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# ELECTRONIC STRUCTURES AND MOLECULAR ORBITAL CALCULATIONS OF *OPPOSITELY* DINAPHTHALO- AND DIANTHRACO-SUBSTITUTED $D_{2h}$ TYPE METAL-FREE PHTHALOCYANINE CONGENERS

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**Abstract** – Phthalocyanine congeners substituted with two naphthalene or anthracene units on opposite sides (**1** and **2**) have been synthesized and their spectroscopic properties investigated by electronic absorption and magnetic circular dichroism (MCD) spectroscopy in conjunction with quantum chemical calculations. These compounds exhibited several intense absorption peaks in the 600-900 nm region. The geometry of possible tautomers for these macrocycles were optimized at the density functional level (B3LYP/6-31G*), and the absorption spectra were reproduced using Hartree-Fock theory based on ZINDO/S Hamiltonian.

## INTRODUCTION

Metalloporphyrins and phthalocyanines can often be approximated as compounds with $D_{4h}$ symmetry.[1] Since the first report on $D_{2h}$ symmetry zinc phthalocyanine in 1992,[2] however, low symmetry tetraazaporphyrins have attracted the attention of many laboratories, particularly, because they can be relatively easily prepared and the correspondence between the spectroscopic properties and calculated properties are generally good.[3] In synthesizing these low symmetry compounds, researchers are apt to choose diamagnetic metal ions such as zinc, magnesium, and silicon, since the resultant compounds can

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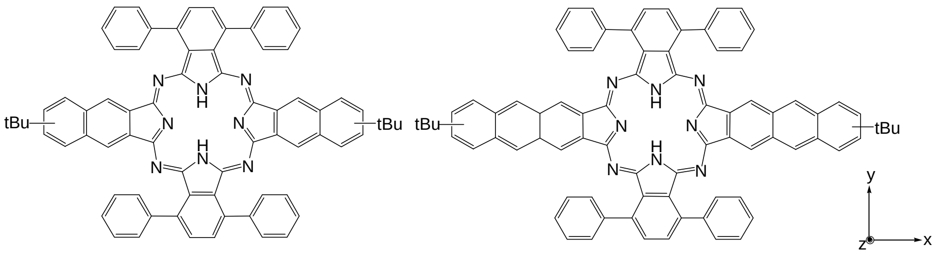
This paper is dedicated to Prof. Dr. Ekkerhard Winterfeldt on the occasion of his 75th birthday.

be characterized by NMR spectroscopy. However, the stability of large tetraazaporphyrin compounds containing these metal ions was not sufficient enough that a metal-free tetraanthracotetraazaporphyrin was reported as a sole diamagnetic tetraazaporphyrin larger than naphthalocyanines.[4] The properties of metal-free species are important in understanding the properties of macrocycles *per se* before examining metal complexes. In this paper, we report the synthesis and spectroscopic properties of oppositely substituted dinaphthalo- and dianthraco-substituted phthalocyanine analogues. i.e. compounds **1** and **2**, respectively. As spectroscopy, we used electronic absorption and magnetic circular dichroism (MCD) spectroscopy, and they were interpreted with the help of molecular orbital (MO) calculations.



**1**

**2**

**Figure 1**. Structures of the compounds in this study.

## RESULTS AND DISCUSSION

Compounds **1** and **2** were synthesized by using 3,6-diphenylphthalonitrile[2,5] as one of the two starting phthalonitriles, since it is established that the use of this dinitrile in the presence of zinc salts can give oppositely di-substituted phthalocyanines preferentially due to steric hindrance between phenyl groups.[3] In the present case, however, the zinc ion was removed by acid treatment after the condensation reaction, since the zinc complexes of **1** and **2** were found not to be stable under column chromatography conditions required for purification. The formation of macrocycles was confirmed by elemental analysis, $^1$H NMR, mass, and electronic absorption spectroscopy.

The electronic absorption and MCD spectra of **1** and **2** measured in chloroform are shown in Figure 2(a). Both the macrocycles exhibited several intense absorption bands in the 600-900 nm region, which is characteristic of $D_{2h}$-type phthalocyanine derivatives with extended $\pi$-conjugation.[6] The dinaphthalo-fused compound (**1**) has three Q absorption peaks at 792, 740, 691 nm and a Soret band at 353 nm, while four Q absorption peaks (855, 784, 728, and 662 nm) and a Soret band (357 nm) were observed for the anthraco-fused compound (**2**). Since the Q band peak positions in the MCD spectra of **1** and **2** were nearly identical to those in these absorption spectra, these MCD signals can be assigned to Faraday *B* terms, indicating split Q absorption bands. The MCD sign corresponding to the lowest-energy absorption band was negative for **1** and **2**. It is noted that the lowest-energy absorption bands of the metal-free compounds shifted to the red, compared with the absorption spectra of the corresponding cobalt(II) complexes reported previously.[3]

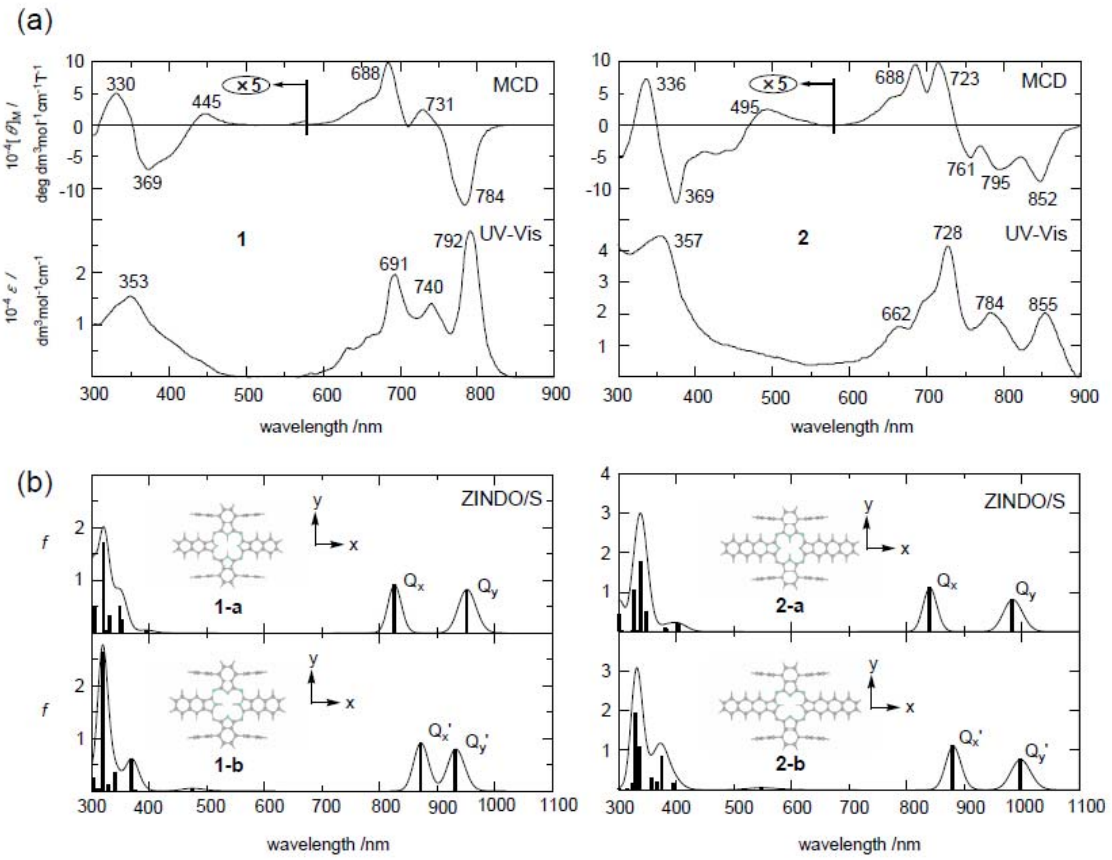


**Figure 2**. (a) Experimental electronic absorption and MCD spectra of **1** (left) and **2** (right) measured in $CHCl_3$ at room temperature. (b) Calculated absorption spectra (ZINDO/S). In **1-a** and **2-a**, the inner two protons are along the y-axis, while in **1-b** and **2-b**, they are along the x-axis.

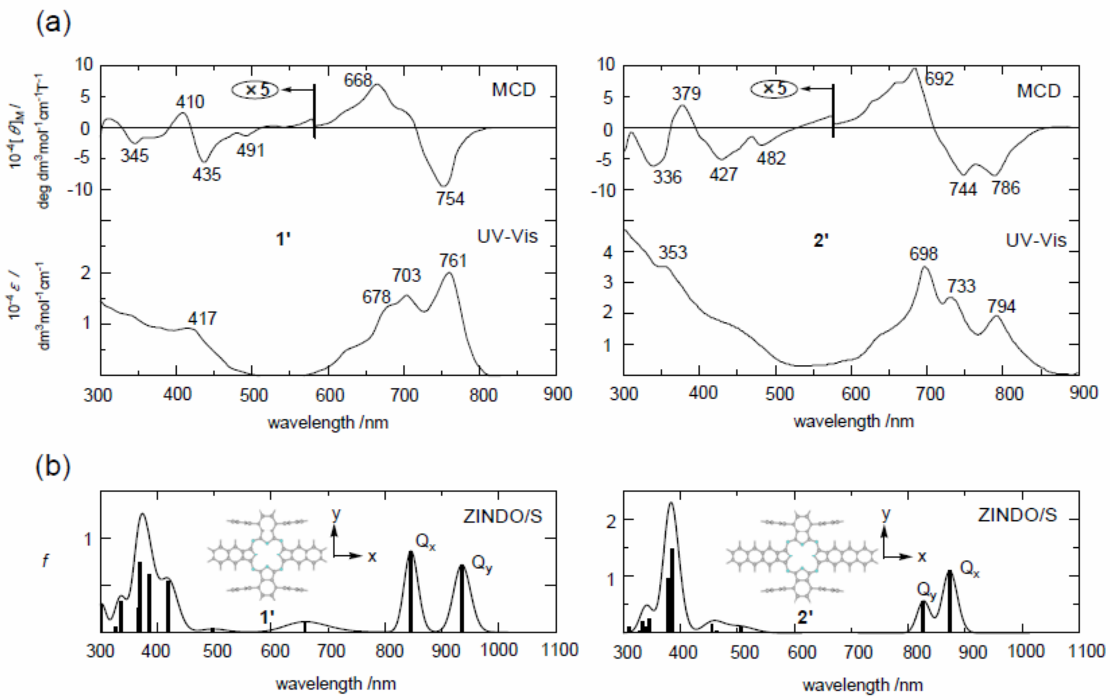
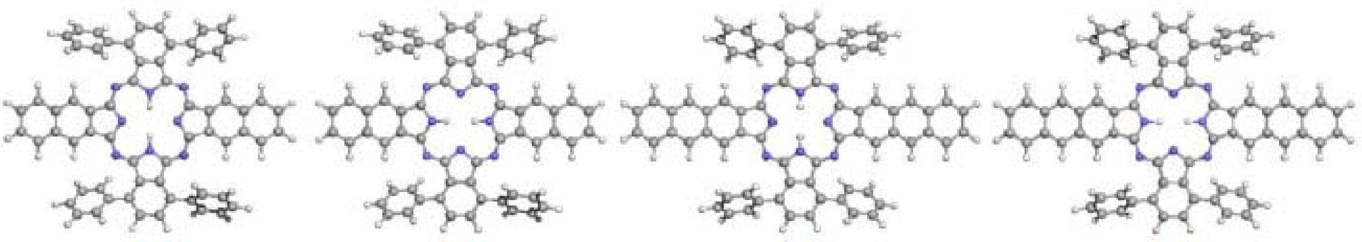


**Figure 3**. (a) Experimental electronic absorption and MCD spectra of the deprotonated forms of **1** (left) and **2** (right) measured in $CHCl_3$ at room temperature. (b) Calculated absorption spectra (ZINDO/S).

Figure 3(a) shows the experimental spectra of the deprotonated forms (**1’** and **2’**) generated by the addition of tetra-*n*-butylammonium hydroxide to a solution of the macrocycles. The dinaphthalo-fused compound (**1’**) has Q absorptions at 761, 703, 678 nm and a Soret band at 417 nm, while the anthraco-fused compound (**2’**) possesses Q absorptions at 794, 733, and 698 nm and a Soret band at 353 nm. The spectral patterns and peak positions for the Q region are similar to those of the cobalt(II) complexes.

Geometry optimizations of the macrocycles were carried out using density functional theory (DFT) at the B3LYP/6-31G* level. As expected, two stable tautomers were calculated for each macrocycle (Figure 4). These optimized geometries do not have ideal $D_{2h}$ symmetry but have $D_2$ symmetry due to different rotation angles of the phenyl groups. It was found that, in the both compounds, the relative energy ($E_{rel}$) of tautomer **1-a** (or **2-a**), in which the inner hydrogens are attached parallel to the short axis (y-axis), is somewhat lower than the other tautomer **1-b** (or **2b**). The results may be related to the previous experimental and computational results that central hydrogen atoms are located along the short molecular axis for several metal-free low-symmetrical tetraazaporphyrin derivatives.[7,8]



**1-a** $E_{rel}$ = 0 kcal/mol

**1-b** $E_{rel}$ = +1.57 kcal/mol

**2-a** $E_{rel}$ = 0 kcal/mol

**2-b** $E_{rel}$ = +2.68 kcal/mol

**Figure 4**. B3LYP/6-31G* structures of possible tautomers of **1** and **2**. The relative energies ($E_{rel}$) were based on total energies corrected with the zero-point vibrational energies.

The absorption spectra for these molecules and their deprotonated species were calculated and analyzed using the Hartree-Fock (HF) method based on the ZINDO/S Hamiltonian.[9] The method has been shown to reproduce the electronic excitations of porphyrins with relatively less expensive levels of computation. The optimized structures with ideal $D_{2h}$ symmetry were used for the calculations. The calculated spectroscopic properties for the optimized $D_2$ structures are essentially identical to those for the $D_{2h}$ structures, suggesting that the rotation of the peripheral phenyl groups does not affect the spectroscopic properties. The calculated spectra are shown in Figure 2(b) and 3(b), and Table 1 lists the results for the Q band region. The partial MO diagrams and contour plots of the MOs associated with the Q transitions are shown in Figure 5.

**Table 1**. Selected ZINDO/S results for the B3LYP-optimized structures of the oppositely substituted dinaphthalo- and dianthraco-substituted phthalocyanine congeners and their deprotonated species. H and L indicate, respectively, the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO).

| | Assign. | Symm. | $\lambda$(nm) | *f* | major contribution (%) |
|---|---|---|---|---|---|
| **1-a** | $Q_y$ | $B_2$ | 951 | 0.83 | H→L(90), H – 5→L + 1(4.5) |
| | $Q_x$ | $B_3$ | 826 | 0.91 | H→L + 1(92), H – 5→L(3.9) |
| **1-b** | $Q_y$’ | $B_2$ | 932 | 0.79 | H→L(93), H – 3→L + 1(2.7) |
| | $Q_x$’ | $B_3$ | 872 | 0.91 | H→L + 1(90), H – 3→L(3.9) |
| **2-a** | $Q_y$ | $B_2$ | 984 | 0.81 | H→L(90), H – 5→L + 1(4.5) |
| | $Q_x$ | $B_3$ | 840 | 1.10 | H→L + 1(92), H – 5→L(3.8) |
| **2-b** | $Q_y$’ | $B_2$ | 998 | 0.76 | H→L(93) |
| | $Q_x$’ | $B_3$ | 881 | 1.10 | H→L + 1(90), H – 3→L(2.4) |
| **1’** | $Q_y$ | $B_2$ | 935 | 0.72 | H→L(90), H – 1→L + 1(5.1) |
| | $Q_x$ | $B_3$ | 846 | 0.86 | H→L + 1(86), H – 1→L(7.0) |
| **2’** | $Q_x$ | $B_3$ | 873 | 1.10 | H→L+2(82), H – 1→L + 3(5.3) |
| | $Q_y$ | $B_2$ | 827 | 0.56 | H→L + 3(82), H→L(7.0), H – 1→L + 2(3.7) |

As shown in Figure 2(b), the calculated absorption spectrum of each tautomer shows two well-separated absorption bands in the Q region and several bands in the Soret band region. The lowest- and next-lowest-energy absorption bands are assigned, respectively, to the $Q_y$ and $Q_x$ transitions for all the tautomers. The $Q_y$ transition is associated predominantly with the HOMO→LUMO transition and polarized along the short axis of the molecule, while the $Q_x$ transition is the HOMO→LUMO+1 transition and the polarization is parallel to the molecular long axis. As seen in Figure 5, these MOs correspond to Gouterman’s orbitals.[10] Since electronic transitions of different polarizations generally exhibit MCD signals of opposite sign, the negative and positive MCD signal observed for the Q region can be assigned to the $Q_y$ and $Q_x$ transitions, respectively. Each pair of tautomers has different excitation energies in the Q region, which can be related to the experimental observation that these metal-free macrocycles have more than two Q band peaks, which is in contrast to the essentially two peaks observed for the corresponding cobalt complexes.[3] Detection of these kinds of tautomers was recently reported for some low-symmetry tetraazaporphyrins.[11] The excitation energies for the Q band of the deprotonated forms are higher than those of the neutral forms, which is in agreement with the experimental results. Although the band assignment of **1’** is similar to that of **1**, the properties of the deprotonated form of the anthraco-substituted systems (**2’**) were different from those of **2**. The lowest- and second-lowest-energy transitions for **2’** are assigned, respectively, to the $Q_x$ and $Q_y$ transitions, since the energy ordering of the Gouterman’s LUMOs is different from the other systems.

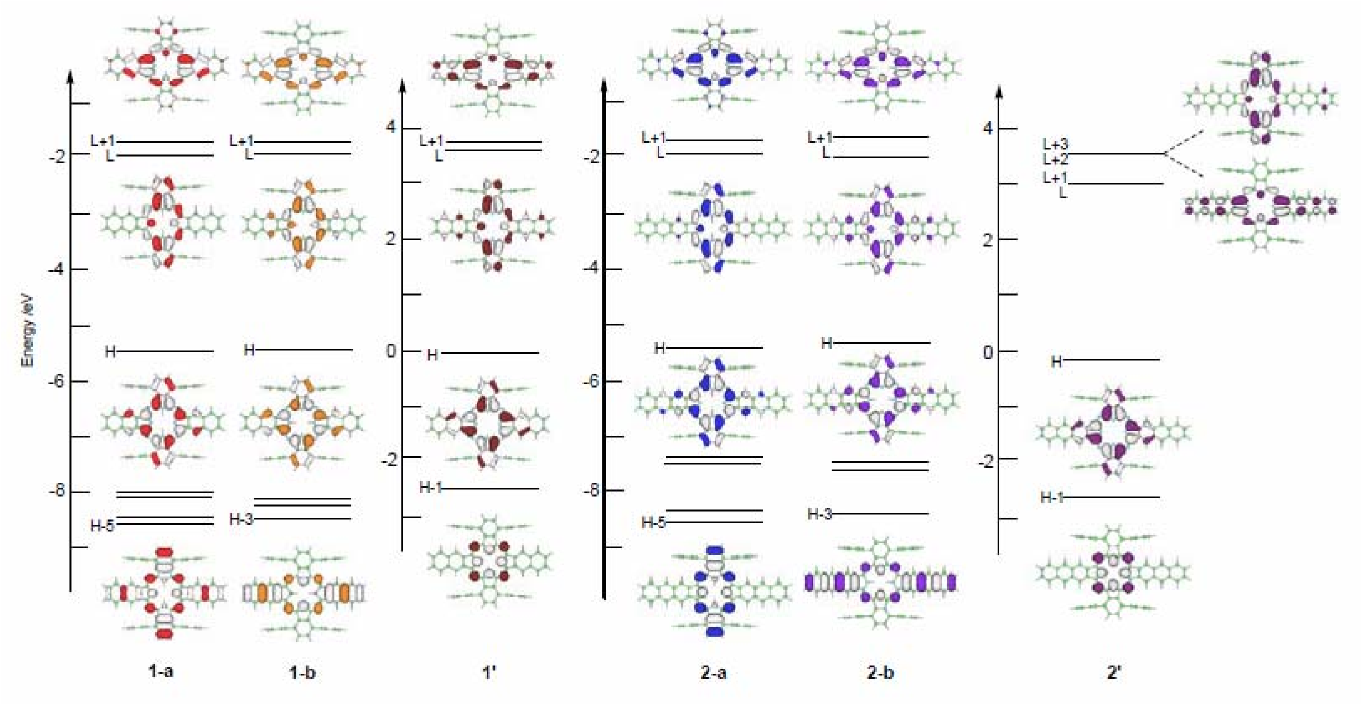


**Figure 5**. Frontier molecular orbitals of possible tautomers of **1** and **2** and their deprotonated forms (ZINDO/S). The MOs whose structures are not shown are either naphthalene or anthracene-centered orbitals.

## CONCLUSION

We have reported the synthesis, spectroscopic properties, and theoretical calculations of opposite type of di-aromatic ring fused phthalocyanine derivatives (**1** and **2**) and their deprotonated forms (**1'** and **2'**). These compounds exhibited several intense Q absorption bands in the 600-900 nm region. Geometry optimizations of possible tautomers were carried out at the level of B3LYP/6-31G* and their absorption spectra were predicted and analyzed using the ZINDO/S method. The computational studies suggest that several Q absorption peaks observed for the metal-free macrocycles are associated with the presence of equilibria between the two tautomers in solution.

## EXPERIMENTAL

### Measurement

Electronic absorption spectra were recorded with a Shimadzu UV-360 spectrophotometer. The MCD spectra were recorded with a JASCO J-500 spectropolarimeter equipped with a JASCO electromagnet that produces parallel and antiparallel magnetic fields of up to 1.5 T. The magnitude of the MCD signal is expressed in terms of molar ellipticity per tesla $[\theta]_M$ deg $mol^{-1}dm^3cm^{-1}T^{-1}$. $^1H$ NMR spectra were recorded with a Jeol GX-500 spectrometer, and are reported in ppm (δ) relative to tetramethylsilane in deuterated chloroform. The mass spectra were obtained with a Kratos MS-50 triple analyzer using *o*-nitrophenyloctylether as a matrix.

### $2^1,2^4,12^1,12^4$-Tetraphenyldibenzo[*b,l*]-$7^3$(or $7^4$),$17^3$(or $17^4$)-di-*tert*-butyldinaphthalo[*g,q*]-21*H*,23*H*-5,10,15,20-tetraazaporphyrin (1)[12]

A mixture of 3,6-diphenylphthalonitrile[5] (500 mg, 1.79 mmol), 6-*tert*-butyl-2,3-dicyanonaphthalene[13] (139 mg, 0.60 mmol), and zinc acetate (157 mg, 0.72 mmol) was heated in a glass cylinder at 270 °C for 40 min. After cooling, the residue was washed with MeOH. The residue (46.6 mg) was dissolved in a mixture of acetic acid (15 mL) and concentrated HCl (5 mL) and refluxed for ca. 3 h, and diluted with cold water. The precipitate was collected and purified by basic alumina column (act. I) using $CCl_4$-toluene = 2:1 v/v as eluent, and the portion of $R_f$ = 0.3 was collected (6 mg, 1.9 %) as a green powder. MS (FAB) *m/z* 1031 $[M+1]^+$. *Anal.* Calcd for $C_{72}H_{54}N_8$: C, 83.86 ; H, 5.28 ; N, 10.87. Found: C, 83.50; H, 5.61; N, 10.25. UV-VIS ($CHCl_3$) $\lambda_{max}$ (log ε) 792 (4.44), 740 (4.15), 691 (4.29), 353 (4.19).

### $2^1,2^4,12^1,12^4$-Tetraphenyldibenzo[*b,l*]-$7^4$(or $7^5$),$17^4$(or $17^5$)-di-*tert*-butyldianthraco[*g,q*]-21*H*,23*H*-5,10,15,20-tetraazaporphyrin (2)

A mixture of 3,6-diphenylphthalonitrile[5] (500 mg, 1.79 mmol), 6-*tert*-butyl-2,3-dicyanoanthracene[14,15] (169 mg, 0.72 mmol), and zinc acetate (157 mg, 0.72 mmol) was heated in a glass cylinder at 270 °C for 40 min. After cooling, the residue was washed with MeOH. The residue (28 mg) was dissolved in a mixture of acetic acid (15 mL) and concentrated HCl (5 mL) and refluxed for ca. 2.5 h, and diluted with cold water. The precipitate was collected and purified by basic alumina column (act. I) using $CCl_4$-toluene = 2:1 v/v as eluent, and the portion of $R_f$ = 0.15 was collected (6 mg, 1.9 %) as a green powder. MS (FAB) *m/z* 1131 $[M+1]^+$. *Anal.* Calcd for $C_{80}H_{58}N_8$ C, 84.93; H, 5.17; N, 9.90. Found: C, 84.43; H, 5.56; N, 9.26. $^1$H NMR (500MHz, $CDCl_3$) δ 7.3-9.0 (38H, m, arom), 1.23-1.28 (18H, br s, butyl), 0.07 (2H, br s, pyrrole H). UV-VIS ($CHCl_3$) $\lambda_{max}$ (log ε) 855 (4.31), 784 (4.31), 728 (4.62), 662 (4.20), 357 (4.65).

### Computational details

All calculations were carried out using the Gaussian 03 program package.[16] Geometry optimizations were performed using Becke's gradient corrected three-parameter exchange functional with the correlation functional of Lee, Yang, and Parr (B3LYP). The peripheral *tert*-butyl groups were omitted for these calculations. The 6-31G* basis set was used for all geometry optimizations. For all conformations, B3LYP/6-31G* frequency calculations were carried out to discern between minima and transition states. The lowest-energy conformations of both **1** and **2** have $D_2$ symmetry. Forty excitation energies, oscillator strengths for the optimized structures with $D_{2h}$ symmetry restriction were calculated using Hartree-Fock (HF) method based on the ZINDO/S Hamiltonian. Gaussian bands with half-bandwidth of $400^{-1}$ cm (Q region) or 2000 $cm^{-1}$ (Soret region) were used to produce calculated spectra.

## ACKNOWLEDGEMENTS

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