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COMMUNICATION

Sizeable red-shift of absorption and fluorescence of subporphyrazine induced by peripheral push and pull substitution

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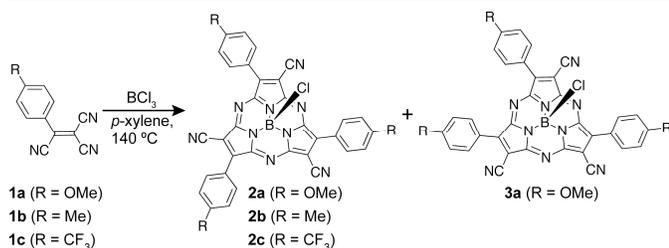
Peripheral substitution with electron-donating (push) and electron-withdrawing (pull) substituents caused a sizeable red-shift of the Q band absorption and fluorescence of subporphyrazine, and the red-shift was controlled by the push substituents. Control of the chromophore symmetry and inherent molecular chirality arising from the pattern of substitution were also investigated.

Control of electronic absorption and fluorescence in the UV/visible and near infrared regions in a simple manner such as introduction of substituents or changes in molecular symmetries has been central to the molecular design of functional dyes. Its importance has been accelerated due to the recent growth of fields related to photo-energy conversion. As a result, attention has been refocused on conventional chromophore molecules, for which these kinds of modification are possible. From this point of view, subporphyrazine (SubPz),¹ a contracted analogue of tetraazaporphyrin (TAP)² or in other words the *meso*-nitrogen-substituted congener of subporphyrin,^{3,4} has become an attractive class of chromophore molecules because of its intense Q band absorption and fluorescence in the visible region. Despite their potential control by peripheral substituents, it has been possible to introduce only a limited kinds of substituents to the periphery of SubPz, mainly due to poor stability of SubPz molecules. The synthesis of SubPz was pioneered by three different groups, Hanack,⁵ Torres,⁶ and us⁷ and unequivocally established for the first time by Torres and Rodríguez-Morgade *et al.*⁶ They reported the synthesis of several peripherally alkyl and alkylthio-substituted SubPzs in moderate yields from a one-pot reaction of the corresponding substituted maleonitriles in the presence of boron trichloride at 140 °C. Recently the same group succeeded in the post-modification of the peripheral substituents with aryl groups using Pd-catalyzed copper(I) thiophene-2-carboxylated (CuTC)-mediated coupling of boronic acids with heteroaromatic thioethers.⁸ With these peripherally substituted SubPzs in hand, they also revealed a perturbed nature of absorption spectral morphologies by peripheral aryl-substituents, which was

mainly observed as shift and intensification of intramolecular charge transfer (CT) bands at the higher energy region than the Q band, whereas the changes in the Q band absorption were modest. With the aim of controlling the Q band absorption and fluorescence of SubPzs, we envisioned introduction of both electron-donating (push) and electron-withdrawing (pull) substituents. Push and pull substituents respectively cause destabilization and stabilization of the HOMO and LUMO, and the synergetic effect of the push-pull substituents generally results in the decrease in the HOMO-LUMO energy gap and hence a red-shift of the Q band absorption mainly comprising the HOMO-LUMO transition. This push-pull strategy worked perfectly in the previous attempt at shifting the Q band absorption of TAP molecules to the red.^{9,10} In addition to the perturbation by the push and pull substituents, molecular symmetries defined by arrangement of the push and pull substituents also had a marked effect on the morphologies of the Q band absorption of TAP molecules.¹⁰ In the case of SubPzs, formation of two positional isomers with C₃ and C₁ symmetry can be expected from the reaction of a tricyanoethylene substituted with a push group. Furthermore, these push-pull SubPzs are inherently chiral due to the absence of any symmetric mirror plane in the structures, which is similar to the chirality of low-symmetry subphthalocyanines, a peripherally benzene-annulated homologue of SubPz.¹ The inherent chirality of subphthalocyanines was disclosed for the first time by Torres and Claessens¹¹ and recently developed by us¹² to elucidate the relationship between the absolute structures and the circular dichroism spectra. In this manuscript, the first synthesis of push-pull SubPzs and their properties are described with a special focus on correlation of the red-shift of the Q band absorption and fluorescence to the donor ability of the push substituents and on the inherent molecular chirality.

From the reaction of 1,1,2-tricyano-2-*p*-methoxyphenylethylene **1a** and BCl₃ in xylene at 140 °C for 45 min, two diastereomers **2a** and **3a** with C₃ and C₁ molecular symmetry were obtained in 3.3% and

0.2% isolated yields, respectively (Scheme 1). The discrepancy in the ratio of the isolated yields from the statistical ratio (C_3 isomer : C_1 isomer = 1 : 3) is simply explained by instability of the push-pull SubPzs in solution. In particular, **3a** is less stable than **2a**. For this reason, in the cases of *p*-tolyl or *p*-trifluoromethylphenyl-substituted SubPz, only the C_3 symmetric isomers (**2b** and **2c**) were obtained in 5.6% and 7.2% yields, respectively, and formation of the C_1 isomer could not be observed (Scheme 1).



Scheme 1. Synthesis of push-pull SubPzs.

These push-pull SubPzs were characterized by high-resolution MALDI-TOF mass analysis, and the molecular symmetries were confirmed by ^1H NMR spectroscopy (see the ESI). In the case of the C_3 symmetric compounds **2a–c**, a pair of doublets was observed at 8.88 and 7.24 ppm for **2a**, 8.71 and 7.55 ppm for **2b**, and 8.68 and 7.39 ppm for **2c**, while a singlet due to the methoxy and methyl substituents at *para*-positions of the push substituents in **2a** and **2b** was observed at 4.00 and 2.63 ppm, respectively (see the ESI). In contrast to the symmetric patterns of the proton signals observed for **2a–c**, **3a** exhibited three pairs of doublets of the phenyl substituents at 8.91, 8.78, 8.71, 7.30, 7.23, and 7.20 ppm and three singlets of methoxy groups at 4.01, 3.98, and 3.96 ppm due to the C_1 molecular symmetry. The structure of the C_3 symmetric isomer was unambiguously elucidated by X-ray structural analysis on single crystals of **2c** obtained from slow diffusion of hexane into a toluene solution of a racemic mixture of **2c** (Fig. 1).

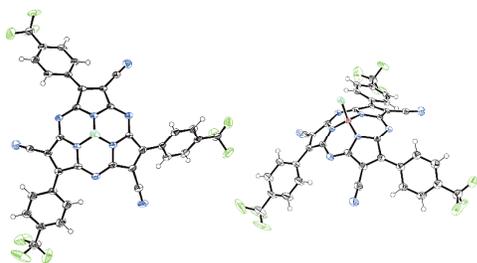


Fig. 1. X-ray single crystal structure of **2c**, top view (left) and side view (right). The thermal ellipsoids were scaled to the 50% probability level.

The crystal structure of **2c** exhibited C_3 symmetric arrangement of cyano and *p*-trifluoromethylphenyl substituents. The structures of both enantiomers with clockwise and anticlockwise arrangement of these substituents were also confirmed (see the ESI). In the crystal packing, **2c** formed slipped-stack columns in a convex-concave manner, in which solvent toluene molecules resided between each **2c** molecule. A structural feature which should be emphasized is the high co-planarity of the phenyl substituents with the core structure of SubPzs. This results from small steric hindrance of the neighbouring

cyano groups so that a significant perturbation of the optical properties by the push-substituents can be expected.

Compared to the Q band absorption of hexakis-alkyl-substituted SubPzs at ca. 500 nm⁶ and hexakis-aryl-substituted SubPzs at 560–580 nm,⁸ the push-pull SubPzs exhibited red-shift of the Q band absorption; **2a**: 633 nm, **2b**: 594 nm, and **2c**: 571 nm (Fig. 2). The extent of the red-shift is proportional to the donor ability of the push-substituent, which is broadly supported by a linear correlation between the position of the Q band absorptions and the Hammett σ_p parameters of the substituents of the aryl groups (see the ESI). Between the Q band and Soret band absorptions at around 300 nm, a broad absorption was observed. The absorption maxima of this broad band was also red-shifted in the same order as observed for the Q band absorptions (**2a**: 435 nm, **2b**: 419 nm, and **2c**: 390 nm). In the magnetic circular dichroism (MCD) spectra, a derivative-shaped Faraday A term with an inflection point close to the maximum of the Q band absorption was observed for these C_3 symmetric compounds, which is indicative of degenerate excited states due to the high molecular symmetry (Fig. 2). The C_1 symmetric compound **3a** exhibited its Q band absorption at a very similar position to that of **2a** at 626 nm. A derivative-shaped MCD corresponding to the Q band absorption of **3a** was assigned as a pseudo Faraday A term, which can be observed if molecules with less than three-fold molecular symmetry accidentally possess nearly degenerate excited states. From these spectroscopic results, insignificant perturbation of the Q band absorption by molecular symmetries is inferred in the case of SubPzs. This is in marked contrast to the push-pull TAPs.¹⁰ Despite the small difference in the Q band region, significant changes in the absorption spectral morphologies featured by two broad absorptions at 499 and 435 nm were observed in the higher energy region.

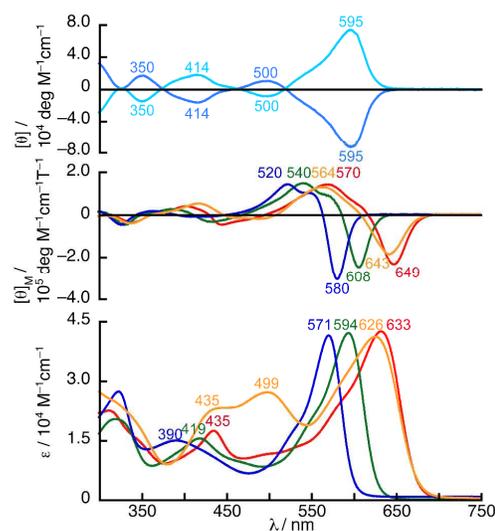


Fig. 2. UV/vis absorption (bottom) and MCD (middle) spectra of **2a** (red line), **2b** (green line), **2c** (blue line), and **3a** (orange line) in toluene and CD spectra of enantiomers of **2b** in toluene (top).

Similar to regular SubPzs and subphthalocyanines,¹ the push-pull SubPzs also exhibited moderately intense fluorescence with a similar trend in the red-shift as observed for the Q band absorptions (Fig. 3, **2a**: 662 nm, $\Phi_f = 0.16$, **2b**: 620 nm, $\Phi_f = 0.16$, **2c**: 593 nm, $\Phi_f = 0.14$,

3a: 668 nm, $\Phi_f = 0.18$). The larger Stokes shift with respect to those of SubPzs and subphthalocyanines reflect structural dynamics in the excited states mainly due to the peripheral aryl groups. The circular dichroism spectra of enantiomers of **2b** separated using HPLC equipped with a chiral column exhibited a mirror imaged spectra, clearly indicating the inherent molecular chirality of the push-pull SubPzs (Fig. 2).

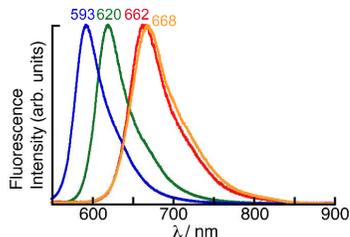


Fig. 3. Fluorescence spectra of **2a** (red line), **2b** (green line), **2c** (blue line), and **3a** (orange line) in toluene.

DFT and time-dependent (TD) DFT calculations at the B₃LYP/6-31G(d) level provided a detailed insight into the perturbed electronic structures of the push-pull SubPzs as well as spectral morphologies in the Q band region. As a reference compound, calculations on unsubstituted SubPz **4** were also carried out (Fig. 4). The TDDFT calculations demonstrated that in the cases of **2a–c**, the transitions from the HOMO to the degenerate LUMO mainly contribute the Q band absorption, which were followed by transitions from the HOMO–1 and HOMO–2 to the LUMO and transitions from the HOMO–3 to the LUMO (Fig. 4 and see the ESI). The distribution patterns of the molecular orbitals in the HOMO and HOMO–3 indicate that these orbitals are derived from the same a₂ HOMO of **4** upon linear combination with molecular orbitals of the peripheral push and pull substituents, whereas the HOMO–1 and HOMO–2 localize on the push-pull substituents. The broad absorption observed between the Q band and Soret band in the absorption spectra of **2a–c**, is, therefore, considered to be composed of both intramolecular CT transitions from the HOMO–1 and HOMO–2 to the LUMO and π - π^* transitions between the SubPz-centred HOMO–3 and LUMO. The peripherally aryl-substituted SubPzs⁸ also exhibit similar CT absorption in this region. Since a Faraday A term like MCD signal was observed for the band at 435 nm for **2a**, 419 nm for **2b**, and 390 nm for **2c** in the MCD spectra, this band can be assigned as the π - π^* transitions, which accompanies angular momentum change (Fig. 2). Based on the TDDFT calculations, which indicates that the π - π^* transitions follow the CT transitions, the CT transitions contribute broad absorption between the Q band and the π - π^* transitions (ca. 575–450 nm for **2a**, 550–450 nm for **2b**, and 525–425 nm for **2c**). The broadening of the observed Q band absorption upon increasing the donor ability of the push-substituents from **2c** to **2b** and to **2a** can be explained in terms of enhanced contribution of the CT transition to the absorption in the Q band region. This also illustrates the low R square value of 0.8 for the regression line of the Hammett plot (see the ESI). In the case of **3a**, based on the TDDFT calculation, the absorption spectral morphologies in the Q band and the higher energy regions can be similarly explained: the Q band absorption comprises transitions from the HOMO to the non-degenerate LUMO and LUMO+1, whereas the

higher-energy broad band at 499 and 435 nm can be assigned as intramolecular CT-like transitions and π - π^* transitions between the SubPz-centred orbitals.

In order to give an insight into the perturbation of the electronic structures by the push-pull substituents, the energy levels of the HOMO and LUMO of **2b** were compared with those of **4**. The LUMO is significantly stabilized, whereas the HOMO remains at the same energy probably due to cancellation of stabilization by the pull substituents with destabilization by the push substituents. Changing the substituents at the *p*-positions from methyl to methoxy and trifluoromethyl results in destabilization and stabilization of the HOMO and LUMO, respectively. In both cases, the extent of stabilization or destabilization is more significant for the HOMO. The MO diagram, therefore, clearly reproduces the trend of the red-shift of the Q band absorption. In the case of **3a**, the energy difference between the LUMO and LUMO+1 is not large. This is also in good agreement with the broad single Q band absorption of **3a** (Fig. 2).

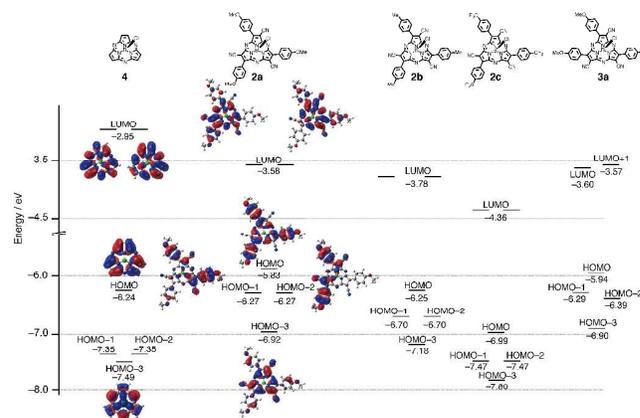


Fig. 4. Partial frontier MO diagrams, in which MOs of **2a** and **4** are shown. For the complete partial frontier MO diagrams, see the ESI.

In summary, a series of push-pull SubPzs were synthesized for the first time, and their diastereomers and enantiomers related to the arrangement of the peripheral substituents were successfully separated. The electronic absorption spectra revealed a perturbation of the spectral morphologies and positions of the Q band absorption by the push-pull substituents. The red-shift of absorption and fluorescence were clearly dependent on the donor ability of the push substituents, which affects the HOMO-LUMO energy gaps based on the DFT calculations. The TDDFT calculations also demonstrated that the broad absorption in the energy region higher than the Q band absorption is characteristic of the electronic structures of these push-pull SubPzs. With this information on the push-pull SubPzs in hand, it is anticipated that the absorption, fluorescence, and chiroptical properties can be further controlled, and the research along this direction is currently being pursued in our laboratory.

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Notes and references

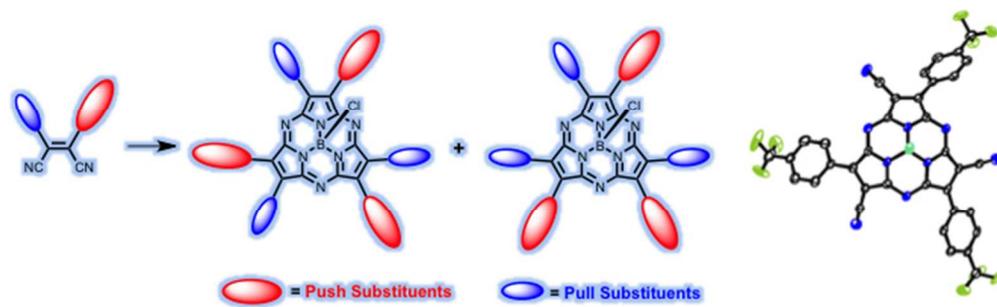
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† Crystallographic data for **2c**: C₈₆H₄₀B₂Cl₂F₁₈N₁₈, *M*_w = 1759.88, triclinic, space group *P*-1 (no. 2), *a* = 7.441(2) Å, *b* = 17.725(5) Å, *c* = 30.886(9) Å, α = 104.188(4)°, β = 91.911(4)°, γ = 91.436(4)°, *V* = 3945(2) Å³, *Z* = 2, ρ_{calcd} = 1.482 g cm⁻³, *T* = -173(2) °C, 34390 measured reflections, 13504 unique reflections (*R*_{int} = 0.0389), *R* = 0.0652 (*I* > 2σ(*I*)), *R*_w = 0.1481 (all data), goodness-of-fit on |*F*²| = 1.054, largest diff. peak/hole 0.722/-0.544 e Å⁻³, CCDC-1015544.

Electronic Supplementary Information (ESI) available: synthesis, spectroscopic data, Hammett plot, and theoretical calculations. See DOI: 10.1039/c000000x/

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