10.03 (s, 1 H), 9.46 (s, 1 H), 9.14 (d, $J = 5.0$ Hz, 2 H), 8.85 (d,

$J = 4.8$ Hz, 2 H), 8.82 (d, $J = 5.0$ Hz, 2 H), 8.63 (d, $J = 4.8$ Hz, 2 H), 7.90–7.93 (m, 4 H), 7.65–7.74 (m, 6 H); vis [λ_{max} nm (log ϵ)] 385 (5.14), 444 (5.52), 607 (4.66); HRMS (LSI) m/z calcd for $\text{C}_{36}\text{H}_{20}\text{N}_6\text{Ni}$ (M^+) 594.1103, found 594.1064. Anal. Calcd for $\text{C}_{36}\text{H}_{20}\text{N}_6\text{Ni}$: C, 72.64; H, 3.39; N, 14.12. Found: C, 72.41; H, 3.42; N, 14.01.

[10-(2'-Formylethenyl)-5,15-diphenylporphyrinato]nickel(II) (11) and [5,15-Bis(2'-formylethenyl)-10,20-diphenylporphyrinato]nickel(II) (12). In a 50 mL round-bottomed flask connected to a nitrogen inlet was added freshly distilled POCl₃ (0.8 mL, 8.6 mmol) dropwise to a solution of 3-(dimethylamino)acrolein (0.8 mL, 8.0 mmol) in CH₂Cl₂ (4.0 mL) at 0 °C. The red mixture was kept at room temperature for 30 min, and then a portion of this Vilsmeier reagent (2.0 mL, 2.9 mmol) was transferred via a syringe to a solution of **3** (156 mg, 0.3 mmol) in CH₂Cl₂ (50 mL). The mixture was heated at 50 °C for 7 h, cooled to room temperature, and then mixed with saturated aqueous NaOAc (100 mL). The mixture was vigorously stirred at 60 °C for 2 h. The organic layer was separated and washed with water (3 \times 80 mL). After being dried over anhydrous Na₂SO₄, the volatiles were removed under reduced pressure and the crude product was purified by chromatography with toluene as eluent. A dark red band followed by a green band developed, which were collected and evaporated to give **11** (94 mg, 55%) and **12** (10 mg, 5%), respectively. **11**: $R_f = 0.39$; ^1H NMR (300 MHz) δ 10.03 (d, $J = 9.3$ Hz, 1 H), 9.66 (s, 1 H), 9.61 (d, $J = 18.6$ Hz, 1 H), 9.27 (d, $J = 6.0$ Hz, 2 H), 9.02 (d, $J = 5.7$ Hz, 2 H), 8.82 (d, $J = 6.0$ Hz, 2 H), 8.75 (d, $J = 5.4$ Hz, 2 H), 7.94–7.98 (m, 4 H), 7.66–7.74 (m, 6 H), 6.60 (dd, $J = 9.3, 18.6$ Hz, 1 H); vis [λ_{max} nm (log ϵ)] 426 (5.76), 541 (4.78), 584 (4.71); HRMS (LSI) m/z calcd for $\text{C}_{35}\text{H}_{23}\text{N}_4\text{NiO}$ (MH^+) 573.1225, found 573.1229. Anal. Calcd for $\text{C}_{35}\text{H}_{23}\text{N}_4\text{NiO}$: C, 73.33; H, 3.87; N, 9.77. Found: C, 73.27; H, 3.89; N, 9.80. **12**: $R_f = 0.13$; ^1H NMR (300 MHz) δ 10.06 (d, $J = 7.8$ Hz, 2 H), 9.54 (d, $J = 15.6$ Hz, 2 H), 9.23 (d, $J = 5.1$ Hz, 4 H), 8.72 (d, $J = 4.8$ Hz, 4 H), 7.90–7.93 (m, 4 H), 7.68–7.73 (m, 6 H), 6.61 (dd, $J = 7.8, 15.6$ Hz, 2 H); vis [λ_{max} nm (log ϵ)] 444 (5.50), 622 (4.59); HRMS (LSI) m/z calcd for $\text{C}_{38}\text{H}_{25}\text{N}_4\text{NiO}_2$ (MH^+) 627.1331, found 627.1322.

[10-(4',4'-Dicyano-1',3'-butadienyl)-5,15-diphenylporphyrinato]nickel(II) (13). According to the procedure described for **10**, compound **11** (115 mg, 0.2 mmol) was treated with malononitrile (44 mg, 0.7 mmol) and triethylamine (0.4 mL) in THF (25 mL) to give **13**, which was further purified by recrystallization from CHCl₃/hexane (120 mg, 96%): $R_f = 0.56$; ^1H NMR (300 MHz) δ 9.64 (s, 1 H), 9.24 (d, $J = 14.7$ Hz, 1 H), 9.15 (d, $J = 5.1$ Hz, 2 H), 9.00 (d, $J = 4.5$ Hz, 2 H), 8.79 (d, $J = 5.1$ Hz, 2 H), 8.69 (d, $J = 4.8$ Hz, 2 H), 7.94–7.97 (m, 4 H), 7.83 (d, $J = 11.7$ Hz, 1 H), 7.67–7.74 (m, 6 H), 7.00 (dd, $J = 11.7, 14.7$ Hz, 1 H); vis [λ_{max} nm (log ϵ)] 393 (5.40), 469 (5.68), 626 (5.05).

10-Bromo-5,15-diphenylporphyrin (15). To a solution of porphyrin **14** (545 mg, 1.18 mmol) and pyridine (1 mL) in CH₂Cl₂ (180 mL) was added slowly NBS (340 mg, 1.71 mmol). The mixture was stirred at room temperature for 4 h, and then acetone (20 mL) was added. After being stirred for a further 15 min, the mixture was rotary-evaporated, and the residue was subjected to chromatography with CH₂Cl₂/hexanes (3:7) as eluent. The first and third portion contained the *meso*-dibromoporphyrin and the starting material **14**, respectively, while the second band contained the desired product **15** (320 mg, 50%): $R_f = 0.23$; ^1H NMR (250 MHz) δ 10.17 (s, 1 H), 9.75 (d, $J = 5.0$ Hz, 2 H), 9.29 (d, $J = 4.5$ Hz, 2 H), 8.97 (d, $J = 4.8$ Hz, 2 H), 8.96 (d, $J = 4.8$ Hz, 2 H), 8.20–8.24 (m, 4 H), 7.78–7.82 (m, 6 H), –3.02 (s, 2 H); vis [λ_{max} nm (log ϵ)] 414 (5.46), 511 (4.12), 544 (3.57), 586 (3.60), 646 (3.22); HRMS (LSI) m/z calcd for $\text{C}_{32}\text{H}_{21}\text{BrN}_4$ (M^+) 542.0930, found 542.0969.

(10-Bromo-5,15-diphenylporphyrinato)nickel(II) (17). A mixture of **15** (320 mg, 0.59 mmol) and Ni(OAc)₂·4H₂O (440 mg, 1.77 mmol) in DMF (30 mL) was refluxed for 4 h. The resulting bright red mixture was cooled slowly to –20 °C, and the microcrystals formed were filtered. The filtrate was mixed with water (20 mL) to give a second crop of product (300 mg, 85%): $R_f = 0.80$ (CH₂Cl₂/hexanes 1:1); ^1H NMR (300 MHz) δ 9.76 (s, 1 H), 9.55 (d, $J = 4.8$ Hz, 2 H), 9.08 (d, $J = 4.8$ Hz, 2 H), 8.83 (d, $J = 4.8$ Hz, 2 H), 8.82 (d, $J = 5.1$ Hz, 2 H), 7.98–

8.02 (m, 4 H), 7.68–7.74 (m, 6 H); vis [λ_{\max} nm (log ϵ)] 408 (5.19), 523 (4.09); HRMS (LSI) m/z calcd for $C_{32}H_{19}^{81}BrN_4^{58}Ni$ (M^+) 598.0127, found 598.0161. Anal. Calcd for $C_{32}H_{19}BrN_4Ni$: C, 64.26; H, 3.20; N, 9.37. Found: C, 65.06; H, 3.19; N, 9.40.

(10-Iodo-5,15-diphenylporphyrinato)nickel(II) (18). According to the above procedure, treatment of **16** (100 mg, 0.16 mmol) with $Ni(OAc)_2 \cdot 4H_2O$ (110 mg, 0.43 mmol) afforded **18** (115 mg, 95%): $R_f = 0.94$ (toluene); 1H NMR (300 MHz) δ 9.75 (s, 1 H), 9.55 (d, $J = 5.1$ Hz, 2 H), 9.08 (d, $J = 4.8$ Hz, 2 H), 8.81 (d, $J = 4.8$ Hz, 2 H), 8.78 (d, $J = 5.1$ Hz, 2 H), 7.98–8.01 (m, 4 H), 7.69–7.74 (m, 6 H); vis (λ_{\max} nm) 407, 523; HRMS (LSI) m/z calcd for $C_{32}H_{19}IN_4^{58}Ni$ (M^+) 644.0010, found 644.0051.

[5-Bromo-15-(2'-formylethenyl)-10,20-diphenylporphyrinato]nickel(II) (19). $POCl_3$ (0.78 mL, 8.4 mmol) was added dropwise to a solution of (3-dimethylamino)acrolein (0.78 mL, 7.8 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The mixture was kept at this temperature for 30 min and then added to a red solution of **17** (156 mg, 0.26 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred at room temperature for 30 h to give a dark green solution. Saturated aqueous Na_2CO_3 (200 mL) was then added, and the mixture was stirred for a further 8 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×150 mL). The combined organic portions were washed with water (3×200 mL), dried over anhydrous Na_2SO_4 , and evaporated to dryness. The residue was chromatographed with toluene as eluent to give **19** as a green solid (83 mg, 49%): $R_f = 0.36$; 1H NMR (250 MHz) δ 9.96 (d, $J = 7.8$ Hz, 1 H), 9.38 (d, $J = 15.5$ Hz, 1 H), 9.31 (d, $J = 5.0$ Hz, 2 H), 9.08 (d, $J = 5.0$ Hz, 2 H), 8.64 (d, $J = 5.0$ Hz, 2 H), 8.57 (d, $J = 5.0$ Hz, 2 H), 7.82–7.87 (m, 4 H), 7.52–7.71 (m, 6 H), 6.48 (dd, $J = 7.8, 15.5$ Hz, 1 H); vis [λ_{\max} nm (log ϵ)] 432 (5.49), 552 (4.28), 595 (4.31); HRMS (LSI) m/z calcd for $C_{35}H_{21}^{81}BrN_4^{58}NiO$ (M^+) 652.0233, found 652.0214.

[5-(2'-Formylethenyl)-15-iodo-10,20-diphenylporphyrinato]nickel(II) (20). A mixture of **18** and (5,15-diiodo-10,20-diphenylporphyrinato)nickel(II) (5:1, 120 mg) in CH_2Cl_2 (50 mL) was treated with the Vilsmeier reagent prepared from (3-dimethylamino)acrolein (1.5 mL), $POCl_3$ (1.5 mL), and CH_2Cl_2 (6 mL). The mixture was stirred at room temperature overnight, and then a saturated aqueous $NaOAc$ (100 mL) was added. The mixture was stirred vigorously at 50 °C for 2 h, and then the organic portion was separated and washed with water. After being dried over anhydrous Na_2SO_4 , the solution was evaporated in vacuo and the residue was chromatographed with toluene as eluent. The first fraction contained a mixture of the starting iodoporphyrins, and the second fraction contained a small amount of unidentified side products. The last green fraction was collected and evaporated to afford the desired product (62 mg, 50%): $R_f = 0.36$; 1H NMR (300 MHz) δ 10.03 (d, $J = 7.7$ Hz, 1 H), 9.50 (d, $J = 15.6$ Hz, 1 H), 9.34 (d, $J = 5.0$ Hz, 2 H), 9.19 (d, $J = 5.0$ Hz, 2 H), 8.71 (d, $J = 5.0$ Hz, 2 H), 8.58 (d, $J = 5.0$ Hz, 2 H), 7.87–7.90 (m, 4 H), 7.64–7.72 (m, 6 H), 6.56 (dd, 1 H, $J = 7.7, 15.6$ Hz); $^{13}C\{^1H\}$ NMR (75.4 MHz) δ 192.0, 150.9, 144.2, 143.7, 141.5 (two overlapping signals), 139.5, 138.5, 134.4, 133.7, 133.5, 131.3, 128.1, 127.1, 120.4, 108.8; vis [λ_{\max} nm (log ϵ)] 436 (5.70), 556 (4.48), 602 (4.58). Anal. Calcd for $C_{35}H_{21}IN_4NiO$: C, 60.13; H, 3.03; N, 8.01. Found: C, 59.95; H, 2.99; N, 7.72.

[5-(2'-Formylethenyl)-15-[[4'-(*N,N*-dimethylamino)phenyl]ethynyl]-10,20-diphenylporphyrinato]nickel(II) (21). By employing the procedure described for **7**, compound **19** (40 mg, 60 μ mol) was treated with $Pd(PPh_3)_2Cl_2$ (4 mg, 6 μ mol), CuI (3 mg, 16 μ mol), [4-(*N,N*-dimethylamino)phenyl]ethyne (12 mg, 80 μ mol), and triethylamine (1 mL) in THF (8 mL) to give **21** as a dark green solid (35 mg, 80%): $R_f = 0.30$; 1H NMR (250 MHz) δ 9.97 (d, $J = 7.8$ Hz, 1 H), 9.44 (d, $J = 15.5$ Hz, 1 H), 9.40 (d, $J = 5.0$ Hz, 2 H), 9.09 (d, $J = 5.0$ Hz, 2 H), 8.62 (d, $J = 5.0$ Hz, 2 H), 8.56 (d, $J = 5.0$ Hz, 2 H), 7.85–7.88 (m, 4 H), 7.75 (d, $J = 8.7$ Hz, 2 H), 7.55–7.72 (m, 6 H), 6.80 (d, $J = 8.7$ Hz, 2 H), 6.56 (dd, 1 H, $J = 7.8, 15.5$ Hz); vis [λ_{\max} nm (log ϵ)] 448 (4.70), 635 (4.23); HRMS (LSI) m/z calcd for $C_{45}H_{31}N_5^{58}NiO$ (M^+) 715.1882, found 715.1818.

X-ray Diffraction Studies of 8 and 21. Purple single crystals of **8** and **21** were grown by slow evaporation from THF solutions. Crystal data are given in Table 3, together with refinement details. Data for both crystals were collected with

Table 3. Crystal Data and Structure Refinement for 8 and 21

	8	21
emp formula	$C_{43}H_{29}N_5NiO$	$C_{45}H_{31}N_5NiO$
formula wt	690.42	716.46
T (K)	293(2)	293(2)
wavelength (\AA)	0.710 73	0.710 73
cryst syst	monoclinic	orthorhombic
space grp	$C2/c$	$Pbca$
unit cell dimens (\AA , deg)		
a	26.44(2)	27.02(2)
b	10.242(11)	8.679(9)
c	24.43(2)	35.25(3)
β	100.966(10)	(90)
volume (\AA^3)	6496	2976
Z	8	8
density (calcd) ($Mg\ m^{-3}$)	1.412	1.151
absorptn coeff (mm^{-1})	0.642	0.507
$F(000)$	2864	2976
cryst size (mm)	$0.45 \times 0.10 \times 0.10$	$0.40 \times 0.20 \times 0.20$
θ range for data collection (deg)	2.35–25.07	2.72–26.11
index ranges	$0 \leq h \leq 31$ $-10 \leq k \leq 10$ $-28 \leq l \leq 28$	$-30 \leq h \leq 29$ $0 \leq k \leq 10$ $-42 \leq l \leq 43$
reflns collected	9938	17792
independent reflns [$R(int)$]	5280 (0.0430)	6639 (0.0817)
data/restraints/param	5280/0/442	6630/0/488
weighting scheme (a, b) ^a	0.254, 0.000	0.137, 20.002
final R indices [$I > 2\sigma(I)$]		
R_1	0.0832	0.0981
wR_2	0.2381	0.2537
R indices (all data)		
R_1	0.1386	0.1567
wR_2	0.2920	0.3288
largest diff. peak and hole ($e\ \text{\AA}^{-3}$)	1.655, -0.525	0.761, -0.343

^a Weighting scheme $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$, where $P = (F_o^2 + 2F_c^2)/3$.

MoK α radiation using the MARresearch Image Plate System. The crystals were positioned at 75 mm from the Image Plate. Ninety-five frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.³² Both structures were solved using direct methods with the Shelx86 program.³³ In both structures, the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Both structures were then refined using SHELXL.³⁴ All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.³⁵

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Supporting Information Available: X-ray crystallographic data for compounds **21** and **8** (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(35) The authors have deposited atomic coordinates for **8** and **21** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.