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meso-(4-(*N*,*N*-Dialkylamino)phenyl)-Substituted Subporphyrins: Remarkably Perturbed Absorption Spectra and Enhanced Fluorescence by Intramolecular Charge Transfer Interactions

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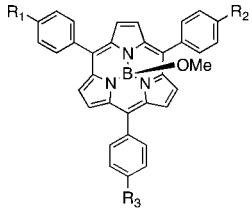
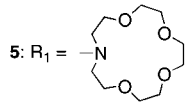
Since our synthesis in 2006,[1] subporphyrin, a ring contracted congener of porphyrin, has emerged as a promising macrocycle in light of the bowl-shaped triangular structures, distinct aromaticity along its 14π-electronic circuit, bright green fluorescence, and theoretical interest.[2−4] Despite this progress, the chemistry of subporphyrin still remains in its rudimentary stage compared to that of subphthalocyanine.[5] One of the remarkable characteristics of subporphyrin is the large substituent effects of the *meso*-aryl group on the electronic property of subporphyrin, which are arising from its small rotational barrier. An interesting example is *meso*-tri(4-nitrophenyl)-substituted subporphyrin that exhibits strongly solvent-dependent optical properties due to the intramolecular charge transfer (CT) interaction with the subporphyrin core as an electron donor.[4a] Here we report the synthesis and full characterizations of *meso*-(4-(*N*,*N*-dibenzylamino)phenyl)-substituted subporphyrins that exhibit unique absorption properties and remarkably enhanced fluorescence emission due to the intramolecular CT interaction in the opposite direction.



1: $R_1 = NBn_2$, $R_2 = R_3 = H$
2: $R_1 = R_2 = NBn_2$, $R_3 = H$
3: $R_1 = R_2 = R_3 = NBn_2$
4: $R_1 = R_2 = R_3 = H$



Subporphyrins **1**−**3** were prepared by means of a palladium catalyzed Buchwald−Hartwig amination protocol[6] from corresponding 4-bromophenyl-substituted subporphyrins and dibenzylamine (Supporting Information, SI). The ^{1}H NMR spectrum of subporphyrin **1** indicates C_s molecular symmetry, featuring a singlet at 8.08 ppm and a couple of doublets at 8.16 and 8.07 ppm due to the peripheral β-protons. Appearance of a pair of doublets at 7.92 and 7.07 ppm due to the protons of the aminophenyl substituent indicates its free rotation. Similar molecular symmetry was confirmed for **2** by its ^{1}H NMR spectrum (SI). In contrast, **3** exhibits C_3-symmetry by displaying a singlet at 8.08 ppm due to the β-protons and a single set of signals due to the *meso*-aryl-substituents.

The solid-state structures of **1** and **3-OEt**, a B-OEt analogue of **3**, were unambiguously elucidated by X-ray diffraction analysis (Figure 1 and SI).[7] The dihedral angles between the subporphyrin mean plane and *N*,*N*-dibenzylaniline moiety are 40.9° for **1** and 42.7°−48.6° for **3-OEt**. Interestingly, each 4-aminophenyl group

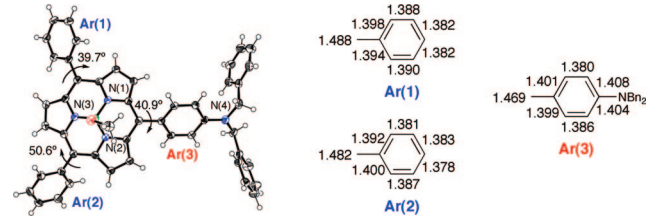


Figure 1. X-Ray crystal structure of **1**. Selected bond lengths and dihedral angles are shown.

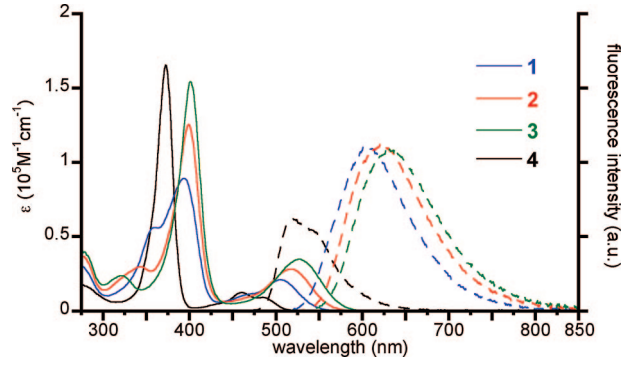


Figure 2. UV−vis absorption (solid lines) and fluorescence (dashed lines; excited at 394, 401, 401, and 373 nm for **1**, **2**, **3**, and **4**, respectively) spectra of subporphyrins **1**−**4** in CH_2Cl_2.

exhibits a slight but distinct distortion toward a quinodimethene-like form. Namely, the bond lengths of C2−C3 and C5−C6 are shorter than the other bonds in the 4-aminophenyl substituent in **1** (Figure 1) and all the 4-aminophenyl substituents in **3** (SI). These features are similar to those of donor−acceptor molecules such as 4-cyano- and 4-nitro-substituted *N*,*N*-dimethylanilines.[8] Such a structural distortion is trivial in corresponding *meso*-(4-aminophenyl)porphyrins.

The UV−vis absorption spectra of **1**−**3** are clearly different depending on the number of 4-aminophenyl substituents (Figure 2). Subporphyrin **1** exhibits a split Soret band at 359 and 394 nm and a red-shifted Q-like band at 505 nm compared to that of triphenylsubporphyrin **4**. Subporphyrin **2** also displays a split Soret band, but its shape is changed; a high-energy band at 343 nm is attenuated, and a low-energy band at 401 nm is intensified. Interestingly, subporphyrin **3** shows a nonsplit sharp Soret band at 401 nm. To understand these spectral features, MO calculations were performed at the B3LYP/6-31G* level. Among the four frontier orbitals of subporphyrin **4**, HOMO (a_1) and HOMO−1 (a_2) are energetically close to the HOMO of the *N*,*N*-dialkylaminophenyl group but only the a_1 orbital can be well hybridized with the HOMO

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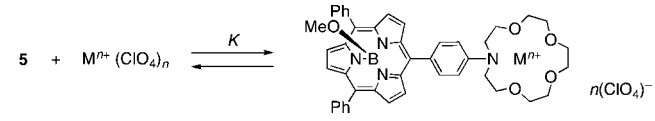
of the *N*,*N*-dimethylaniline moiety, since the *meso*-positions of the a_2 orbital are nodes. In subporphyrin **1**, such orbital hybridization results in the formation of stabilized HOMO−2 and destabilized HOMO, while HOMO−1 (a_2) remains at the same energy level. According to Gouterman's four orbital theory,[9] the Soret band of porphyrin consists of energetically degenerated transitions from HOMO (a_1) or HOMO−1 (a_2) to LUMO (e) or LUMO+1 (e) (i.e., B_x and B_y transitions). In the case of **1**, B_x and B_y are no longer equivalent, since the a_1 level is split into two different energy levels. This situation leads to the split Soret band. The similar feature was predicted and was actually observed as a split Soret band for **2**. Importantly, the degeneracy of the HOMO is recovered for **3**, due to its C_3 molecular symmetry. These spectral changes in the Soret band underscore the characteristic substituent effects of subporphyrin. The calculations also indicate that HOMOs of **1**−**3** are progressively destabilized in this order through the orbital interactions with the dimethylaminophenyl moiety, which is in good agreement with the first oxidation potentials measured by cyclic voltammetry; **1** (0.38 V), **2** (0.30 V), **3** (0.26 V), and **4** (0.71 V). This trend leads to a larger energy difference between HOMO (a_1) and HOMO−1 (a_2), which may account for the gradual increase and bathochromic shift in the Q-like bands of **1**−**3**. Therefore, these spectral characteristics are still understandable within Gourterman's four orbital theory.

Subporphyrins **1**−**3** emit reddish-orange fluorescence tailing over 800 nm as mirror images of their Q-like bands. Remarkably, the fluorescence quantum yields of **1**−**3** recorded in CH_2Cl_2 are drastically enhanced; Φ = 59, 60, and 58%, respectively, which are more than 4-fold that of **4** (Φ_F = 13%). The fluorescence lifetimes of **1**−**3** determined by a time-correlated single photon counting method are considerably longer than those of **4** in solvents examined (SI), hence suggesting suppression of a nonradiative decaying route in the singlet excited state. Subporphyrins **1**−**3** also exhibit solvatochromic behaviors in the absorption and fluorescence spectra. These fluorescence spectral changes were analyzed by a Lippert−Mataga plot,[10] which provided large slopes of 2210, 1550, and 1510 cm^{-1} for **1**, **2**, and **3** (SI), suggesting substantial CT characters for the excited singlet states. On the contrary, the fluorescence quantum yields and lifetimes remain insensitive to the solvent polarity, implying that the fluorescence comes not from an ion-pair state but from a singlet excited state with considerable CT character.

Strong electronic interaction between the 4-aminophenyl substituent and the subporphyrin core is attractive in view of a chemical sensing system. Along this line, aza-crown-substituted subporphyrin **5** was designed and prepared via the similar Pd-catalyzed amination route (SI). Similarly to **1**, the subporphyrin **5** shows a split Soret band at 358 and 394 nm and a Q-band at 508 nm in acetonitrile due to the electron-donating character of the nitrogen atom embedded in the crown ether. The cation binding ability of **5** was examined by UV−vis absorption and fluorescence titration in acetonitrile using perchlorate salts (Table 1 and SI). Upon addition of $Ca(ClO_4)_2$, the perturbed absorption spectrum of **5** was gradually changed to an unperturbed one that was quite similar to that of triphenylsubporphyrin **4** with several clear isosbestic points (SI), allowing accurate determination of the binding constants (Table 1). This Ca^{2+} binding can be monitored by a vivid color change of solution from orange to yellow. During the titration, the perturbed reddish-yellow fluorescence of **5** was changed to a normal subporphyrin-like green yellow fluorescence. The similar binding events

Table 1. Binding Constants of **5** with Alkali and Alkaline Earth Metal Perchlorates Measured by Absorption Titration in Acetonitrile



cation	Li^+	Na^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
log K	2.80	2.30	3.54	4.51	3.69	3.68

were confirmed with other metal cations examined (Table 1). As an advantageous propensity, the fluorescence spectra of solutions of cation-bound **5** were found to vary among orange, yellow, and green, depending upon the binding cation (SI). The determined binding constants are roughly similar to the previously reported trend of 1-aza-15-crown-5 attached chromoionophores,[11] and it can be concluded that cation-induced spectral changes in the absorption and fluorescence spectra are attributed to the suppression of the electron-donating character of the amine nitrogen atom by coordination to metal cation. Protonation of the amino group in **5** with trifluoroacetic acid resulted in a fluorescence color change to green. While the cation selectivity is low for this prototype, coordination-induced changes in the absorption and fluorescence are large enough to be distinguishable by the naked eye and thus promising.

In summary, we have demonstrated tunable characteristics of subporphyrins by incorporating electron donating 4-aminophenyl substituents. Distinct CT interactions in **1**−**3** lead to large changes in the absorption spectra and drastic enhancement of the fluorescence intensity, which has been utilized to explore a new chemosensor. Further tuning and fabrications of subporphyrins through *meso*-aryl substituents are actively in progress in our laboratories.

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Supporting Information Available: Detailed experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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