

How big is big? Separation by conventional methods, X-ray and electronic structures of positional isomers of bis-*tert*butylisocyano adduct of 2(3),9(10),16(17),23(24)-tetrachloro-3(2),10(9),17(16),24(23)-tetra(2,6-di-*iso*-propylphenoxy)phthalocyaninato iron(II) complex

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Dedicated to Professor Kevin M. Smith on the occasion of his 70th birthday

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ABSTRACT: A presence of bulky 2,6-di-*iso*-propylphenoxy groups in bis-*tert*-butylisocyano adduct of 2(3),9(10),16(17),23(24)-tetrachloro-3(2),10(9),17(16),24(23)-tetra(2,6-di-*iso*-propylphenoxy)-phthalocyaninato iron(II) complex allows separation of two individual positional isomers and a mixture of the remaining two isomers using conventional chromatography. X-ray structures of " D_{2h} " and " C_{4h} " isomers were confimed by X-ray crystallography. Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations of each individual positional isomer allowed insight into their electronic structures and vertical excitation energies, which were correlated with the experimental UV-vis and MCD spectra.

KEYWORDS: iron phthalocyanine, positional isomers, X-ray crystallography, UV-vis, MCD, density functional theory, time-dependent density functional theory.

INTRODUCTION

Phthalocyanines are a well-known class of organic compounds which is widely used as dyes and pigments [1] as well as high tech applications such as optical recording [2], optical limiting [3], catalysis [4], photodynamic therapy of cancer [5], liquid crystalline materials [6], materials for light harvesting [7], and bio imaging [8]. Because of the low solubility of standard unsubstituted phthalocyanine complexes, there is a continuous effort to improve synthetic strategies for the preparation of substituted phthalocyanines. Indeed, peripheral substitutions as well as axial coordination through the central metal allows not only to tune the solubilities of phthalocyanine molecules but also adjusts their photophysical, redox, and aggregation properties [9]. Because of the well-known application of iron phthalocyanines in catalysis [10], a lot of attention was focused on the preparation of well soluble iron phthalocyanines with relatively high first oxidation potentials. In order to increase the solubility of the iron phthalocyanine in common organic solvents, one might think about peripheral substituents with bulky aryl or alkyl groups, which will both prevent aggregation and increase the solubility of target molecules. One of the most popular strategies for the introduction of such groups is the aromatic nucleophilic substitution of the nitro or chloro group(s) with aryloxo or arylthiol substituents [9]. Although this strategy is very simple and useful for the creation of symmetric, octa-substituted phthalocyanines, the presence of eight electron-donating groups on the periphery of the

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macrocycle results in a significant decrease of the first oxidation potential of the phthalocyanine core, which is not a desirable property for oxidative chemical catalysis. It has been shown that the presence of both halogens and aryloxo groups at the periphery of the phthalocyanine macrocycles allows the achievement of both oxidative stability and the solubility of the macrocycles [11]. In a series of publications originating from McKeowns group, it has been shown that the 2,3,9,10,16,17,23,24-octa(2,6-di-*iso*-propylphenoxy) phthalocyanines can form highly unusual cubic symmetry crystals with large nano-scale voids accessible for a variety of small substrate molecules [12]. Although such crystals can be directly used in catalytic transformations of organic substrates, it is expected that they will have a relatively low stability due to the eight electron-donating groups. Thus, in this paper we prepared 2(3),9(10),16(17),23(24)-tetrachloro-3(2), 10(9),17(16),24(23)-tetra(2,6-di-iso-propylphenoxy)phthalocyaninato iron(II) in which four electron acceptor chlorine groups should stabilize the energy of the HOMO orbital and thus improve potential catalytic properties of this iron macrocycle. Because of the asymmetric nature of precursor, 4-chloro-5-(2,6-di-*iso*-propylphenoxy)phthalonitrile, the target phthalocyanine is expected to be formed as a statistical mixture of four positional isomers (Scheme 1). Thus, our second aim was to study whether or not is possible to separate the individual positional isomers using standard chromatography techniques as it was mentioned before that the separation of similar metalfree, zinc, aluminum, gallium, and indium complexes by column chromatography or high performance liquid chromatography (HPLC) is very difficult [13].



Scheme 1. Synthesis of nitriles 1 and 2 and phthalocyanines 3 and 4

RESULTS AND DISCUSSION

Synthesis and attempted separation of individual positional isomers

The degree of nucleophilic substitution in 4,5-dichlorophthalonitrile by 2,6-di-iso-propylphenol depends on the reaction temperature. Thus, when the reaction was conducted in DMSO at 120°C, in the presence of excess phenol, the major reaction product was 4,5-(2,6-di-iso-propylphenoxy)phthalonitrile with a minor presence of 4-chloro-5-(2,6-di-iso-propylphenoxy) phthalonitrile. When the reaction was conducted at 70°C in acetonitrile or DMF or at 90°C in DMSO, the major reaction product was 4-chloro-5-(2,6-di-isopropylphenoxy)phthalonitrile contaminated by a small amount of 4,5-(2,6-di-iso-propylphenoxy)phthalonitrile. A template reaction of the 4-chloro-5-(2,6-di-isopropylphenoxy)phthalonitrile in the presence of iron salt after the standard reaction mixture workup followed by interaction of the crude product with a large excess of tert-butylisonitrile as a axial ligand, resulted in the formation of axially coordinated by tert-butylisonitrile 2(3),9(10),16(17),23(24)-tetrachloro-3(2),10(9),17(16), 24(23)-tetra(2,6-di-iso-propylphenoxy)phthalocyaninato iron(II) complex 3 as a mixture of all four positional isomers 3a-3d (Scheme 1). Target blue-colored product is stable in a solid state and solution, as expected, but sensitive to the photophysical dissociation of the axial ligand, which is similar to the earlier reported compounds [14]. To our surprise, both analytical and preparative aluminum plates allow separation of three fractions of 3 (Fig. 1). We were able to confirm by X-ray crystallography discussed below that the first and the third fractions correspond to the " C_{4h} " and " D_{2h} " individual isomers **3a** and 3d, respectively, while the most abundant second fraction consists of a mixture of the two remaining " $C_{2\nu}$ " and " C_s " positional isomers. Thus, at least in our hands, we were able to separate two pure fractions of positional isomers 3a and 3d and thus one can conclude that, at least for the phthalocyanines with in-plane central ion the presence of bulky 2,6-di-iso-propylphenoxy groups, separation of individual isomers can be achieved by conventional chromatography methods.

Spectroscopy

The high-resolution ESI mass spectrum of the mixture of positional isomers **3** is shown in Fig. 2. It is dominated by three major peaks which correspond to the $[M]^+$, $[M + THF + O]^+$, and $[M + THF + O_2]^+$ ions. In addition, low intensity ions which originate from a loss of one or two axial ligands were also observed in ESI mass spectrum at the lower masses. The molecular ion isotope distribution and mass of the $[M]^+$ are in excellent agreement with the simulated pattern. The UV-vis and MCD spectra of the mixture of the positional isomers **3** is present in Fig. 3.



3

Fig. 1. Photograph of separation of individual isomers of complex 3



Fig. 2. High-resolution ESI mass spectrum of 3

The UV-vis spectra of fractions 1–3 in Q-band region are virtually the same, indicating that the influence of the asymmetric pattern of peripheral substituents on the energy splitting between the LUMO and LUMO+1 energy levels is rather small. Such a small energy difference between LUMO and LUMO+1 was further supported by DFT calculations on the individual isomers **3a–3d** and indicative of the effective four-fould symmetry in these isomers. The B-band in the UV-vis spectrum of **3** was observed at 343 nm and is more intense in comparison to the Q-band at 665 nm due to the contributions from the four peripheral



Fig. 3. UV-vis and MCD spectra of 3 in DCM

2,6-di-iso-propylphenoxy groups. In addition, a weak band around 415 nm was observed in the UV-vis spectrum of the target compound **3**. This low-intensity band is associated with the very weak MCD Faraday A-term and, based on the similarity with the energy of earlier reported phthalocyanine iron(II) complexes axially coordinated with organic isonitriles, was assigned to the metal to ligand charge transfer (MLCT) band originating from the excitation from the Fe d_{xz} , d_{yz} MOs to phthalocyanine centered π^* orbital [14]. The MCD spectrum of **3** is dominated by the Faraday MCD A-term centered at 663 nm which corresponds to the UV-vis absorption peak at 665 nm. In addition, another prominent Faraday MCD A-term has been observed at 342 nm, which corresponds to the UV-vis peak at 343 nm. As expected for Fe $(d_{xx}, d_{yx}) \rightarrow$ Pc (π^*) MLCT transition, the MCD A-term observed at ~415 nm is very weak. Overall, the position of Q- and B-bands in 2(3),9(10),16(17),23(24)-tetrachloro-3(2),10(9),17(16),24(23)-tetra(2,6-di-iso-propylphenoxy)phthalocyaninato iron(II) complex is typical for the bis-axially coordinated by two isonitrile ligands iron phthalocyanines except for the large intensity B-band in the UV-vis spectrum, which reflects the presence of four additional phenoxy groups in our compound. It is also worthwhile to note that the UV-vis spectrum of phthalocyanine 3 and, in particular its Q- and B-band positions (665 and 343 nm), is very close to that observed in the reported earlier [12a] symmetric analogue 4 (Q-band at 664 and B-band at 349 nm [12a]).

The ¹H NMR spectra of the reaction mixture as well as fraction 3 are similar to each other on a qualitative level. The presence of four positional isomers on the NMR spectra of the reaction mixture can be clearly seen from the twelve signals for α -phthalocyanine protons between 9.0 and 9.4 ppm (6 singlets) and 7.9–8.3 ppm (6 singlets). In addition, two diastereotopic isopropyl C–H signals were observed between 3.1 and 3.5 ppm. Finally, several multiplets which correspond to the terminal methyl groups in **3** were observed in the ¹H NMR of the reaction mixture. In contrast, in the case of pure fraction 3 (which corresponds to " D_{2h} " isomer **3d**), only one signal of α_1 -phthalocyanine and α_2 -phthalocyanine as well as only one signal from C–H isopropyl groups have been observed in ¹H NMR spectrum (we were not able to get a good quality ¹H NMR of fraction 1 due to its small quantities), Fig. 4.

X-ray crystallography

The X-ray structures of nitriles 1 and 2 as well as individual isomers of phthalocyanine 3a and 3d are shown in Figs 5–8 while the important crystallographic information (refining parameters, crystallographically determined distances and bond angles) are listed in Tables 1 and 3. The asymmetric nitrile 1 crystalizes in P1 symmetry unit cell with two unique molecules per cell, while symmetric nitrile 2 crystallizes in hexagonal space group R-3 and a single unique nitrile molecule per unit cell. In addition, a solvent water molecule has been seen on the inversion center of the unit cell in the structure of nitrile 2. In both nitriles, the 2,6-di-iso-propylphenoxy group are almost perpendicular to the molecular plane of the dicyanobenzene fragment thus eliminating any conjugation between the substituents and the core aromatic ring. The C≡N, C–Cl, and C–O bond distances are in the typical range. Nitrile 1 has a very clear 2D intermolecular packing motif which originates from CN-Cl and CN-H intermolecular interactions. CN-Cl contacts range between 3.262 and 3.293 Å, while the CN-H close contacts range between 2.590 and 2.596 Å (Fig. 5). In both cases, close contacts are smaller than the sum of the Van der Waals radius of corresponding atoms. There are no such clear structural motifs in the case of the packing in the symmetric nitrile 2 observed by X-ray crystallography. The 3D structure of nitrile 2 predetermined by CN-H and CH-C intermolecular contacts, which are expected to be weak compared to the CN-Cl contacts seen in nitrile 1. The X-ray structures of the individual isomers **3a** and **3d** are shown in Figs 7 and 8. Fraction 1 consists of the " C_{4h} " isomer **3a**, which crystallizes in monoclinic P21/c space group and has iron center located at the crystallographic center of symmetry. Fraction 3 consists of the " D_{2h} " isomer 3d, which crystalizes in the triclinic P-1 space group and has two independent molecules in a unit cell. The iron center is located at the center of symmetry in each individual molecule. In the case of individual positional isomers 3a and 3d, the first coordination sphere of the iron center resembles the previously published bis isonitrilecoordinated iron phthalocyanines [14]. In particular, the



Fig. 4. ¹H NMR spectrum of positional isomer 3d. Solvent impurities are labeled with asterisk



Fig. 5. X-ray structure of nitrile 1 (a), two crystallographically independent molecules in the unit cell) and its packing diagram (b)



Fig. 6. X-ray structure of nitrile 2

first coordination sphere of the iron center resembles a distorted octahedral environment with the axial Fe–C bond distances being shorter compared to the equatorial Fe–N bond distances (Table 1). The phthalocyanine ligands are planar in **3a** and **3d**. The axial isonitrile

ligands have close-to-linear geometry and a typical Fe–C and C≡N bond distances. Simillar to nitriles 1 and 2, the 2,6-di-iso-propylphenoxy groups in 3a and 3d are almost perpendicullar to the phthalocyanine plane. Although isomer **3a** has small voids which are occupied by dichloromethane solvent, both molecules do not have nanometer scale channels which were observed in X-ray structures of the symmetric octa-substituted phthalocyanine 4. Thus, one can conclude that the presence of chlorine substituents in phthalocyanines **3a–3d** results in a disruption in the hydrophobic isopropyl-to-isopropyl groups interactions observed in the case of symmetric octa-substituted phthalocyanine 4. We were also able to grow the crystal structure of phthalocyanine 4 and determine that the unit cell of the complex was almost indistinguishable with the crystal structure published by McKeown and coworkers [12].

Electronic structures and vertical excitation energies of individual positional isomers 3a–3d

The insight into the electronic structure and vertical excitation energies of individual positional isomers 3a-3d



Fig. 7. X-ray crystal structure of positional isomer 3a. (a) General view; (b) core structure; (c) packing diagram



(a)



Fig. 8. X-ray crystal structure of positional isomer 3d. (a) General view of two crystallographically independent molecules in the unit cell; (b) packing diagram

was gained on the basis of density functional theory (DFT) and time-dependent DFT (TDDFT) calculations. The energy diagram for **3a–3d** is shown in Fig. 9, the selected frontier orbitals are listed in Fig. 10, and the frontier molecular orbital contributions are presented in Table 2. The DFT-predicted electronic structures of the individual positional isomers 3a-3d are very close to each other and correlate well with the observed PcFe(CNR)₂ complexes optical and redox properties [14]. In particular, the HOMO, LUMO, and LUMO+1 MOs in 3a-3d are phthalocyanine-centered, which correlate well with the electrochemical data on similar systems. A compression of the octahedral environment along C-Fe-C z-axis results in higher energies of predominantly Fe-centered d_{xz} (HOMO-1) and d_{yz} (HOMO-2) MOs compared to the Fe-centered d_{xy} (HOMO-3) orbital. In the case of isomers 3a and 3c, LUMO and LUMO+1 are degenerate, while a small splitting (up to 0.08 eV) of these orbitals was predicted for isomers 3b and 3d. The classic Gouterman's orbitals [15] in isomers **3a–3d** were identified as HOMO, HOMO-6, LUMO, and LUMO+1, which correspond to the " a_{1u} ", " a_{2u} ", and " e_g " type orbitals in Gouterman's D_{4h} point group notation.

In order to get insight in the optical spectroscopy of the individual isomers 3a-3d, we have conducted TDDFT calculations, which were proven to provide reliable assignments of the UV-vis spectra of transition-metal phthalocyanines and in particular PcFeL₂ complexes [16]. The TDDFT-predicted UV-vis spectra for isomers 3a-3d along with experimental spectrum of 3 are shown in Fig. 11. From Fig. 11, it is clear that TDDFTpredicted UV-vis spectra of 3a-3d correlate well with an experimental spectrum of 3. Because of its actual C_i symmetry, " C_{4h} " isomer **3a** is the only individual isomer, which has "gerade" and "ungerade" orbitals, which simplifies analysis of TDDFT data as only ${}^{1}A_{\mu}$ symmetry excited states will have non-zero intensities. In agreement with the UV-vis spectra of PcFe(CNR)₂ complexes [14], the visible region of UV-vis spectrum of 3a is dominated by two nearly degenerate excited states 1 and 2 of ${}^{1}A_{u}$ symmetry, which are dominated by the classic Gouterman's " $a_{1\mu} \rightarrow e_{g}$ " in common D_{4h} point group notation (HOMO \rightarrow LUMO and HOMO \rightarrow LUMO+1) single-electron excitations. Similarly, the most intense band in UV region of the UV-vis spectrum of **3a** is dominated by the nearly degenerate excited

1			
C(21)≡N(22)	1.146 (7)	C(29)≡N(30)	1.134 (7)
C(23)≡N(24)	1.146 (7)	C(47)≡N(48)	1.140 (7)
Cl(1)-C(2)	1.717 (6)	Cl(25)-C(26)	1.731 (5)
C(3)-O(4)	1.360 (6)	C(33)-O(34)	1.364 (6)
C(2)-C(3)-C(5)-C(6)	92.58 (6)	C(26)-C(33)-C(35)-C(36)	114.04 (7)
2			
C(19)≡N(20)	1.151 (3)	C(23)≡N(24)	1.146 (3)
O(1)-C(2)	1.364 (3)	O(4)-C(3)	1.369 (3)
C(3)-C(2)-C(25)-C(26)	81.95 (3)	C(2)-C(3)-C(5)-C(6)	102.68 (3)
3a			
Fe(1)-N(2)	1.955 (5)	Fe(1)-N(6)	1.950 (5)
Fe(1)-C(50)	1.907 (6)	C(50)≡N(51)	1.131 (8)
C(1)-N(5)-C(52)	171.2 (7)	Fe(1)-C(50)-N(5)	169.1 (6)
N(2)-Fe(1)-C(1)	86.7 (2)	N(6)-Fe(1)-C(1)	92.5 (2)
C(27)-C(13)-C(15)-C(16)	132.99 (7)	C(33)-C(35)-C(38)-C(39)	125.97 (6)
3d			
Fe(1)-N(1)	1.941 (3)	Fe(1)-N(2)	1.929 (3)
Fe(1)-C(1)	1.935 (3)	$C(1)\equiv N(5)$	1.137 (4)
C(1)-N(5)-C(52)	175.0 (4)	Fe(1)-C(1)-N(5)	174.0 (3)
N(1)-Fe(1)-C(1)	88.60 (13)	N(2)-Fe(1)-C(1)	91.39 (13)
C(13)-C(15)-C(18)-C(19)	132.61 (9)	C(33)-C(35)-C(38)-C(39)	115.79 (8)
Fe(2)-N(6)	1.950 (3)	Fe(2)-N(7)	1.939 (3)
Fe(2)-C(2)	1.924 (4)	C(2)≡N(10)	1.157 (5)
C(2)-N(10)-C(107)	172.2 (4)	Fe(2)-C(2)-N(10)	169.9 (3)
N(6)-Fe(2)-C(2)	85.80 (14)	N(7)-Fe(2)-C(2)	89.73 (13)
C(68)-C(70)-C(73)-C(74)	73.88 (8)	C(88)-C(90)-C(93)-C(94)	73.80 (7)

 Table 1. Selected bond lengths and bond angles for nitriles 1, 2, and complexes 3a and 3d

states 20 and 21 of ${}^{1}A_{\mu}$ symmetry, which originate from the Gouterman's " $a_{2u} \rightarrow e_g$ " in common D_{4h} point group notation (HOMO-6 \rightarrow LUMO and HOMO-6 \rightarrow LUMO+1) single-electron excitations. Finally, TDDFT predicts that the MLCT band in 3a, which predominantly originates from the Fe $(d_{xz}, d_{yz}) \rightarrow Pc(\pi^*)$ single-electron transitions should be located at 319 nm (${}^{1}A_{\mu}$ symmetry excited states 46 and 47). Although TDDFT-predicted energy for these transitions is overestimated from the experimentally observed for 3 MCD Faraday A-term at ~415 nm, such energy overestimation is typical for CT states predicted by B3LYP exchange-correlation functional [16]. Nevertheless, agreement between TDDFT-predicted and experimental UV-vis spectra of 3a is quite good. Since actual symmetries of positional isomers **3b–3d** are C_2 and C_1 , parity rule for excited states in these systems does not apply anymore, which results in numerous weak CT transitions predicted by TDDFT in visible region of their spectra. Since MCD



Fig. 9. DFT-predicted molecular orbital energy diagram for positional isomers 3a-3d

spectrum of **3** is clearly indicative of the high-symmetry excited states, which result in observation of the MCD Faraday *A*-terms, such MLCT transitions should have negligible intensities as the Fe-centered d_{xz} , d_{yz} , and d_{xy}



Fig. 10. DFT-predicted profiles of selected frontier orbitals of 3a

MOs as well as phthalocyanine-centered LUMO and LUMO+1 should have "gerade" character.

EXPERIMENTAL

Materials

A symmetric iron phthalocyanine complex **4** was prepared following described earlier procedure [12*a*]. Dichloromethane (DCM), acetonitrile, DMF, and DMSO

were obtained from Aldrich Co. DCM and acetonitrile were dried and distilled over CaH_2 . DMF and DMSO were dried over molecular sieves (4 Å) for 24 h prior use. 4,5-Dichlorophthalonitrile, 2,6-di-*iso*-propylphenol, and potassium carbonate were obtained from Aldrich Co. and were used as received. 9

Physical measurements

Jasco-720 spectrophotometer was used to collect UV-vis data. OLIS DCM 17 CD spectropolarimeter with a 1.4 T DeSa magnet was used to collect MCD data. The MCD spectra were measured in mdeg = $[\theta]$ and converted to $\Delta \epsilon$ (M⁻¹.cm⁻¹.T⁻¹) using the regular conversion formula. Complete spectra were recorded at room temperature in parallel and antiparallel directions with respect to the magnetic field. ¹H and ¹³C NMR spectra were recorded using Varian ANOVA instrument with 500 MHz frequence for protons. High-resolution ESI MS data were collected using Bruker microTOF-III instrument and THF as a solvent.

Computational aspects

All DFT calculations were conducted using the Gaussian 09 software package [17] running under either Windows or UNIX OS. All positional isomers **3a–3d** were optimized at the DFT level using the B3LYP exchange-correlation functional [18]. Wachter's full electron basis set [19] for iron and 6–31G(d) basis sets [20] for all other atoms. The PCM method [21] was used to calculate the solvent effects for all DFT and TDDFT calculations using DCM as a solvent. In all calculations, tight energy (10^{-8} au) SCF convergence criterion has been used. Molecular orbital composition analysis was conducted using QMForge program [22]. TDDFT calculations were conducted for the 80 lowest energy excited states.

X-ray analysis

X-ray quality crystals of nitriles 1 and 2 were obtained by slow evaporation of methanol/DCM mixtures. Dark blue crystals of complexes 3a and 3d were obtained by slow evaporation of DCM/hexane solution. All X-ray diffraction data were collected on Rigaku RAPID-II diffractometer using either Mo-K_{α} ($\lambda = 0.71073$ Å) or Cu-K_{α} (λ = 1.54187 Å) radiation selected by graphite monochromator at -150°C. Structures were solved by direct method implemented into SIR92 software [23] and refined by full-matrix least square method using Crystals for Windows software [24]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were localized from the difference Fourier map and refined using a riding mode approximation $U(H) = 1.2U_{eq}(C)$. All final refinement parameters are presented in Table 3. PLATON SQUEEZE program was used for elimination of the disordered DCM molecule in the structure of 3a

% MO	Composition						
MO	Energy (eV)	Symmetry	Fe	Pc	tbutyl	Cl	OPh
3a							
411	-6.238	a_u	0.21	55.52	2.08	8.73	33.47
412	-6.054	a _g	68.64	31.17	0	0.09	0.1
413	-5.666	a _g	40.41	44.36	3.57	3.88	7.78
414	-5.663	a_g	40.3	44.39	3.55	3.86	7.89
415	-4.923	$\mathbf{a}_{\mathbf{u}}$	0.01	92.98	0.04	1.56	5.41
416	-2.613	a _g	3.88	92.27	0.19	1	2.67
417	-2.61	a_g	3.85	92.43	0.2	1	2.51
418	-1.195	a_u	0	90.62	0.01	2.89	6.48
3b							
411	-6.226	b	0.75	56.7	6.82	7.3	28.44
412	-6.046	а	68.6	31.2	0	0.09	0.1
413	-5.664	а	40.76	44.49	3.63	4.61	6.51
414	-5.657	b	40.49	44.48	3.57	3.84	7.62
415	-4.916	a	0.17	92.8	0.01	1.47	5.55
416	-2.606	а	3.86	92.29	0.19	1.01	2.64
417	-2.602	b	3.85	92.4	0.2	1.01	2.54
418	-1.147	b	0.08	90.49	0.03	2.4	7
3c							
411	-6.055	а	10.03	52.29	3.21	4.01	30.46
412	-6.048	а	65.42	32.39	0.19	0.3	1.69
413	-5.711	а	44.12	42.68	4.15	4.26	4.78
414	-5.544	а	29.41	48.57	2.39	1.13	18.5
415	-4.931	а	0.13	93.16	0.02	2.05	4.64
416	-2.652	а	3.78	92.7	0.19	1.71	1.62
417	-2.573	а	3.93	92.22	0.19	0.58	3.06
418	-1.175	а	0.08	91.66	0.04	2.86	5.36
3d							
411	-6.248	b	0.79	63.58	8.85	7.79	18.99
412	-6.042	а	68.59	31.23	0	0.09	0.08
413	-5.681	а	41.97	43.93	3.86	5.69	4.54
414	-5.628	b	39.78	45.05	3.36	2.46	9.35
415	-4.917	а	0	93.21	0	1.61	5.18
416	-2.628	а	4.21	92.24	0.18	1.55	1.82
417	-2.571	b	3.51	92.31	0.2	0.41	3.57
418	-1.148	b	0.17	89.41	0.27	2.43	7.72

Table 2. DFT-predicted compositions of the frontier MOs for individual isomers 3a-3d

HOMO and LUMO are in bold.



Fig. 11. Comparison between experimental UV-vis spectrum of 3 and TDDFT-predicted UV-vis spectra of isomers 3a–3d

[25]. Mercury program was used for packing diagram generation [26].

Synthesis

4-Chloro-5-(2,6-di*-iso*-propylphenoxy)phthalonitrile (1).

<u>Method A</u>. Dry potassium carbonate (4.0 g, 29 mmol) was added in 8 portions over period of 8 h to a stirred solution of 4,5-dichlorophthalonitrile (1.02 g, 5 mmol) and 2,6-di-*iso*-propylphenol (1.97 g, 11 mmol) in 80 mL of dry acetonitrile under argon atmosphere. A light yellow solution was heated to 70 °C for 24 h. Resulting light brown solution was cooled to the room temperature, poured into 200 mL of water and neutralized by diluted hydrochloric acid. The target compound was filtered and recrystallized from methanol. Yield 0.83 g (47.3%) of a white crystals with mp 180–182 °C.

<u>Method</u> <u>B</u>. Dry potassium carbonate (2.26 g, 16 mmol) was added in 8 portions over period of 30 min to a stirred solution of 4,5-dichlorophthalonitrile (1.12 g, 5.7 mmol) and 2,6-di-*iso*-propylphenol (3.04 g, 17 mmol) in 50 mL of dry DMF under argon atmosphere. A light yellow solution was heated to 70 °C for 1 h. Resulting light brown solution was cooled to the room temperature, poured into 200 mL of water and neutralized by diluted hydrochloric acid. The target compound was filtered and recrystallized from methanol. Yield 1.24 g (64.4%) of a white crystals with mp 180–182 °C.

<u>Method C</u>. Dry potassium carbonate (3.00 g, 22 mmol) was added in 8 portions over period of 30 min to a stirred solution of 4,5-dichlorophthalonitrile (1.00 g, 5 mmol) and 2,6-di-*iso*-propylphenol (5.34 g, 30 mmol) in 15 mL

of dry DMSO under argon atmosphere. A light yellow solution was heated to 90 °C for 1 h. Resulting light brown solution was cooled to the room temperature, poured into 100 mL of water and neutralized by diluted hydrochloric acid. Precipitate was filtered and recrystallized from methanol. Yield 1.04 g (61.4%) of a white crystals with mp 180–182 °C. Anal. calcd. for C₂₀H₁₉ClN₂O: C, 70.90; H, 5.65; N, 8.27%. Found C, 70.97; H, 5.75; N, 8.13%. ¹H NMR (500 MHz, CDCl₃, 20 °C): δ , ppm 1.11 (*d*, *J* = 6.5 Hz, 6H, $-CH_3$), 1.20 (*d*, J = 6.5 Hz, 6H, $-CH_3$), 2.73 (septet, J = 6.5 Hz, 2H, Ar-CH), 6.73 (s, 1H, Ar-H), 7.29 (*d*, *J* = 7.5 Hz, 2H, Ar-H), 7.38 (*t*, *J* = 7.5 Hz, 1H, Ar-H). ¹³C NMR (125 MHz, CDCl₃, 20 °C): δ, ppm 22.40 (-CH₃), 24.42 (-CH₃), 27.57 (Ar-CH), 109.18, 114.54, 114.67, 115.59, 118.15, 125.45, 127.95, 128.31, 135.61, 140.66, 147.06, 158.43.

4,5-Bis-(2,6-di-iso-propylphenoxy)phthalonitrile (2). This compound was prepared by slight modification of the reported earlier procedure. Dry potassium carbonate (3.00 g, 22 mmol) was added in 8 portions over period of 30 min to a stirred solution of 4,5-dichlorophthalonitrile (1.00 g, 5 mmol) and 2,6-di-iso-propylphenol (5.34 g, 30 mmol) in 15 mL of dry DMSO under argon atmosphere. A light yellow solution was heated to 120 °C for 1 h. Resulting pale blue-brown solution was cooled to the room temperature, poured into 100 mL of water and neutralized by diluted hydrochloric acid. Precipitate was filtered and recrystallized from methanol. Yield 1.43 g (59.5%) of a white crystals with mp 160–162 °C. 1 H NMR (500 MHz, CDCl₃, 20 °C): δ , ppm 1.18 (*d*, *J* = 5.5 Hz, 6H, $-CH_3$), 1.24 (*d*, J = 5.5 Hz, 6H, $-CH_3$), 2.95 (septet, J = 5.5 Hz, 2H, Ar-CH), 6.76 (s, 2H, Ar-H), 7.26-7.35 (m, 3H, Ar-H).

2(3),9(10),16(17),23(24)-Tetrachloro-3(2),10(9),17(16),24(23)-tetra(2,6-di-iso-propylphenoxy) phthalo cyaninato iron(II) di-tert-butylisocyanide (3). Dry ferrous chloride (0.16 g, 1.3 mmol) and 4-chloro-5-(2,6di-iso-propylphenoxy)phthalonitrile (0.25 g, 0.7 mmol) were added in one portion to a stirred solution of lithium N,N-dimethylaminoethoxide (prepared from 8 mg, 1.2 mmol, of Li metal) in 3 mL of dry N,N-dimethylaminoethanol under argon atmosphere. Reaction mixture was reflux for 2.5 h, cooled to the room temperature, poured into 20 mL of water, filtered and dried overnight. Yield of the crude green product is 0.127 g (48.8%). The crude green product was dissolved in 10 mL of dry toluene and 1.5 mL of tert-butylisocyanide was added to the reaction mixture. Reaction mixture was heated at 50 °C for 24 h, solvent and an excess of the axial ligand were evaporated in vacuum and dried. A small portion of blue precipitate was filtered through a 5 cm of alumina using 1:1 (v/v) DCM:hexanes mixture and the mixture of positional isomers 3a-3d was isolated upon evaporation of the solvents in vacuum. This sample was used for UV-vis, MCD, ESI MS, and ¹H NMR spectra of the mixture of positional isomers **3a–3d**. The rest of the blue precipitate was loaded on thin layer chromatography

Empirical formula	$C_{20}H_{19}Cl_1N_2O_1$	$C_{32}H_{36}N_{2}O_{2}\cdot H_{2}O$	$C_{90}H_{90}Cl_4Fe_1N_{10}O_4$	$C_{90}H_{90}Cl_4Fe_1N_{10}O_4$
Formula weight	338.84	483.66	1573.43	1573.43
Temperature, K	123	123	123	123
Space group, Z	P1, 2	R-3, 18	$P2_1/c, 2$	P-1, 2
a, Å	6.28110 (10)	35.808 (2)	10.0746 (6)	13.7969 (6)
b, Å	8.49460 (10)	35.808 (2)	13.7552 (8)	17.5859 (6)
c, Å	17.1438 (12)	11.2600 (7)	33.739 (2)	19.3592 (13)
α,°	98.929 (7)	90	90	111.393 (8)
β,°	98.759 (7)	90	105.411 (7)	92.374 (7)
γ, °	93.962 (7)	120	90	99.803 (7)
V, Å ³	889.05 (7)	12503.4 (13)	4507.4 (5)	4282.1 (5)
D _{calc} , g/cm ³	1.266	1.156	1.159	1.221
μ, mm ⁻¹	1.957 (Cu)	0.072 (Mo)	0.338 (Mo)	0.356 (Mo)
$2\theta_{\text{max}}$, °	68.213	26.371	26.372	26.370
$GoF(F^2)$	0.8695	0.9379	0.9845	0.9525
$R_1, wR_2 [I > 2\sigma(I)]$	0.0651, 0.1472	0.0638, 0.1694	0.0982, 0.2407	0.0591, 0.1498
R_1, wR_2 [all data]	0.0827, 0.1573	0.1025, 0.1967	0.1778, 0.3020	0.1022, 0.1912
ρ_{max}/ρ_{min} , $e/Å^3$	-0.47, 0.62	-0.45, 0.78	-0.88, 1.06	-0.57, 1.11

Table 3. Crystal data collection and refinement for nitriles 1, 2, and complexes 3a and 3d

plates and separated in three blue fraction using 1:1 (v/v) DCM:hexanes mixture as eluent. Three fractions were collected. The first fraction, based on X-ray crystallography results, (1.5 mg) was found to be a pure isomer **3a**. A second fraction has a mixture of positional isomers 3b and 3c (23 mg). The third fractions was identified by X-ray crystallography as positional isomer **3d** (4 mg). ¹H NMR for **3d** (500 MHz, CDCl₃, 20 °C): δ, ppm -0.55 (s, 18H, CNC(CH₃)₃), 1.16 (d, J = 6.5 Hz, 24H, $-CH_3$), 1.36 (*d*, J = 6.5 Hz, 24H, $-CH_3$), 3.28 (septet, *J* = 6.5 Hz, 8H, Ar-CH), 7.43 (*d*, *J* = 7.5 Hz, 8H, OAr-H), 7.54 (t, J = 7.5 Hz, 4H, OAr-H), 7.99 (s, 4H, α_1 -Pc), 9.26 (s, 4H, α_2 -Pc). ¹³C NMR (125 MHz, CDCl₃, 20 °C): δ , ppm 22.58 (-CH₃), 24.84 (-CH₃), 27.58 (Ar-CH), 28.67 $(-C(CH_3)_3), 31.74 (-C(CH_3)_3), 105.99, 122.88, 123.38,$ 124.84, 126.61, 134.94, 140.35, 141.81, 145.63, 146.11, 149.26, 155.31. The isonitrile C≡N carbon signal was not observed in ¹³C NMR spectrum, which is typical for this class of compounds [14, 27].

CONCLUSION

In this paper, we have prepared bis-axially coordinated with *tert*-butylisonitrile 2(3),9(10),16(17),23(24)tetrachloro-3(2),10(9),17(16),24(23)-tetra(2,6-di*iso*-propylphenoxy)phthalocyaninato iron(II) complexes**3**which were characterized by UV-visible spectroscopy,MCD, ESI MS, and ¹H NMR spectroscopy. The presenceof all four positional isomers in the reaction mixture wasproven by the ¹H NMR spectroscopy. The UV-vis andMCD spectra of**3a–3d**are typical for iron phthalocyanine complexes axially coordinated with organic isonitrile groups and are dominated by the intense Q- and B-bands as well as low intensity MLCT transitions. Two out of the four positional isomers (3a and 3d) can be separated using conventional chromatography methods. The structures of these two individual positional isomers 3a and 3d were determined by X-ray crystallography. The central iron atoms in both cases were observed in distorted octahedral N₄C₂ environment with Fe-C bond distances shorter compared to the Fe-N bond distances. The presence of the four chlorine substituents of the phthalocyanine core results in disruptions of the hydrophobic intermollecular interactions between isopropyl groups. As a result, X-ray structures of 3a and 3d do not have large solvent-accesable voids which were observed in symmetric octasubstituted phthalocyanine 4. Electronic structures of individual isomers 3a-3d were calculated using the DFT approach and are very close to each other. The HOMO, LUMO, and LUMO+1 orbitals are dominated by the contribution from the phthalocyanine core. The influence of the asymmetric pattern in 3a–3d on the energy separation between LUMO and LUMO+1 is rather mild. The TDDFT calculations predict that the UV-vis absorption spectrum of individual isomers **3a–3d** should be dominated by four strong bands resulting from two pairs of nearly-degenerate excited states. The first pair of nearly-degenerate states would contribute into the intensity of the Q-band region and the other pair of degenerate states would contribute to the intensity of the B-band region. In addition, TDDFT also correctly predicts the presence of the MLCT band at ~415 nm spectral window.

Supporting information

Crystallographic CIF files for **1**, **2**, **3a** and **3d** are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet. com/jpp/jpp.shtml.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC) under numbers CCDC 1441635 (1), 1441634 (2), 1441632 (3a), and 1441633 (3d). Copies can be obtained on request, free of charge, *via* www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: data_request@ccdc.cam.ac.uk).

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