Pyrrole-Inverted Isomer of 5,10,15,20-Tetraaryl-21-Selenaporphyrin†

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A novel 5,10,15,20-tetraaryl-21-selenaporphyrin isomer with an inverted pyrrole ring, i.e., 5,10,15,20-tetraaryl-2-aza-21-carba-22-selenaporphyrin (*SeC*-TArPH) has been produced by a [3 + 1] condensation of 2,5-bis(phenylhydroxymethyl)selenophene and 5,10-ditolyltripyrrin. The reaction yielded 5,20-diphenyl-10,15-bis(*p*-tolyl)-21-selenaporphyrin *Se*-DPDTPH (19%) and its isomer with an inverted pyrrole ring, i.e., 5,10-diphenyl-15,20-bis(*p*-tolyl)-2-aza-21-carba-22-selenaporphyrin, *SeC*-DPDTPH (1%). Mechanistically the synthesis of *SeC*-DPDTPH requires one *β*-condensation at the pyrrole moiety of 5,10-ditolyltripyrrin instead of the stereotypical α-condensation. The identity of inverted selenaporphyrin has been confirmed by high-resolution mass spectrometry and ^{1}H NMR spectroscopy. A saddle distortion mode for the inverted selenaporphyrin macrocycle *SeC*-DPDTPH has been determined by X-ray crystallography. NMR spectra are consistent with the existence of tautomeric equilibria that involve three tautomeric species of the neutral form of *SeC*-DPDTPH. The preference for the tautomer with the labile proton located at the peripheral N(2) nitrogen atom has been detected in pyridine-d_5 solution. The density functional theory (DFT) has been applied to determine the molecular and electronic structure of three tautomers of 2-aza-21-carba-22-selenaporphyrin: {2-N, 23-N, 24-NH}, {2-N, 23-NH, 24-N}, and {2-NH, 23-N, 24-N} formally created from *SeC*-DPDTPH by a replacement of phenyl and tolyl groups with hydrogen. The total energies calculated using the B3LYP/6-311G//B3LYP/6-311G approach, demonstrate that relative stability of postulated tautomers decreases in the order {2-N, 23-NH, 24-N} > {2-N, 23-N, 24-NH} > {2-NH, 23-N, 24-N}. The small energy differences between tautomeric species suggests their simultaneous presence in equilibrium.

Introduction

The accessibility of 5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin (inverted porphyrin, N-confused porphyrin, *C*-TPPH$_2$) in the reaction of arylaldehyde with pyrrole gave rise to a revision of the view that tetraarylporphyrin is a sole macrocyclic product of the Rothemund-type synthesis.[1,2] Subsequently, apart from tetraphenylporphyrin and inverted tetraphenylporphyrin, two other aromatic macrocycles were identified among the products of the pyrrole−arylaldehyde condensation: tetraarylsapphyrin[3] and trisarylcorrole.[4−7] The synthesis of *C*-TPPH$_2$ has been recently optimized.[8,9] The peralkylated, *meso*-unsubstituted, inverted porphyrin has been synthesized in the course of the stepwise process.[10,11] An inversion of one pyrrole ring results in the creation of the porphyrin-like skeleton of 5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin, which locates an "exotic" carbon atom in the center of the macrocyle.[1,2,12−14] Formally the inverted porphyrin can be related to the class of core-modified tetraarylporphyrins created by the introduction of various heteroatoms (O, S, Se, Te) in place of the NH group.[5,15,16]

The emerging class of carbaporphyrinoid macrocycles with one pyrrole ring replaced by an all-carbon ring provides a novel route to modify porphyrin properties.[17−19] Eventually, the isomers of 21-oxaporphyrin and 21-thiaporphyrin with an inverted pyrrole ring in the position *trans* to the furan or thiophene rings combine

† Dedicated to Professor A. L. Balch on his 60th birthday.

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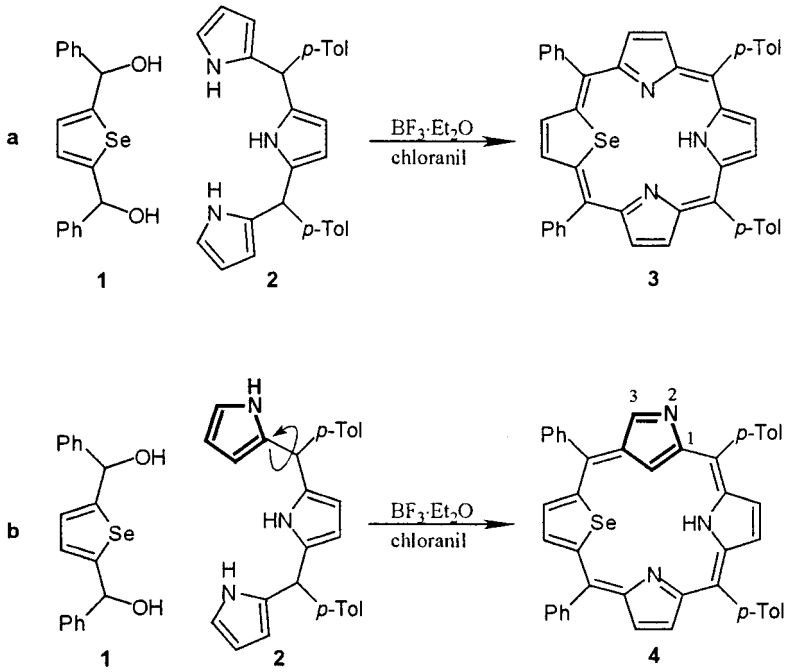
Scheme 1



features of standard heteroporphyrins and inverted porphyrins.[20−22] A new 5,10,15,20-tetraphenyl-21-thiaporphyrin isomer with an inverted thiophene ring, i.e., 5,10,15,20-tetraphenyl-21-carba-2-thiaporphyrin (*SC*-TPPH) has been lately synthesized as well.[23]

We have previously established that the routine procedures, i.e., condensation of pyrrole, arylaldehyde, and 2,5-bis(arylhydroxymethyl)furan or 2,5-bis(arylhydroxymethyl)-thiophene, gave 5,10,15,20-tetraaryl-26,28-dioxasapphyrin and 5,10,15,20-tetraaryl-26,28-dithiasapphyrin in addition to 5,10,15,20-tetraaryl-21-oxaporphyrin or 5,10,15,20-tetraaryl-21-thiaporphyrin, respectively.[24] Remarkably, the acid-catalyzed condensation of 16-oxatripyrrane, 16-thiatripyrrane, or 16-selenatripyrrane gave 18-π, 22-π, and 26-π macrocycles (*meso*-aryl diheteroporphyrins, diheterosaphyrins, and diheterorubyrins), respectively.[25,26] The formation of diheterosaphyrin and diheteroporphyrin requires fragmentation of tripyrranes followed by condensation of the formed moieties.[26] Recently it has been mentioned that in a condensation of 5-(*p*-tolyl)dipyrromethane and furylpyrromethanediol, 5,10,15-trisaryl-21-oxacorrole has been obtained in addition to expected 5,10,15,20-tetraaryl-21-oxaporphyrin.[27]

All these observations resulted in an anticipation that, in analogy to the inverted porphyrin formation, heteroporphyrins inverted on a pyrrole ring might be produced in the course of any typical synthesis used to produce heteroporphyrins or expanded heteroporphyrins. As a matter of fact the condensation of benzaldehyde with unsubstituted pyrrole at the β-position instead of the α seems to be quite common[1,2,8] and has been detected in the synthesis of 5-substitued dipyrromethanes.[8] Significantly, it has been demonstrated that the preference for the formation of the regular or inverted porphyrinogen depends strongly on the choice and concentration of the acidic catalysts.[8,27]

Here we report a route in heteroporphyrin synthesis that leads to an unpremeditated inversion of a pyrrole ring. Thus we describe the synthesis and the spectroscopic properties of a 5,10,15,20-tetraaryl-21-selenaporphyrin isomer which can be formally constructed by the exchange of a nitrogen atom and a β-methine carbon atom of the *cis*-pyrrole ring to create the porphyrin-like skeleton of 5,10,15,20-tetraaryl-2-aza-21-carba-22-selenaporphyrin.

Results and Discussion

Synthesis. In light of the currently renewed interest in application of the [3 + 1] strategy in the synthesis of porphyrins, expanded porphyrins, and heteroporphyrins,[20−22,25,26,28−33] we have decided to explore this route in the synthesis of 5,10,15,20-tetraaryl-21-selenaporphyrin. This macrocycle was previously obtained by one-pot condensation from 2,5-bis(phenylhydroxymethyl)-selenophene, *p*-tolylaldehyde, and pyrrole under typical Lindsey conditions.[34] The new procedure combines two

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fundamental building blocks, i.e., 2,5-bis(phenylhydroxymethyl)selenophene **1** and 5,10-bis(*p*-tolyl)tripyrrane **2**[25] in dichloromethane. The condensation was catalyzed by $BF_3 \cdot Et_2O$ and followed by oxidation with *p*-chloranil (Scheme 1a). The reaction gives 5,20-diphenyl-10,15-bis-(*p*-tolyl)-21-selenaporphyrin (*Se*-DPDTPH, **3**) with 19% yield, which is comparable to that found in a typical methodology,[34] although with a remarkably simplified purification procedure as the amount of tetraphenylporphyrin, the typical side product, was negligible.

Apart from the original target, 21-selenaporphyrin, we have detected a new aromatic macrocycle that was formed in ca. 1% yield (Scheme 1b). This compound has been identified as a 5,10-diphenyl-15,20-bis(*p*-tolyl)-21-selenaporphyrin isomer with an inverted pyrrole ring, i.e., 5,10-diphenyl-15,20-bis(*p*-tolyl)-2-aza-21-carba-22-selenaporphyrin (*SeC*-DPDTPH **4**). The identity of **4** has been confirmed by X-ray crystallography, high-resolution mass spectrometry, and ^{1}H NMR spectroscopy as described below. The replacement of **2** with 5,10-diphenyltripyrrane **2a** gave 5,10,15,20-tetraphenyl-21-selenaporphyrin (*Se*-TPPH **3a**) and its "inverted" isomer, i.e., 5,10,15,20-tetraphenyl-2-aza-21-carba-22-selenaporphyrin (*SeC*-TPPH **4a**).

Mechanistically the synthesis of *SeC*-DPDTPH requires one β-condensation instead of the ordinary α-condensation at the pyrrole moiety. In the course of our investigations we have realized that the stereotypically presented Scheme 1a describing the [3 + 1] strategy seems to unjustly favor only one from several possible orientations of the terminal pyrrole ring(s) of **2** or 16-heterotripyrranes.[20−22,25,26,28−33] In terms of the reaction mechanism it would strongly suggest the steric preference for the electrophilic attack of **1** or analogous 2,5-bis(phenylhydroxymethyl)heterocyclopentadienes at the α-pyrrole position as shown at Scheme 1a. For the mechanism of inverted selenaporphyrin formation we propose that two helical conformations of **2**, differing only by a 180° rotation of the terminal pyrrole ring around the α-carbon−*meso*-carbon bond, contribute in the selenaporphyrinogen or inverted selenaporphyrinogen ring closure (Scheme 1a and 1b). They provide two optimal orientations for the electrophilic attack, to afford regular or inverted selenaporphyrinogen and consequently after oxidation *Se*-DPDTPH **3** or inverted *SeC*-DPDTPH **4**.

This mechanism has been suggested by analogy to the formation of an inverted porphyrin where two helical conformation of tetrapyrromethane differing only by an orientation of the terminal pyrrole ring contributed to the porphyrinogen or inverted porphyrinogen formation.[1]

Crystal and Molecular Structures of *SeC*-DPDTPH. The structure has been studied by X-ray crystallography. The perspective views of the molecule are shown in Figure 1.

The structure of *SeC*-DPDTPH displays disorder in the location of the peripheral N(2) nitrogen atom and β-pyrrolic C(13)′ carbon located at the trans pyrrole ring. Simultaneously the structure suffers from disorder that involves the location of the internally located C(21) carbon atom and the N(23)′ pyrrole nitrogen in the trans position. Thus the N(2) and C(13) as well C(21) and N(23) atoms share common positions, respectively. The structure has been refined with fixed 50% occupancy for each

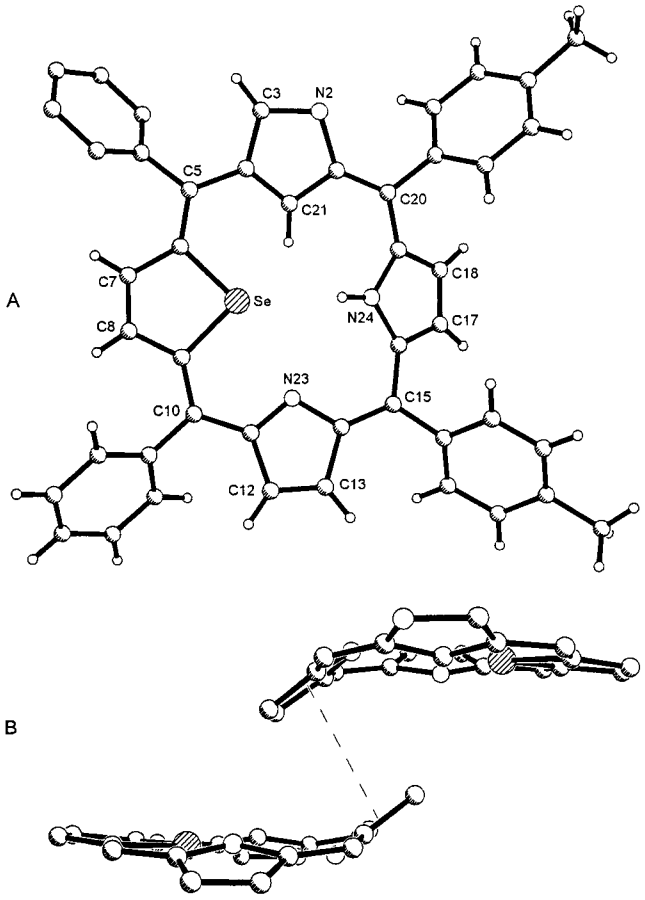

Figure 1. The crystal structure of *SeC*-DPDTPH: (A) perspective view and (B) side view of a pair of molecules, positioned about the center of symmetry; aryl groups omitted for clarity. The vibrational elipsoids represent 50% probability. One of the two equally possible molecular orientations with respect to the N(2)−C(13), C(21)−N(23) permutations has been shown.

disordered pair of atoms. Two alternative positions of the 5-phenyl have been observed, which are differentiated by the orientation with respect to the mean porphyrin plane as given by 44.5° and 70.5° dihedral angles, respectively, with the relative occupation equal to 46% and 54%. The crystal also contains the disordered molecule of toluene. The deviation of the pyrrole planes from the plane defined by dihedral angles between the pyrrole, selenophene, and inverted pyrrole and C(5)C(10)C(15)C-(20) planes are as follows: C(21){N(23)} −16°, Se(22) 6°, N(24) 35°. This can be described as a saddle distortion mode for the inverted selenaporphyrin macrocycle. The determined disorders in the positions of the inverted and regular pyrrole rings do not allow for the detailed structural analysis of *SeC*-DPDTPH. However we have found that an extensive delocalization exists through the *SeC*-DPDTPH macrocycle and extends on the selenophene fragment. There is an appreciable effect of the aromatic character of the macrocycle on the selenophene portion. The Se−C_α distance is practically unchanged in inverted selenaporphyrin (1.893(8) Å) and selenaporphyrin (1.850(7) Å)[34] relative to free selenophene (1.855(1) Å.)[35] The C_α−C_β (1.451(12) Å) and C_β−C_β (1.346(11) Å)

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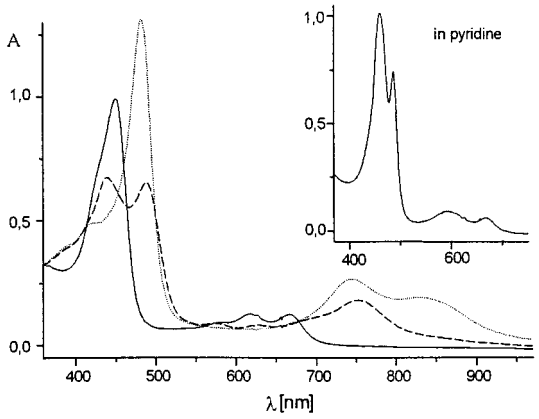


Figure 2. The electronic spectra of *SeC*-DPDTPH (solid line), *SeC*-DPDTPH$_2^+$ (dashed line), and *SeC*-DPDTPH$_3^{2+}$ (dotted line) in dichloromethane. The inset presents the spectrum of *SeC*-DPDTPH in pyridine.

distances of *SeC*-DPDTPH are similar as in regular 21-selenaporphyrin ($C_\alpha-C_\beta$ 1.420(10) Å and $C_\beta-C_\beta$ 1.384-(10) Å) but distinctly different than in free selenophene ($C_\alpha-C_\beta$ 1.369(1) Å and $C_\beta-C_\beta$ 1.433(3) Å).[35] These selenophene bond length changes indicate that the π-delocalization of the selenophene moiety is altered in inverted selenaporphyrin in a similar manner as determined previously for 21-selenaporphyrin.[34]

In the solid pairs of *SeC*-DPDTPH are positioned about centers of symmetry so there is face to face $\pi-\pi$ contact (Figure 1B). The two molecules do not fully overlay one another, but they are offset. The marked overlap within the pair has been only observed between pyrrole rings containing N(24) nitrogen atoms. Within this fragment the mean N(24) pyrrole plane separation is 3.3 Å and the N(24)−N(24)′ distance equals 4.4 Å.

Spectroscopic Characterization. Inverted selenaporphyrin demonstrates spectroscopic properties typical for core-modified porphyrins and carbaporphyrinoids. The UV−vis spectrum of *SeC*-DPDTPH **4** is porphyrin-like, with the strong Soret band, which is bathochromically shifted (∼20 nm) when compared to regular 21-selenaporphyrin **3**.[34] *SeC*-DPDTPH acts as a base. Titration of a dichloromethane solution of *SeC*-DPDTPH with TFA has been followed by UV−vis electronic spectroscopy (Figure 2). The isosbestic points between the neutral and the monocationic form, and between mono- and dicationic forms, have been detected. The acid titration is accompanied by the distinct color change from bright green to brown.

The representative ^{1}H NMR spectral patterns of *SeC*-DPDTPH are shown in Figure 3. As a matter of fact the neutral form of **4** produces well resolved NMR spectra but only under certain well-defined, deliberately chosen conditions. The visibility of diagnostic features depends strongly on a choice of solvent and temperature. In chloroform-*d* or in benzene-d_6 the severe broadening of all resonances has been observed (Figure 3, trace A). The analogous spectrum in dichloromethane-d_2 demonstrated slightly better resolved multiplets with the broad 2-NH resonance at ca. 9.61 ppm and one for 21-CH at 2.45 ppm (295 K). The gradual addition of pyridine-d_5 to chloroform-*d* or dichloromethane-d_2 solutions of **4** produced the remarkable modifications of the line widths of all resonances to yield finally the well resolved spectrum presented at trace B of Figure 3 (dichloromethane-d_2/pyridine-d_5, 1:1 v/v, 245 K). The spectrum of similar quality has been collected when neat pyridine-d_5 has been used as a solvent. The broadening of all resonances detected for the neutral form of *SeC*-DPDTPH in chloroform-*d* has been accounted by an equilibrium between three tautomers of *SeC*-DPDTPH, ({2-N, 23-N, 24-NH} **4′**, {2-N, 23-NH, 24-N} **4″**, and {2-NH, 23-N, 24-N} **4‴**), differentiated by the position of the labile NH proton (Scheme 2).

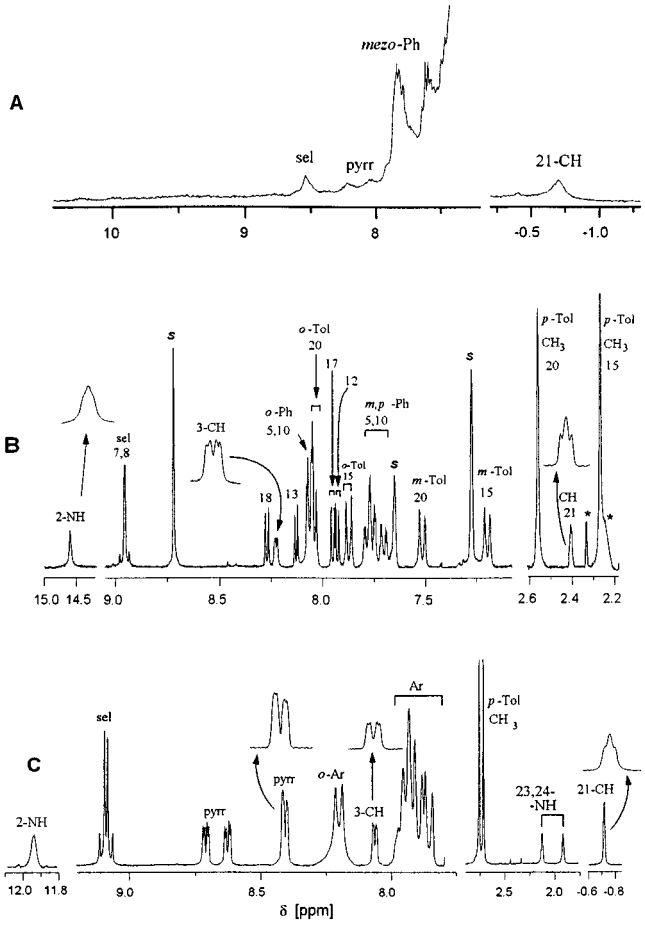
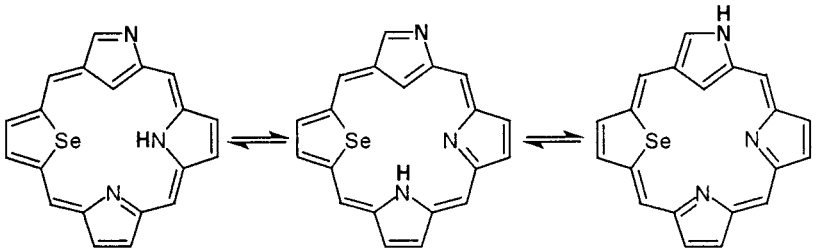


Figure 3. ^{1}H NMR spectra (selected downfield and upfield regions presented): (A) *SeC*-DPDTPH (chloroform-*d*, 293 K), (B) *SeC*-DPDTPH (dichloromethane-d_2/pyridine-d_5, 1:1 v/v, 245 K, *s* solvent) and (C) *SeC*-DPDTPH$_3^{2+}$ (TFA/dichloromethane-d_2, 5:95 v/v, 260 K). Peak labels follow systematic position numbering of the porphyrin ring or denote proton groups: *o*, *m*, *p* are ortho, meta, and para positions of *meso*-phenyl (Ph) or *meso*-*p*-tolyl (Tol) rings, respectively.

The tautomer **4‴** with the NH proton localized on the outer nitrogen has been exclusively formed in the presence of pyridine-d_5. In chloroform-*d* the tautomeric equilibrium is shifted toward **4′** and **4″**. Contribution of these two tautomers in the equilibrium results in the marked upfield relocation of the 21-CH resonance relative to **4‴** (Figure 3, trace A).

The tautomeric equilibrium of *SeC*-DPDTPH resembles those determined for 2-aza-21-carbaporphyrin (*C*-TPPH$_2$)[1,10] and 5,20-diphenyl-10,15-dimesityl-2-aza-21-carba-23-thiaporphyrin (*SC*-DMDPPH).[22] In the fundamental structure of the inverted porphyrin two labile NH protons are located on their inner pyrrole nitrogens.[1,2,10] However the alternative tautomer with one inner and one outer NH protons, 2-NH-*C*-TPPH, prevails in more polar solvents, including pyridine-d_5.[36] This tautomer

Scheme 2



4' **4''** **4'''**

preserves strongly the pyrrolic nature of the inverted ring. Two tautomeric forms of *SC*-DMDPPH were detected in chloroform-*d* (296 K), where the most stable one has the labile proton located at the peripheral nitrogen, and its third tautomer was detected at 223 K.[22]

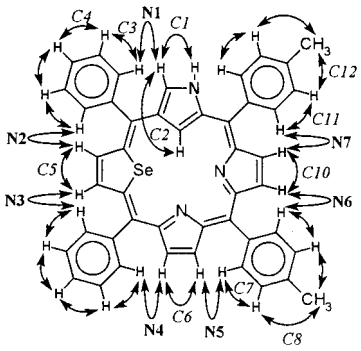
Consequently, the specific resonance assignment has been carried out for the tautomeric form **4'''** (Figure 3, trace B) as this is the species that presents the well resolved ^{1}H NMR spectrum in the presence of pyridine-d_5. In the 7−14 ppm region the ^{1}H NMR spectrum of **4'''** exhibits two AB patterns of the regular pyrroles and one more assigned to the selenophene fragment. The inverted pyrrole ring contributes one proton signal of 3-H at 8.29 ppm (doublet of doublets in dichloromethane-d_2/pyridine-d_5). The proton located on the outer pyrrole nitrogen (2-NH) gave a broad singlet located at 14.61 ppm. The 2-NH proton can be selectively exchanged by deuterium after addition of D_2O. All other resonances including the upfield located 21-CH resonance remained unchanged in the course of this experiment. The important confirmation of the inverted structure is provided by the upfield position of the unique 21-CH proton at 2.82 ppm (pyridine-d_5). The 3-H and 21-H resonances are split into doublets as a result of mutual scalar coupling ($^4J_{3,21}$ = 1.3 Hz, pyridine-d_5). Once the solvent has been changed to dichloromethane-d_2/pyridine-d_5 mixture and the temperature lowered to 245 K, the additional splitting due to 2-NH proton has been revealed producing the doublet of doublets ($^3J_{2,3}$ = 3.6 Hz, $^4J_{3,21}$ = 1.3 Hz) for the 3-H proton and the triplet-like multiplet for 21-CH one ($^4J_{3,21}$ = 1.3 Hz, $^4J_{2,21} \approx$ 1 Hz. The complete assignment of all resonances shown in trace B of Figure 3 has been obtained by means of 2D ^{1}H NMR COSY and NOESY experiments.

Here, as a starting point for making requisite assignments the unique 3-H resonance has been used. The connectivity pattern determined from these COSY (*C*) and NOESY (**N**) analyses is shown in Scheme 3 with specific assignments given in Figure 3.

Three isomers of 21-selenaporphyrin with inverted pyrrole ring are feasible, as shown in Scheme 4. The mechanistic route, discussed previously (Scheme 1b) suggested the isomer **a** as an "inverted" reaction product. However, in the worst case scenario, which includes the fragmentation in the course of the acid-catalyzed condensation of tripyrranes,[26] two other isomers **b** and **c** should be considered as well. As the consequence of the substantial disorder the X-ray crystallography could not distinguish between these three isomers. Moreover, the NMR analysis provides the definitive confirmation of the structure. The spatial proximity between the 3-H and

(36) Furuta, H. Private communication, see ref 15, p 402.

Scheme 3

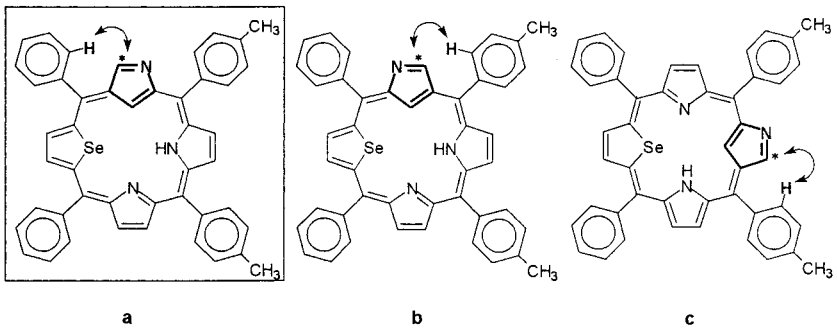


ortho phenyl protons is expected in isomer **a**. Contrary, in the case of isomers **b** and **c** the spatial contact between 3-H and ortho protons of the *p*-tolyl fragment is only accessible. The observed NOE connectivity between the 3-H and ortho protons of the 5-phenyl ring is of particular importance as it requires the 3-H−5-phenyl spatial contact. The relevant nuclear Overhauser effect is reflected by the correlation cross-peak in the NOESY map. Thus this correlation serves as a structural marker of the **a** structure. We would like to point out that such an analysis leading to the isomer identification has been possible for *SeC*-DPDTPH **4** but not for 5,10,15,20-tetraphenyl-2-aza-21-carba-22-selenaporphyrin (*SeC*-TPPH **4a**). The relatively minor structural change, namely, a replacement of two *meso*-phenyls by two *p*-tolyls, simplified the spectrum, allowing the detailed analysis.

The molecule *SeC*-DPDTPH essentially preserves aromaticity of its parental isomer *Se*-DPDTPH. All outer pyrrole (7.92−8.27 ppm, pyr-d_5, 298 K), *meso*-phenyl and *meso*-(*p*-tolyl), and selenophene (8.90 ppm) resonances are downfield shifted as a result of the ring current effect, although the effect is markedly (ca 1 ppm) smaller than for *Se*-DPDTPH.[34] The unique inner 21-CH resonance of the inverted pyrrole ring is located at 2.82 ppm. The diagnostic shift difference of ca. 5.5 ppm between the outer and inner pyrrole resonances reflects their location in the deshielding (3-H) and shielding (21-H) zones of the macrocycle diatropic ring current. Altogether the downfield shifts of the regular pyrrole resonances and the upfield shifts of 21-CH are less pronounced than the corresponding values found for 5,10,15,20-tetra-(*p*-tolyl)-2-aza-21-carbaporphyrin *C*-TTPH$_2$[1] or 5,20-diphenyl-2-aza-21-carba-23-oxaporphyrin.[20] Similar π-delocalization at the inverted pyrrole moiety was reported in the doubly N-confused porphyrin.[37]

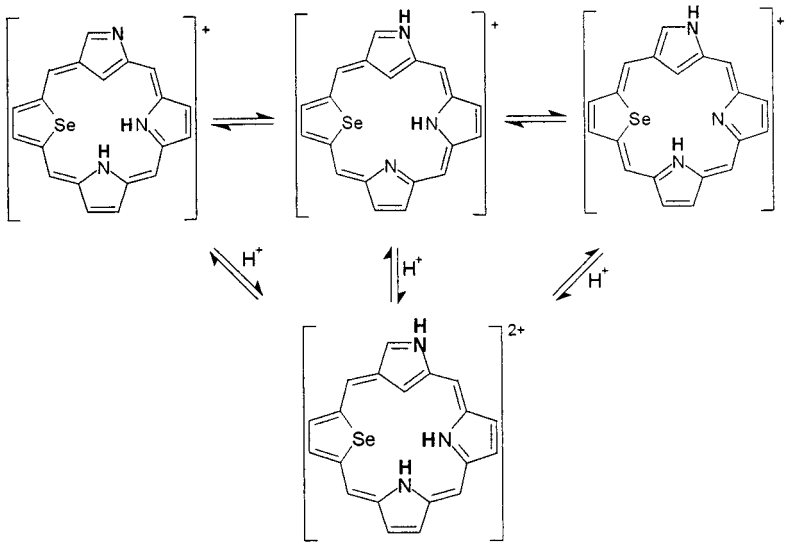
(37) Furuta, H.; Maeda, H.; Osuka, A. *J. Am. Chem. Soc.* **2000**, *122*, 803.

Scheme 4



a **b** **c**

Scheme 5



One can consider the ^{1}H NMR shifts of the internally located 21-CH proton and the peripheral pyrrole (selenophene) resonances as a convenient spectroscopic criterion of the macrocycle aromaticity. The following carbaporphyrinoids presented a relatively small degree of aromaticity: 2*N*-methyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin (21-CH, 0.984 ppm; pyrrole, 7.48−7.96 ppm),[12] 2*N*-methyl-5,10,15,20-tetraphenyl-21-methyl-2-aza-21-carbaporphyrin (pyrrole, 7.910−7.270 ppm),[13] azuliporphyrin (internal CH, 1.5 ppm)[38] and 5,10,15,20-tetraphenyl-2-thia-21-carbaporphyrin (21-CH, 5.18 ppm, pyrrole 8.25−7.20 ppm).[23] In the limiting case of benziporphyrin[17] the strong aromatic structure of benzene completely blocks the π delocalization pathway of the entire macrocycle (internal CH, 7.88 ppm). Thus, the *SeC*-DPDTPH molecule reveals some similarity, as far as the ring current effect is concerned, to 2*N*-methyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin (2-NCH$_3$*C*-TPPH), pointing out the similar π-delocalization pathway particularly at the inverted pyrrole moiety.

Two discrete stages of protonation of **4** in dichloromethane have been demonstrated by UV−vis electronic spectroscopy. However the parallel ^{1}H NMR spectroscopic titration carried out for *SeC*-DPDTPH in dichloromethane-d_2 at 293 K presented a rather complex picture. The broadening of all resonances seen in the NMR spectrum of the neutral form is preserved in the primary protonation stage, suggesting the equilibrium between three tautomeric monocationic species (Scheme 5).

A single dicationic species is formed when an excess of acid is added. The well-resolved spectrum presents the following diagnostic resonances: 8.07 (3-H); −0.72 (21-H); 11.94 (2-NH); 2.13, 1.92 (23,24-NH) (dichloromethane-d_2−TFA, 260 K) (Figure 3, trace C). The 2-NH, 23,24-NH protons can be readily exchanged for deuterons once TFA-*d* has been used for titration, leaving only 21-CH resonance in the upfield region. In the 7−14 ppm region the ^{1}H NMR spectrum of *SeC*-DPDTPD$_3^{2+}$ exhibits two AB patterns of two regular pyrroles and one more assigned to the selenophene fragment. The 3-H and 21-H resonances are split into doublets as a result of mutual scalar coupling. In the case of *SeC*-DPDTPH$_3^{2+}$ the additional splitting by the 2-NH proton has been revealed, producing the doublet of doublets ($^3J_{2,3} = 3.6$ Hz, $^4J_{3,21} = 1.3$ Hz) for the 3-H proton and the triplet-like multiplet for the 21-CH one ($^4J_{2,21} = 1.3$ Hz, $^4J_{3,21} \approx 1$ Hz). Simultaneously the doublet structure has been observed for all pyrrole resonances as a result of four-bond scalar coupling with internal NH protons.

The upfield increase of 21-CH chemical shift has been determined in the dicationic species in comparison with the neutral form observed in pyridine-d_5 or dichloromethane-d_2/pyridine-d_5 solutions. Such a behavior seems to be typical for inverted porphyrins or inverted heteroporphyrins, provided that the peripheral nitrogen atom is protonated or methylated in the neutral form.[12,13,22]

The macrocycle **4** has an unusual SeCNN coordination core combining the features of inverted porphyrin[1] and 21-selenaporphyrin.[34] 21-Selenaporphyrin provided an environment to coordinate the nickel(II) or nickel(I) ions

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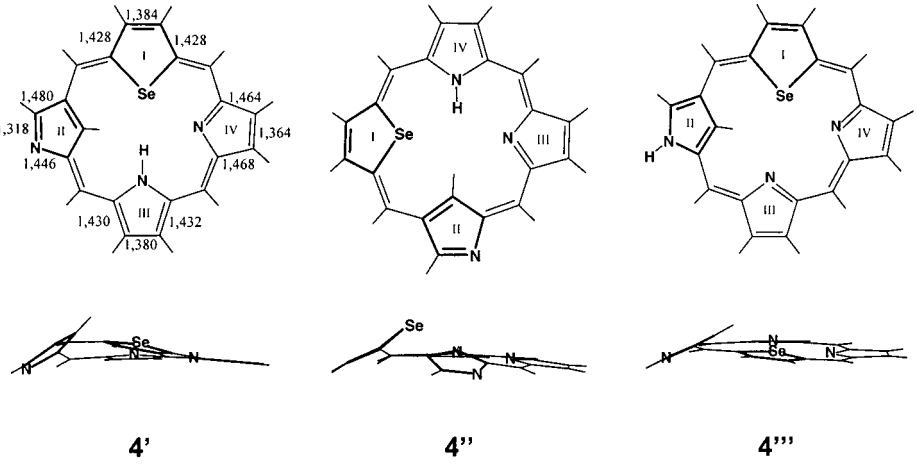

Figure 4. DFT optimized structures of *SeC*-DPDTPH tautomers. Selected bond lengths are in angstroms. Projections emphasize the folding of the macrocycle.

to the selenophene fragment.[34,39] Coordination properties of its inverted isomer are currently under considerations.

DFT Calculations. 5,10,15,20-Tetraaryl-2-aza-21-carba-22-selenaporphyrin contains only one exchangeable proton and the tautomeric process involves its three accessible nitrogen positions (Scheme 2). Consequently the experimentally observed tautomeric equilibria for neutral form of 5,10,15,20-tetraaryl-2-aza-21-carba-22-selenaporphyrin have raised the question of the relative stability of the invoked tautomers of **4**. To approach this problem we have applied the density functional theory (DFT) in the similar way as previously described for inverted porphyrins, sapphyrin, and diheterosapphyrins.[40−42] The density functional theory methods and the high level of ab initio calculations have been recently applied to porphyrins, porphyrin isomers, metalloporphyrins, and related systems.[40−45] The theoretical investigations addressed problems of geometry, NH tautomerization, electronic spectra, and substituent effect on the electronic structure.

For simplification all calculations have been carried out for tautomers of 2-aza-21-carba-22-selenaporphyrin *SeC*-PH. Therefore the corresponding phenyl and tolyl groups of 5,10,15,20-tetraaryl-2-aza-21-carba-22-selenaporphyrin presented in Scheme 3 have been replaced by hydrogen. The density functional theory calculations have been carried out using geometry determined by X-ray crystallography as a starting point of the DFT optimization procedure. The optimized structural parameters and the calculated relative energies are presented in Figure 4 and Tables 1 and 2. The respective structures of three tautomers are presented in two views using the very similar perspective for each tautomer. The second view was deliberately chosen to demonstrate any deviation of the macrocycle from planarity. Similarly to the X-

Table 1. Calculated Relative Energies[a]

tautomer	B3LYP/6-311G//B3LYP/6-311G
4′	0
4″	6.98
4‴	12.70

[a] Energies in kilocalories per mole.

Table 2. Dihedral Angles (deg) between the C(5)C(10)C(15)C(20) and the Five-Membered Ring Planes

	ring			
tautomer	I (Se(22))	II (C(21))	III (N(24))	IV (N(23))
4′	8.3	31.0	3.2	4.0
4″	33.3	18.6	4.7	5.1
4‴	3.7	27.6	4.3	3.6

crystallographic data for *SeC*-DPDTPH the deviation of *SeC*-PH from planarity has been described by the corresponding dihedral angles between the C(5)C(10)C(15)C(20) and the five-membered ring planes as demonstrated in Table 2. It is apparent that the DFT optimized skeleton of the discussed macrocycle is distorted from planarity for each tautomer. This is not unexpected considering the steric crowding in the selenacarbaporphyrin cavity. The selenium atom interacts with the 21-CH proton in the *cis* position in any tautomer considered. In addition the internal NH is located in the position *trans* to selenium but *cis* to 21-CH (**4′**) or in the position *cis* to selenium and *trans* to 21-CH (**4″**). For the obvious reason such an interaction is absent in **4‴**.

Considering the X-ray crystallography the largest deviation form the reference plane could be expected for the pyrrole ring in the position *trans* to the selenophene moiety. The analysis of the respective data clearly demonstrates that the DFT calculation has not reproduced this structural feature. Therefore, the real preference of geometry in solution may be finally determined by other factors not directly included into DFT optimization. For instance this structural difference can be related to the marked overlap within the pair of *SeC*-DPDTPH molecules detected in the crystal structure, which solely involves pyrrole rings containing N(24) nitrogen atoms. The presence of the bulky aromatic *meso*-substituents in *SeC*-DPDTPH but not in *SeC*-PH can be of importance. In this case the established influence of the methyl substitution on geometry of sapphyrin is particularly informative.[42] Analogously, it was recently demonstrated that softness of the ruffling deformation of regular

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porphyrins limits possibility to accurately reproduce a solid-state structure by molecular calculation.[45]

General comparison of bond distances within the pyrrole and inverted pyrrole portions demonstrates that extensive delocalization exists through the macrocycle and extends to the inverted pyrrole fragment. Bond distances of the regular pyrroles $C_\alpha-C_\beta > C_\alpha-C_{meso} > C_\alpha-N > C_\beta-C_\beta$ reproduce the pattern of the regular porphyrin macrocycle PH_2.[39] The largest differences between the bond lengths in tautomers **4**, **4′**, and **4″** are in the range of few hundreds of an angstrom. Therefore the inversion of the pyrrole ring and its essential modification play a rather moderate role in determination of the electronic and molecular structure of the complementary part of the macrocycle. There is an appreciable effect of the aromatic character of the macrocycle on the selenophene moiety. Here the $C_\alpha-C_\beta$ distances are longer and the $C_\beta-C_\beta$ distances are shorter than in free selenophene. The pattern of $C_\alpha-C_\beta$ and $C_\beta-C_\beta$ distances follows that seen in the pyrrole rings. Altogether, these modifications suggest that the π electron density has been altered within the selenophene fragment so that it is increased in the $C_\beta-C_\beta$ bond, decreased in the $C_\alpha-C_\beta$ bond, and unchanged in the $C_\alpha-Se$ bonds. Thus these bond changes indicate that the π delocalization through the selenophene ring is altered in selenacarbaporphyrin as it has been already detected in the crystal structure. The bond length patterns of the inverted pyrrole ring as determined for **4′**, **4″**, and **4‴** suggest two alternative π-delocalization pathways. The C(1)−N(2) and N(2)−C(3) bond lengths of **4′** and **4″** approach limits of isolated single and double carbon−nitrogen bond but acquire more aromatic character for the tautomer **4‴**. The optimized bond lengths of the inverted pyrrole ring of **4‴** resemble those found for 2-NH-*C*-PH.[39] The similarity in the structure of the inverted pyrrole has been found for **4′**, **4″**, and *C*-PH_2.[39] Thus the bond distances of the inverted pyrrole ring are controlled by protonation of the N(2) atom.

The calculated total energies, using the B3LYP/6-311G//B3LYP/6-311G approach, demonstrate that relative stability of postulated tautomers increases in the order **4‴** < **4″** < **4′**. At present the appropriate experimentally determined thermodynamic values to compare quantitatively the calculated relative stability of tautomers are not accessible. The small energy difference between **4′**, **4″,** and **4‴** species accounts for their simultaneous presence in equilibrium. The ^{1}H NMR evidence supports the existence of three tautomers of selenacarbaporphyrin. Their relative population and energy can be efficiently modified for instance by formation of an external hydrogen bond with the solvent molecule, e.g., pyridine-d_5 as the calculated energy differences are in the range of values expected for a single hydrogen bond.

Experimental Section

Preparation of precursors. 2,5-Bis(phenylhydroxymethyl)selenophene **1**[29,46] and 2,5-bis(4-tolyl-2′-pyrrolilmethyl)pyrrole **2**[25] were synthesized according to known procedures.

Synthesis of *SeC*-DPDTPH 4. 2,5-Bis(phenylhydroxymethyl)selenophene (250 mg, 0.73 mmol) and 2,5-bis(4-tolyl-2′-pyrrolilmethyl)pyrrole (crude, 1 g, ca. 2 mmol) were added to freshly distilled dichloromethane (500 mL). The solution was deoxygenated by bubbling N_2 for 20 min, and $BF_3{\cdot}Et_2O$ (1 mL) was added. After 40 min of stirring in dark, *p*-chloranil (0.55 g, 2,5 mmol) was added to the reaction mixture and the solution was refluxed (1 h). Then the solvent was evaporated under reduced pressure. The dry residue was dissolved in chloroform and chromatographed on basic alumina column. The first red fraction containing 5,20-diphenyl-10,15-bis(4-tolyl)-21-selenaporphyrin and $TPPH_2$ was removed, and the next fractions eluted with $CHCl_3$ or MeOH/$CHCl_3$ (5/95 v/v) were subject to further chromatography on basic alumina. Fractions eluted with dichloromethane with increasing concentration of chloroform were monitored by UV−vis and *SeC*-DPDTPH was eluted with chloroform as a bright green solution. Yield 1%.

***SeC*-DPDTPH 4.** UV−vis (λ_{max}[nm] (log ϵ)): 451 (4.73), 541 (3.93), 578 (3.95), 618 (4.00), 666 (3.98). ^{1}H NMR (300 MHz, 298 K, py-d_5): δ 14,33 (bs, 2-NH, inv. pyrr.); 8.93, 8.91 (AB, $^3J_{AB}$ = 6.1 Hz, 7,8-H, sel.); 8.29 (d, ^4J = 1.3 Hz, 3-H, inv. pyrr.); 8.25 (d, ^3J = 4.5 Hz; 18-H, pyrr.); 8.12 (d, ^3J = 4.3, 13-H, pyrr.); 8.04 (m, 5,10-*o*-Ph); 7.98 (d, ^3J = 7.9 Hz, 20-*o*-Tol); 7.94 (d, ^3J = 4.6 Hz, 17-H, pyrr.); 7.92 (d, ^3J = 4.5 Hz, 12-H, pyrr.); 7.83 (d, ^3J = 7.9 Hz, 15-*o*-Tol); 7.73−7.68 (m, 5,10-*m*-Ph); 7.64−7.61 (m, 5,10-*p*-Ph); 7.39 (d, ^3J = 7.9 Hz, 20-*m*-Tol); 7.13 (d, ^3J = 7.9 Hz, 15-*m*-Tol); 2.82 (d, ^4J = 1,3 Hz, 21-CH, inv. pyrr.); 2.42 (s, CH_3, 20-*p*-Tol); 2.19 (s, CH_3, 15-*p*-Tol). ^{1}H NMR (300 MHz, 245 K, CD_2Cl_2/py-d_5, 1:1): δ 14,61 (bs, 2-NH, inv. pyrr.); 8.97, 8.94 (AB, $^3J_{AB}$ = 6.3 Hz, 7,8-H, sel.); 8.27 (d, ^3J = 4.5 Hz; 18-H, pyrr.); 8.23 (dd, ^3J = 3.6 Hz, ^4J = 1.25 Hz, 3-H, inv. pyrr); 8.13 (d, ^3J = 4.5, 13-H, pyrr.); 8.07 (m, 5,10-*o*-Ph); 8.04 (d, 20-*o*-Tol); 7.95 (d, ^3J = 4.5 Hz, 17-H, pyrr.); 7.93 (d, ^3J = 4.5 Hz, 12-H, pyrr.); 7.87 (d, ^3J = 7.95 Hz, 15-*o*-Tol); 7.80−7.75 (m, 5,10-*m*-Ph); 7.72−7.69 (m, 5,10-*p*-Ph); 7.52 (d, ^3J = 7.8 Hz, 20-*m*-Tol); 7.20 (d, ^3J = 7.8 Hz, 15-*m*-Tol); 2.56 (s, CH_3, 20-*p*-Tol); 2.41 (21-CH, inv. pyrr.); 2.27 (s, CH_3, 15-*p*-Tol). *SeC*-$DPDTPH_3^{2+}$ ^{1}H NMR (300 MHz, 260 K, CD_2Cl_2, 5% TFA): δ 11.94 (s, 2-NH, inv. pyrr.); 9.10, 9.07 (AB, $^3J_{AB}$ = 5.9 Hz, 7,8-H, sel.); 8.71, 8.63 (2dd, ^3J = 4.8 Hz, ^4J = 1.8 Hz; 2 pyrr.); 8.41 (d, ^3J = 4.8 Hz, 2 pyrr.); 8.07 (d, ^3J = 4.0, 3-H, pyrr.); 8.20 (d, Ar); 7.96−7.84 (m, Ar); 2.76, 2.71 (2s, CH_3, *p*-Tol); 2.13, 1.92 (2s, 23,24-NH); −0.72 (21-CH, inv. pyrr.). HRMS (EI, 70 eV): *m*/*z* 707.17798 (found for M^+); *m*/z_{calcd} 707.18397 for $C_{46}N_3H_{33}{}^{80}Se$.

Preparation of Samples. Dichloromethane-d_2 and chloroform-*d* for NMR samples were passed through basic alumina column before use. TFA used in high concentration (5%) in NMR samples was prepared from stoichiometric amounts of $(CF_3CO)_2O$ and D_2O.

Calculation Method. The calculations were carried out with the GAUSSIAN94 program.[47] All structures were optimized within unconstrained C_1 symmetry of the system using the density functional theory (DFT) with Becke's three-parameter exchange functionals and the gradient-corrected functionals of Lee, Yang, and Parr (DFT(B3LYP)).[48−51] The final estimations of the total energies were performed at the B3LYP level with the 6-311G basis set using the B3LYP/6-311G fully optimized structures.

X-ray Data Collection and Refinement. Crystals of *SeC*-DPDTPH were prepared by diffusion of cyclohexane into the toluene solution contained in a thin tube. Data were collected at 100 K on a Kuma KM-4 diffractometer. The stability of intensities was monitored by the measurement of three standards every 100 reflections. The data were corrected for Lorentz and polarization effects. No absorption correction was applied.

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The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares method using SHELX-97 with anisotropic thermal parameters for some of the non-H atoms. Scattering factors were those incorporated in SHELXS-97.

The disorder of the two pyrroles adjacent to selenophene was treated by fixing in the positions of N(2), C(13)-H, C(21)-H, and N(23) equally occupied carbon (50%) and nitrogen (50%) atoms. The isotropic thermal parameters of every C/N pair in each position were fixed to be equal. A molecule of toluene in the lattice exhibits a disorder.

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Supporting Information Available: Tables of crystal data, bond lenths and angles, atomic coordinates, anisotropic thermal parameters (1 figure and 6 tables), and computational results (Cartesian coordinates and computed total energies, 3 tables) are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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