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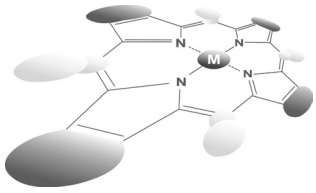

# Synthesis of a doubly $SO_2$-fused phlorin: Tuning the structure and properties by the $SO_2$ groups

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*Dedicated to Professor Naisheng Chen on the occasion of his 80th birthday*

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**ABSTRACT:** A doubly $SO_2$-fused phlorin **4** has been synthesized by the [2 + 2] condensation of dipyrromethanecarbinol **2** and $SO_2$-fused dipyrromenthane **3** in the presence of TFA, followed by DDQ oxidation. The $SO_2$-fused phlorin **4** has been characterized by absorption, fluorescence, mass and NMR spectra, as well as X-ray analysis. Compared to the β-unsubstituted phlorin **5**, the $SO_2$-fused phlorin **4** exhibits a red-shifted absorption spectrum (around 12 nm), a more distorted molecular conformation, as well as nice photostability even with an electron-donating *meso*-3,5-di-*tert*-butylphenyl group. The titration of **4** and **5** with TBAF has been monitored by absorption spectroscopy. The deprotonated phlorin **4** shows a peak at 870 nm which is red shifted by 26 nm compared to that of deprotonated **5**.

**KEYWORDS:** phlorin, sulfolenopyrrole, photostability, crystal structure.



## INTRODUCTION

Porphyrins exist widely in natural functional systems such as heme, chlorophyll and Vitamin $B_{12}$, and they are called life pigments owing to their essential biological functions in respiration and photosynthesis. Various porphyrins, porphyrinoids and oligopyrroles have been synthesized to explore their structural diversities and corresponding applications [1–37]. Among them, calixphyrins exhibit nonplanar conformations, because they contain one or more $sp^3$ *meso*-carbons, which is in contrast to the presence of four $sp^2$ *meso*-carbons in porphyrins, and thus they have been found to be excellent ligands for anion binding [38]. As a special member of calixphyrins, phlorin features one $sp^3$ and three $sp^2$ *meso*-carbons, and was first reported by Woodward in the course of chlorophyll synthesis in 1960 [9]. The existence of one $sp^3$ *meso*-carbon in phlorin endows it unique properties, such as a twisted macrocycle conformation owing to interruption of the conjugation framework by the $sp^3$-carbon, a longer wavelength absorption when compared to that of the corresponding porphyrin, interesting redox properties showing two irreversible reduction and three quasi-reversible oxidation signals at mild potentials, and anion-recognition capability [39–42]. In addition, the one saturated *meso*-carbon in phlorin causes the presence of three inner NHs instead of two in porphyrin, which resembles the structure of corrole and may chelate high valent transition metal ions [43–45]. Thus, phlorins have attracted considerable attention, and many synthetic approaches have been developed. For example, one-pot two-step [46], [2 + 2] condensation [39, 47], stepwise methods [29], and nucleophilic substitution reactions at one of the *meso*-carbons have been employed to construct phlorins and their analogues, such as *N*-confused phlorins [7, 48–50], core-modified phlorins [51, 52] and phlorin-type expanded porphyrins [25, 53–55]. However, phlorins may be labile to oxidation to give linear tetrapyrroles [11, 56], which restricts their further modifications. In the past two decades, the stability of phlorins has been improved by incorporating bulk groups at the inner NH groups [57, 58] or by introducing bulky groups at

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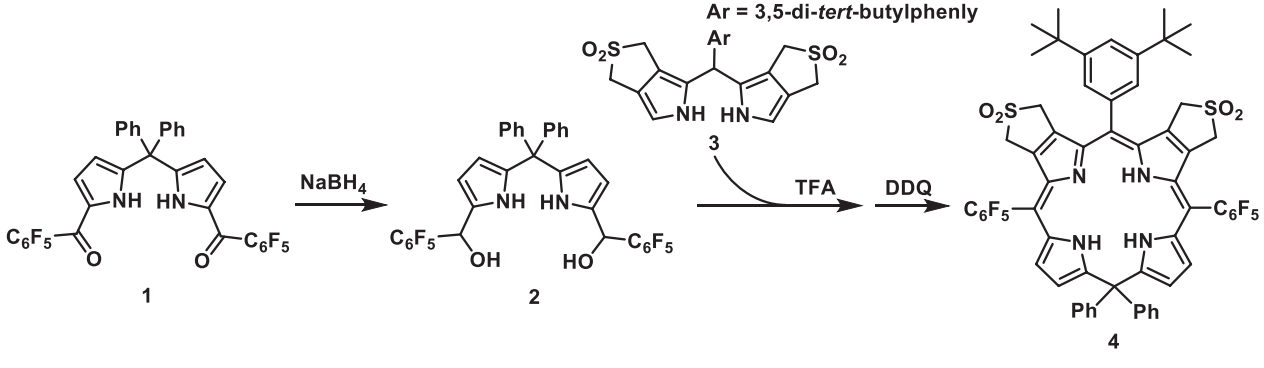
the *meso*-carbons [59]. Recently, Bruce and coworkers obtained stable phlorins by introducing electron-deficient groups like pentafluorophenyl groups to the *meso*-positions [39]. However, most of the trials are focused on modification of the *meso*-positions, and β-substituted phlorins remain relatively unexplored. Herein, we would like to report the synthesis of a β-$SO_2$-fused phlorin **4** (Scheme 1). The effects of the $SO_2$ group on molecular conformation, absorption and photostability have been investigated. In addition, the titration of $SO_2$-phlorin **4** with tetrabutylammonium fluoride (TBAF) has been investigated using absorption and $^1$H NMR spectra.

## RESULTS AND DISCUSSION

The $SO_2$-phlorin **4** was prepared according to the Lindsey-modified MacDonald [2 + 2] approach [8, 60], relying on the optimized procedure by condensation of the corresponding bis(β,β′-sulfoleno)pyrromethane **3** [61] and dipyrromethanecarbinol **2** [48] in the presence of trifluoroacetic acid (TFA), followed by DDQ oxidation (Scheme 1). [62] In detail, the α,α′-di-pentafluorobenzoyl-5,5-diphenyldipyrromethane **1** was synthesized according to the literature [48] and was reduced with $NaBH_4$ to afford the intermediate dipyrromethanecarbinol **2**. The mixture of **2** and **3** in $CH_2Cl_2$ was treated with TFA for 18 h, and then DDQ was added followed by quenching the reaction with triethylamine (TEA). After working up, $SO_2$-phlorin **4** was obtained with a yield of 27% as dark green crystals after purification with silica gel column chromatography and recrystallization from $CH_2Cl_2$/*n*-$C_5H_{12}$.

The absorption spectrum of **4** in $CH_2Cl_2$ (Fig. 1) exhibits a typical absorption of phlorin with a Q band and a Soret band at 678 and 442 nm, respectively, showing a red shift of 12 nm and 14 nm, respectively, as compared to those of phlorin **5** (666 nm for Q band, and 428 nm and 411 nm for Soret band). It is known that electron-withdrawing *meso*-substituents may enhance the stability of phlorins [39]. The $SO_2$-phlorin **4** contains an electron-donation 3,5-di-*tert*-butyl group at one of the *meso*-positions, which is expected to be unfavorable for the stability of the molecule. However, after exposure to ambient light for 4 days, only slight changes in the absorption spectra of **4** and **5** were observed, indicating that **4** exhibits excellent photostability similar to that of phlorin **5**, which contains an additional electron-withdrawing *meso*-$C_6F_5$ substituent [39]. These results imply that the electron-deficient $SO_2$ groups are favorable for reducing the electron-density on the phlorin core, and thus can prevent its oxidative ring opening reaction. Hence, the introduction of electron-withdrawing $SO_2$ groups at the β positions could be an effective strategy for stabilizing phlorin, complementary to that of introducing $C_6F_5$ groups to the *meso*-positions. Corresponding to the absorption peak at 678 nm, the emission band of **4** was observed at 758 nm when its $CH_2Cl_2$ solution was excited at 684 nm. Mass spectra were also recorded to confirm the identity of **4**. As a result, the pseudo-molecular ion $[M - H]^-$ corresponding to $C_{62}H_{46}F_{10}N_4S_2O_4$ was observed at *m/z* = 1163.3 in the ESI mass spectrum. In the MALDI-TOF spectrum, a corresponding characteristic fragment was observed at *m/z* = 1036.3, owing to the loss of the two $SO_2$-groups [32, 61].

The structure of **4** was further established by detailed analysis with one- and two-dimensional NMR spectra ($^1$H,$^1$H COSY and NOESY, and $^1$H,$^{13}$C HSQC spectra). The symmetric sulfolenophlorin **4** showed clear signals in the $^1$H NMR spectrum, including one singlet at the high field, two singlets and one broad singlet at the intermediate field, as well as three doublets, two broad multiplets and one triplet at the low field (see Fig. 2). To complete the assignments, two-dimensional NMR spectroscopy was employed. In the $^1$H,$^1$H COSY spectrum of **4**, the triplet at 7.65 ppm for one proton is coupled with the doublet at 7.33 ppm for two protons, and they are respectively assigned to the protons attached to the *para*- and *ortho*-positions of the 3,5-di-*tert*-butylphenyl substituent. The two doublets, at 6.97 ppm and 6.93 ppm, correlate with each other and are assigned to the pyrrolic β-protons. In the $^1$H,$^{13}$C HSQC spectrum, the singlets at 3.41 ppm and 3.83 ppm are correlated with the carbons at 55.9 ppm and 55.3 ppm, respectively, indicating the typical chemical shifts of the methylene units connected




**Scheme 1.** Synthesis of $SO_2$-phlorin **4** by the Lindsey-modified MacDonald [2 + 2] approach

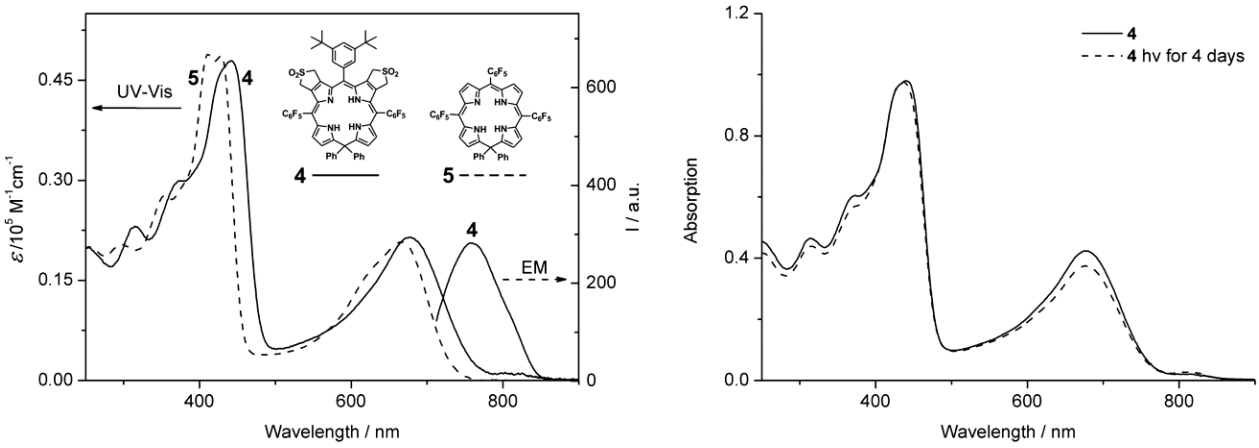



**Fig. 1.** Left, absorption spectra of $SO_2$-phlorin **4** (solid line) and **5** (dashed line) in $CH_2Cl_2$ ($2 \times 10^{-5}$ M) and emission spectrum of **4** in $CH_2Cl_2$ ($5 \times 10^{-6}$ M). Right, absorption spectra of **4** and **5** in $CH_2Cl_2$ ($2 \times 10^{-5}$ M) before/after exposure to ambient light for 4 days at 23 °C under air

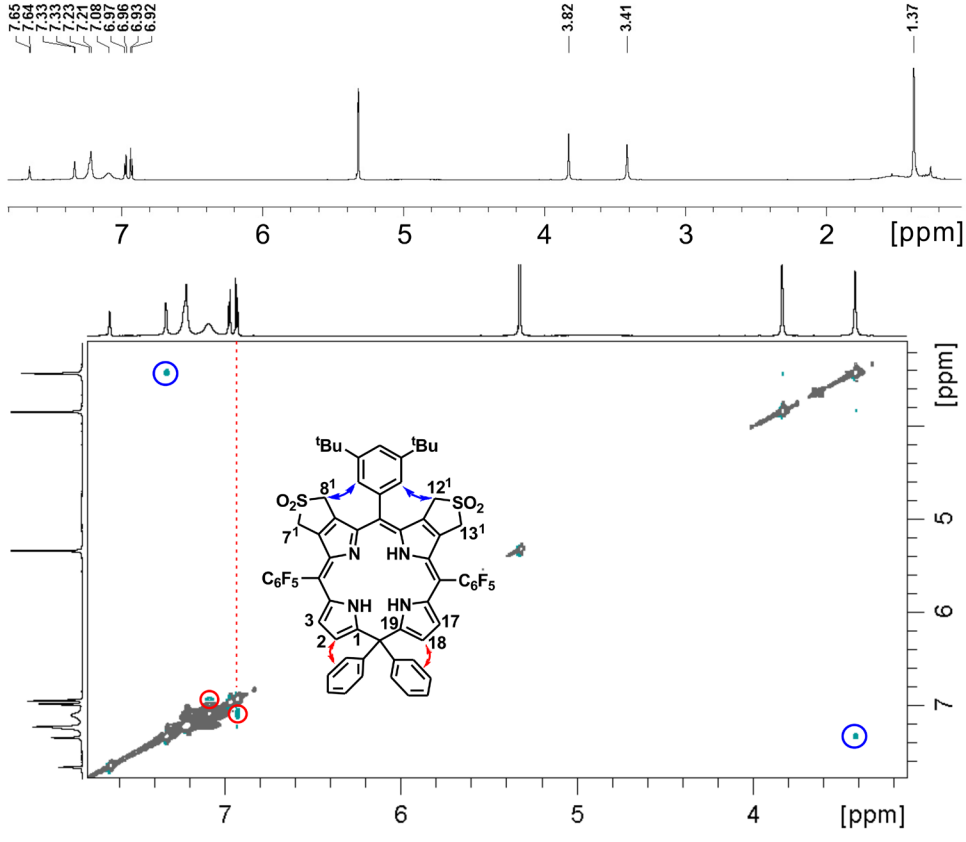



**Fig. 2.** Top, $^1$H NMR spectrum of **4** in $CD_2Cl_2$ (400 MHz, 25 °C). Bottom, the $^1$H,$^1$H NOESY spectrum of **4** in $CD_2Cl_2$ (400 MHz, 25 °C) with the corresponding coupling labeled with blue and red circles

with the $SO_2$ groups. Then, the $^1$H,$^1$H NOESY spectrum assists further detailed assignments (Fig. 2). The *ortho*-proton at 7.65 ppm from 3,5-di-*tert*-butylphenyl group is coupled with the singlet at 3.41 ppm, and thus this signal could be assigned to those attached to $C8^1$ and $C12^1$, while the signal at 3.83 ppm can be assigned to the protons of $C7^1$ and $C13^1$. In addition, the doublet at 6.93 ppm is correlated with the signal from the phenyl group and could be assigned to the protons attached to C2 and C18. Accordingly, the signal at 6.97 ppm can be unambiguously assigned to the protons of C3 and C17.

Single crystals of $SO_2$-phlorin **4** suitable for X-ray analysis were obtained by diffusion of *n*-$C_5H_{12}$ into a solution of **4** in $CH_2Cl_2$ at room temperature. Compound **4** crystalized in the triclinic space group P-1. A unit cell contains two molecules of **4**. In the molecular

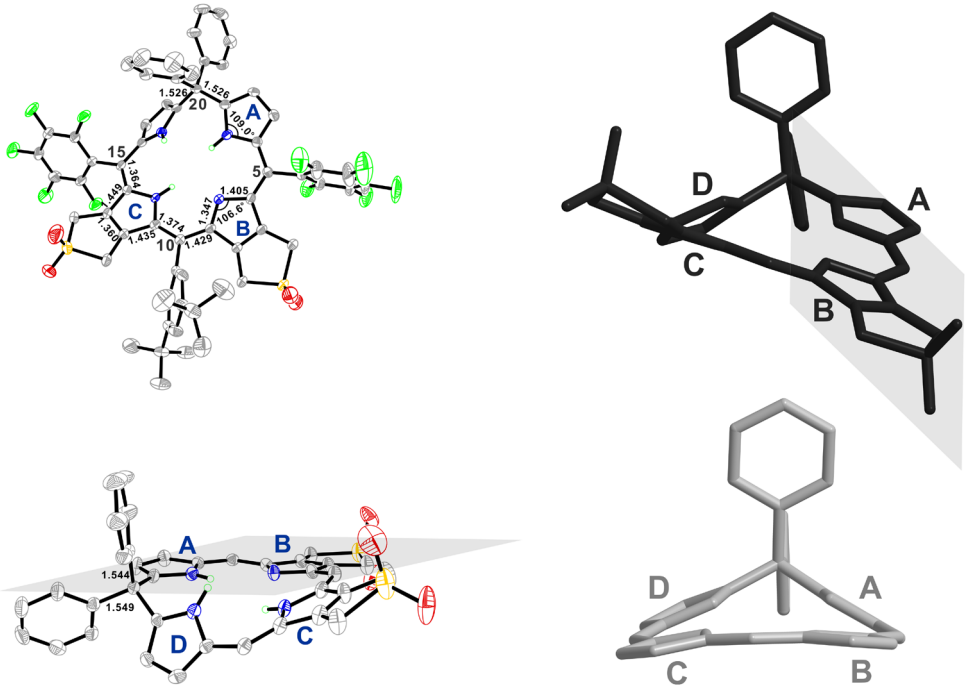



**Fig. 3.** Crystal structure of **4** from front view with partial bond lengths in Å and bond angles (top left, the hydrogens attached to carbons are omitted for clarity) and side view (bottom left, hydrogens attached to carbons and the aryl groups at the 5,10,15-positions are omitted for clarity). The side view of the crystal structures of **4** and **5**, with the latter drawn using the cif file of **5** reported in the Ref. [39] (top right for **4** and bottom right for **5**, the hydrogens, the aromatic substituents at the 5,10,15-positions are omitted for clarity)

structure (Fig. 3, top left), the pyrroles are conjugated with alternate single and double bonds, except for the interruption by the $sp^3$-carbon C20, which shows C–C bond lengths in the range of 1.525 Å–1.549 Å (Fig. 3), and the bond angles around C20 lie within 107.2–111.5°. All these values observed for C20 are typical for $sp^3$-carbons. The presence of the $sp^3$ *meso*-carbon leads to a distortion of the phlorin framework, affording a twisted conformation. It should be noted that the existence of $SO_2$ groups at the β-positions makes the molecule even more distorted owing to the steric hindrance, when compared with **5** (Fig. 3, right). Pyrrolic rings A and B are roughly coplanar in **4**, in sharp contrast to the roughly coplanar rings of B and C observed in **5** (Fig. 3, right). The other two pyrrole rings, C and D, are tilted out of the mean plane composed of A and B with the dihedral angles of 25.0° and 43.7°, respectively. The nitrogen atoms in ring C and D are oriented towards opposite directions of the A/B mean plane. The $C_6F_5$ group at the 5-position is almost vertical to the mean plane of the ring A and B with a large dihedral angle of 82.6°. The two phenyl groups are respectively located above and below the A/B mean plane, with dihedral angles of 84.1° and 60.3°, respectively.

Similar to normal phlorins, the sulfolenophlorin **4** underwent intense interaction with TBAF. Gradual addition of the TBAF solution (24.2 mM) in $CH_2Cl_2$ to the solution of **4** (29.2 μM) in $CH_2Cl_2$ (3 mL) led to a dramatic color change from green to light brown, with clear isosbestic points in the absorption spectra (Fig. 4). During titration with TBAF, the peaks at 371 nm and 678 nm decreased, accompanied with the development of new peaks at 451 nm and 870 nm (see Fig. 4, left), which may be caused by the deprotonation of the NH by $F^-$ [48]. Accordingly, in the negative mode ESI-MS spectrum of the solution of **4** in the presence of TBAF, a peak was observed at $m/z$ = 1163.3, corresponding to $[M - H]^-$. In addition, NMR titration analysis also indicated the deprotonation of the phlorin with the observation of a broad signal at 14.2 ppm, which is proposed to be the signal of $[FHF]^-$ [63]. The $SO_2$ substitution at the β-positions shows noticeable effect on the absorption of the deprotonated form by a 26 nm red shift (870 nm) when compared to that of the normal phlorin **5** (844 nm, Fig. 4, right) [40, 41].

In summary, a $SO_2$-fused phlorin **4** was synthesized, and the effect of $SO_2$-fusion on the structures and properties were systematically investigated. The steric hindrance of the $SO_2$ group distorted the phlorin core when compared to that of the normal phlorin, and the absorption bands are red shifted. Introduction of electron-withdrawing $SO_2$ groups is favorable for stabilizing the phlorin core. Hence, **4** shows excellent photostability comparable to **5**, even though it contains an electron-donating *meso*-3,5-di-*tert*-butylphenyl group. Hence, $SO_2$-fusion could be a new strategy for stabilizing phlorin against light. The interaction of **4** with TBAF has been studied. Compared with titration of the β-unsubstituted phlorin **5**, the fusion of $SO_2$ red shifted the absorption

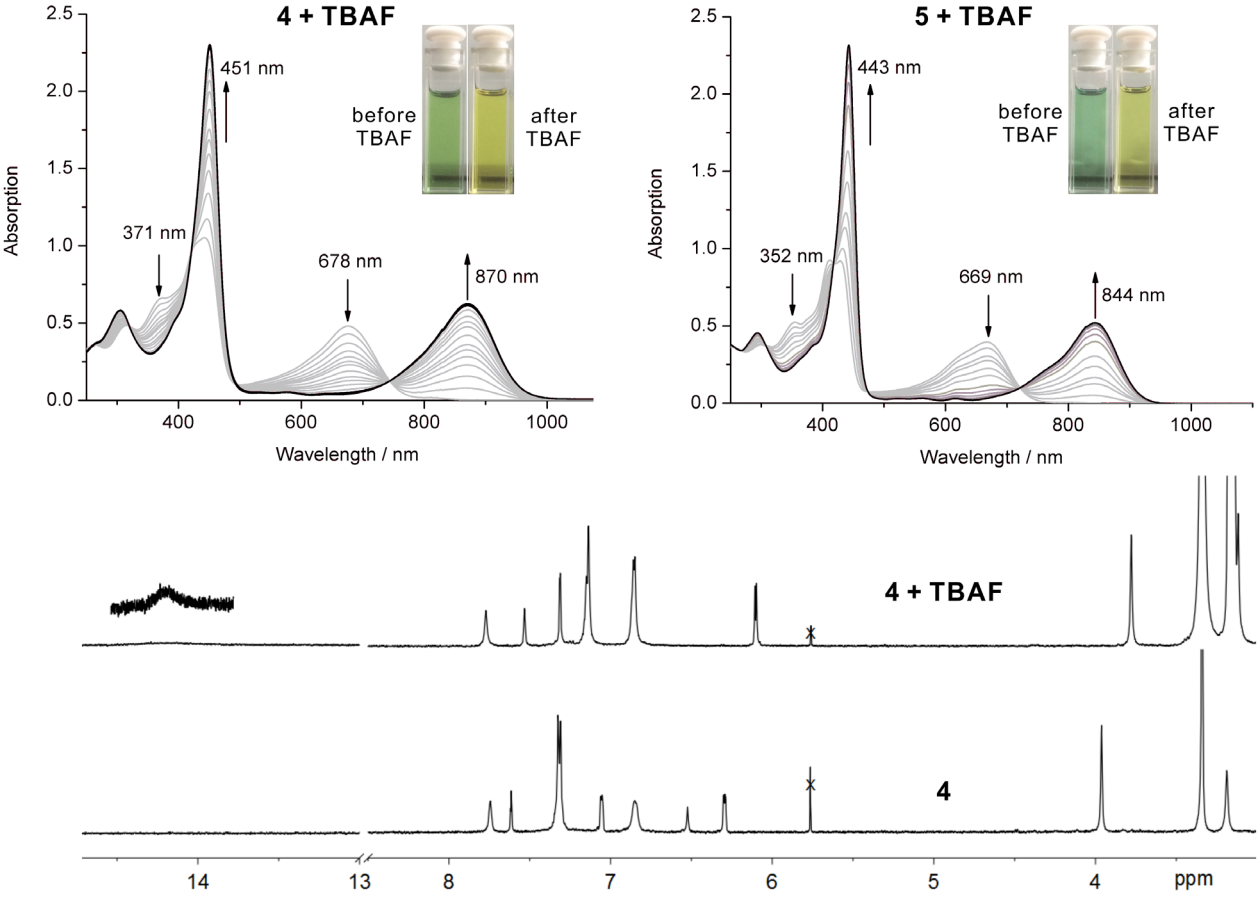



**Fig. 4.** Top left, absorption spectral changes during the titration of the solution of **4** (29.2 μM) in $CH_2Cl_2$ (3 mL) with TBAF (24.2 mM, 1 μL per injection). Top right, absorption spectral changes during the titration of the solution of **5** (28.9 μM) in $CH_2Cl_2$ (3 mL) with TBAF (24.2 mM, 1 μL per injection). Bottom, $^1$H NMR spectra of **4** and of **4** with TBAF (4 eq.) in DMSO-$d_6$ (400 MHz, 25 °C)

of the deprotonated phlorin by *ca.* 26 nm (870 nm). In conclusion, the introduction of $SO_2$ groups is effective for tuning the conformation, absorption and stability of phlorin. Considering the easy functionalization of the sulfolenopyrrole units [61, 64, 65], the $SO_2$-phlorin **4** may open up an efficient pathway for constructing novel functionalized phlorins.

## EXPERIMENTAL

### General

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. $SO_2$-dipyrromethane **3** was synthesized according to the literature [61]. Thin-layer chromatography (TLC) was carried out on glass sheets coated with silica gel 60 F254 (Qingdao Haiyang Chemical Co., Ltd). NMR spectra were obtained using a Bruker AM 400 spectrometer, and chemical shifts were reported relative to the residual peaks of $CD_2Cl_2$ ($\delta = 5.32$), $CDCl_3$ ($\delta = 7.26$) and DMSO-$d_6$ ($\delta = 2.50$) in ppm, where PhH indicates the protons of the phenyl groups, ArH indicates the protons of the 3,5-di-*tert*-butylphenyl group, and PyH indicates the pyrrolic β-H. Mass spectra were collected using a Waters LCT Premier XE spectrometer or an AB Sciex 4800 Plus MALDI-TOF Analyzer. UV-vis absorption spectra were recorded on a Shimadzu UV2600 spectrophotometer and fluorescence spectra were recorded on a Varian Cary Eclipse Fluorimeter.

### Crystallography

Single crystals of **4** were obtained by the slow diffusion of *n*-$C_5H_{12}$ to its solution in $CH_2Cl_2$. X-ray analyses were performed on a SMART APEX Area Detector System equipped with a CCD detector (Bruker) using MoKα (graphite, monochromated, $\lambda = 0.71069$ Å) radiation. The structure was solved by the direct method using SHELXS-97 and refined using the SHELXL-97 program [66]. The positional parameters and thermal parameters of non-hydrogen atoms were refined anisotropically on $F^2$ by the full-matrix least-squares method. Hydrogen atoms were placed at calculated positions and refined riding on their corresponding carbon atoms. CCDC 1827752 contains the supplementary crystallographic data for this paper, and these data are provided free of

charge by the Cambridge Crystallographic Data Centre. Crystal data for **4**: $C_{62}H_{43}F_{10}N_4O_4S_2$, *Mr* = 1165.15, triclinic, space group: *P-1*, *a* = 12.3934 (6), *b* = 16.5275 (12), *c* = 16.8337 (10), α = 97.173 (2)°, β = 109.082 (2)°, γ = 99.489 (2)°, *V* = 3154.4 (3) Å$^3$, *Z* = 2, *R* indices [$I > 2\sigma$ (I)] $R_1$ = 0.0668, $wR_2$ = 0.1339, *R* indices (all data) $R_1$ = 0.1307, $wR_2$ = 0.1558, GOF = 1.041.

## Synthesis

***Preparation of α,α′-di-pentafluorobenzoyl-5,5-diphenyldipyrromethane* 1.** Compound **1** was synthesized according to the literature by acylation of 5,5-diphenyldipyrromethane with $C_6F_5COCl$ in the presence of PhMgBr in THF [48], yield: 32%, $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta_H$, ppm 6.22 (dd, *J* = 2.7, 3.9 Hz, 2H, PyH), 6.71 (dd, *J* = 2.7, 3.9 Hz, 2H, PyH), 7.10 (m, 4H, PhH), 7.41 (m, 6H, PhH), 9.18 (s, 2H, NH).

***Preparation of $SO_2$-phlorin* 4.** To a solution of **1** (24.0 mg, 35 μmol) in THF/MeOH (6 mL, 5/1, v/v) was added $NaBH_4$ (13.3 mg, 350 μmol, 10 eq). After 2 h, compound **1** was completely consumed according to TLC analysis (on silica gel). The reaction was quenched by addition of $H_2O$ (15 mL), and the raw product dicarbinol **2** was extracted with $CH_2Cl_2$ (3 × 10 mL). The organic phase was filtered through a plug of dry cotton wool. The filtrate was dried under reduced pressure and the raw product of **2** was used without further purification.

Dicarbinol **2** and the sulfolenodipyrromethane **3** (18.1 mg, 35 μmol) were dissolved in Ar-purged $CH_2Cl_2$ (14 mL), then TFA (0.11 mL, 1.5 mmol) was added and the reaction mixture was stirred for 18 h under Ar in the dark. DDQ (11.2 mg, 19.3 μmol) was added and the reaction mixture was stirred for 20 min. Triethylamine (0.5 mL) was used to quench the reaction. The mixture was washed successively with saturated *aq*. $NaHCO_3$ (2 × 10 mL) and $H_2O$ (2 × 10 mL). The organic phase passed through a plug of dry cotton wool and the filtrate was dried under reduced pressure. The dark residue was purified by silica gel column chromatography (2 cm × 15 cm). The product **4** was washed by $CH_2Cl_2$/petroleum ether (1/1, v/v) as a green fraction. Finally, dark green crystalline sulfolenophlorin **4** was obtained by recrystallization from $CH_2Cl_2$/*n*-$C_5H_{12}$. Yield: 10.2 mg (27%). UV-vis ($CH_2Cl_2$): $\lambda_{max}$, nm (log ε) 678 (4.33), 442 (4.68), 427 (4.66), 371 (4.48), 314 (4.36). Fluorescence ($CH_2Cl_2$): $\lambda_{max}$, 758 nm. $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta_H$, ppm 1.38 (s, 18H, *t*Bu), 3.41 (s, 2H, $H_2C8^1$ and $H_2C12^1$), 3.83 (s, 2H, $H_2C7^1$ and $H_2C13^1$), 6.93 (d, *J* = 4.1 Hz, 2H, HC2 and HC18), 6.97 (d, *J* = 4.1 Hz, 2H, HC3 and H17), 7.09 (br s, 4H, *o*-PhH), 7.22 (m, 6H, *m*- and *p*-PhH), 7.33 (d, *J* = 1.8 Hz, 2H, *o*-ArH), 7.65 (t, *J* = 1.8 Hz, 1H, *p*-ArH). $^1$H NMR (400 MHz, DMSO-$d_6$, 25 °C): $\delta_H$, ppm 1.34 (s, 18H, *t*Bu), 3.18 (s, 2H), 3.96 (s, 2H), 6.29 (dd, *J* = 2.1/3.9 Hz, 2H, PyH), 6.52 (s, 1H, NH), 6.84 (m, 4H, *o*-PhH), 7.05 (d, *J* = 3.9 Hz, 2H, PyH), 7.31 (m, 8H, *m*- and *p-PhH* + *m*-ArH), 7.61 (t, *J* = 1.6 Hz, 1H, *p*-ArH), 7.74 (br, s, 2H, NH). ESI-MS: *m/z* (%) 1166.3 (11), 1165.3 (38), 1164.3 (70), 1163.3 (100, $[M–H]^-$) calc. $[M–H]^-$ $C_{62}H_{45}F_{10}N_4O_4S_2$: 1163.3.

***Preparation of* 5,10,15-*tripentafluorophenyl*-20,20-*diphenylphlorin* 5.** Phlorin **5** was synthesized according to the reported method [39]. UV-vis ($CH_2Cl_2$): $\lambda_{max}$, nm (log ε) 666 (4.32), 622 shoulder (4.20), 428 (4.69), 411 (4.69), 354 (4.44), 296 (4.31). $^1$H NMR (400 MHz, DMSO-$d_6$, 25 °C): $\delta_H$, ppm 6.13 (dd, *J* = 2.0, 3.7 Hz, 2H, PyH), 6.86 (m, 4H, PhH), 6.96 (dd, *J* = 2.0, 3.7 Hz, 2H, PyH), 7.07 (d, *J* = 5.1 Hz, 2H, PyH), 7.32 (m, 6H, PhH), 7.37 (d, *J* = 5.1 Hz, 2H, PyH), 7.69 (s, 1H, NH), 8.38 (s, 1H, NH).

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## Supporting information

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC-1827752. Copies can be obtained on request, free of charge, *via* http://www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

## REFERENCES

1. Ding Y, Zhu W-H and Xie Y. *Chem. Rev.* 2017; **117**: 2203–2256.
2. Chatterjee T, Srinivasan A, Ravikanth M and Chandrashekar TK. *Chem. Rev.* 2017; **117**: 3329–3376.
3. Lash TD. *Chem. Rev.* 2017; **117**: 2313–2446.
4. Setsune J. *Chem. Rev.* 2017; **117**: 3044–3101.
5. Szyszko B, Bialek MJ, Pacholska-Dudziak E and Latos-Grażyński L. *Chem. Rev.* 2017; **117**: 2839–2909.
6. Anguera G and Sanchez-Garcia D. *Chem. Rev.* 2017; **117**: 2481–2516.
7. Furuta H, Ishizuka T, Osuka A, Uwatoko Y and Ishikawa Y. *Angew. Chem., Int. Ed.* 2001; **40**: 2323–2325.
8. Arsenault GP, Bullock E and MacDonald SF. *J. Am. Chem. Soc.* 1960; **82**: 4384–4389.
9. Woodward RB. *Angew. Chem.* 1960; **72**: 651–662.

10. Xie Y, Wei P, Li X, Hong T, Zhang K and Furuta H. *J. Am. Chem. Soc.* 2013; **135**: 19119–19122.
11. Wei P, Zhang K, Li X, Meng D, Ågren H, Ou Z, Ng S, Furuta H and Xie Y. *Angew. Chem., Int. Ed.* 2014; **53**: 14069–14073.
12. Li M, Wei P, Ishida M, Li X, Savage M, Guo R, Ou Z, Yang S, Furuta H and Xie Y. *Angew. Chem., Int. Ed.* 2016; **55**: 3063–3067.
13. Lu FT, Wang XX, Zhao YM, Yang G, Zhang J, Zhang B and Feng YQ. *J. Power Sources* 2016; **333**: 1–9.
14. Li XF, Meng YK, Yi PG, Stepien M and Chmielewski PJ. *Angew. Chem., Int. Ed.* 2017; **56**: 10810–10814.
15. Liu PP, Hisamune Y, Peeks MD, Odell B, Gong JQ, Herz LM and Anderson HL. *Angew. Chem., Int. Ed.* 2016; **55**: 8358–8362.
16. Fukui N, Kim T, Kim D and Osuka A. *J. Am. Chem. Soc.* 2017; **139**: 9075–9088.
17. Ke XS, Chang Y, Chen JZ, Tian JW, Mack J, Cheng X, Shen Z and Zhang JL. *J. Am. Chem. Soc.* 2014; **136**: 9598–9607.
18. Ke XS, Zhao HM, Zou XR, Ning YY, Cheng X, Su HM and Zhang JL. *J. Am. Chem. Soc.* 2015; **137**: 10745–10752.
19. Roznyatovskiy VV, Lee CH and Sessler JL. *Chem. Soc. Rev.* 2013; **42**: 1921–1933.
20. Zhou ZK, Chang Y, Shimizu S, Mack J, Schutt C, Herges R, Shen Z and Kobayashi N. *Angew. Chem., Int. Ed.* 2014; **53**: 6563–6567.
21. Xu L, Wen B, Kim G, Kim T, Cheng F, Zhou MB, Xu L, Tanaka T, Yin BS, Osuka A, Kim D and Song JX. *Angew. Chem., Int. Ed.* 2017; **56**: 12322–12326.
22. Lu GF, He C, Wang K, Sun JS, Qi DD, Gong L, Wang CM, Ou ZP, Yan S, Zeng SY and Zhu WH. *Inorg. Chem.* 2017; **56**: 11503–11512.
23. Lu G, Kong X, Sun JS, Zhang LL, Chen YL and Jiang JZ. *Chem. Commun.* 2017; **53**: 12754–12757.
24. Liu WB, Pan HH, Wang ZQ, Wang K, Qi DD and Jiang JZ. *Chem. Commun.* 2017; **53**: 3765–3768.
25. Song HL, Liu QY and Xie YS. *Chem. Commun.* 2018; **54**: 1811–1824.
26. Wang YQ, Chen B, Wu WJ, Li X, Zhu WH, Tian H and Xie YS. *Angew. Chem., Int. Ed.* 2014; **53**: 10779–10783.
27. Xie YS, Tang YY, Wu WJ, Wang YQ, Liu JC, Li X, Tian H and Zhu WH. *J. Am. Chem. Soc.* 2015; **137**: 14055–14058.
28. Xie YS, Wu WJ, Zhu HB, Liu JC, Zhang WW, Tian H and Zhu WH. *Chem. Sci.* 2016; **7**: 544–549.
29. Yang GS, Tang YY, Li X, Ågren H and Xie YS. *ACS Appl. Mater. Interfaces* 2017; **9**: 36875–36885.
30. Li CJ, Wurst K, Jockusch S, Gruber K, Podewitz M, Liedl KR and Kräutler B. *Angew. Chem., Int. Ed.* 2016; **55**: 15760–15765.
31. Li CJ, Wurst K, Berghold J, Podewitz M, Liedl KR and Kräutler B. *Chem. —Eur. J.* 2018; **24**: 2987–2998.
32. Li CJ, Zhang JL, Song JX, Xie YS and Jiang JZ. *Sci China: Chem.* 2018; **61**: 511–514.
33. Li CJ, Ulrich M, Liu XJ, Wurst K, Müller T and Kräutler B. *Chem. Sci.* 2014; **5**: 3388–3395.
34. Shao JW, Li CJ, Kong JH, Jiang HR, Zhao SL, Li MZ, Liang X, Zhu WH and Xie YS. *Org. Lett.* 2018; **20**: 1941–1944.
35. Wei XD, Bu LL, Tang WQ, Zhao SL and Xie YS. *Sci China: Chem.* 2017; **60**: 1212–1218.
36. Wang Q, Ma FT, Tang WQ, Zhao SL, Li CJ and Xie YS. *Dyes Pigm.* 2018; **148**: 437–443.
37. Wang Q, Wei XD, Li CJ and Xie YS. *Dyes Pigm.* 2018; **148**: 212–218.
38. Gale PA, Sessler JL, Lynch V and Sansom PI. *Tetrahedron Lett.* 1996; **37**: 7881–7884.
39. Bruce AM, Weyburne ES, Engle JT, Ziegler CJ and Geier GR. *J. Org. Chem.* 2014; **79**: 5664–5672.
40. Pistner AJ, Lutterman DA, Ghidiu MJ, Ma YZ and Rosenthal J. *J. Am. Chem. Soc.* 2013; **135**: 6601–6607.
41. Pistner AJ, Yap GPA and Rosenthal J. *J. Phys. Chem. C* 2012; **116**: 16918–16924.
42. Hong SJ, Ka JW, Won DH and Lee CH. *Bull. Korean Chem. Soc.* 2003; **24**: 661–663.
43. Gross Z. *J. Biol. Inorg. Chem.* 2001; **6**: 733–738.
44. Wasbotten IH, Wondimagegn T and Ghosh A. *J. Am. Chem. Soc.* 2002; **124**: 8104–8116.
45. Golubkov G, Bendix J, Gray HB, Mahammed A, Goldberg I, DiBilio AJ and Gross Z. *Angew. Chem., Int. Ed.* 2001; **40**: 2132–2134.
46. Kim D, Chun HJ, Donnelly CC and Geier GR. *J. Org. Chem.* 2016; **81**: 5021–5031.
47. Gryko DT and Koszarna B. *Eur. J. Org. Chem.* 2005; 3314–3318.
48. Kong JH, Shao JW, Li CJ, Qi DD, Li MZ, Liang X, Zhu WH, Jiang JZ and Xie YS. *Org. Lett.* 2017; **19**: 650–653.
49. Li XF, Chmielewski PJ, Xiang JF, Xu JL, Jiang L, Li YL, Liu HB and Zhu DB. *J. Org. Chem.* 2006; **71**: 9739–9742.
50. Liu B, Li XF, Xu X, Stępień M and Chmielewski PJ. *J. Org. Chem.* 2013; **78**: 1354–1364.
51. Gupta I, Froehlich R and Ravikanth M. *Eur. J. Org. Chem.* 2008: 1884–1900.
52. Skonieczny J, Latos-Grażyński L and Szterenburg L. *Chem. —Eur. J.* 2008; **14**: 4861–4874.
53. Chatterjee T and Ravikanth M. *Inorg. Chem.* 2014; **53**: 10520–10526.
54. Chatterjee T, Ghosh A, Madhu S and Ravikanth M. *Dalton Trans.* 2014; **43**: 6050–6058.
55. Higashino T and Osuka A. *Chem. Asian J.* 2013; **8**: 1994–2002.
56. Jeandon C, Krattinger B, Ruppert R and Callot HJ. *Inorg. Chem.* 2001; **40**: 3149–3153.
57. Krattinger B and Callot HJ. *Chem. Commun.* 1996: 1341–1342.
58. Krattinger B and Callot HJ. *Tetrahedron Lett.* 1996; **37**: 7699–7702.

59. LeSaulnier TD, Graham BW and Geier GR. *Tetrahedron Lett.* 2005; **46**: 5633–5637.
60. Lee CH, Li FR, Iwamoto K, Dadok J, Bothnerby AA and Lindsey JS. *Tetrahedron* 1995; **51**: 11645–11672.
61. Li CJ, Fechtel M, Feng YQ and Kräutler B. *J. Porphyrins Phthalocyanines* 2012; **16**: 556–563.
62. O'Brien AY, McGann JP and Geier GR. *J. Org. Chem.* 2007; **72**: 4084–4092.
63. Wang QG, Xie YS, Ding YB, Li X and Zhu WH. *Chem. Commun.* 2000; **46**: 3669–3671.
64. Rieder A and Kräutler B. *J. Am. Chem. Soc.* 2000; **122**: 9050–9051.
65. Banala S, Ruhl T, Wurst K and Kräutler B. *Angew. Chem., Int. Ed.* 2009; **48**: 599–603.