

## Akzeptierter Artikel

**Titel:** Conformationally Flexible Bis(9-fluorenylidene)porphyrin Diradicaloids

**Autoren:** Jishan Wu, Hejian Zhang, Hoa Phan, Tun Seng Herng, Tullimilli Y. Gopalakrishna, Wangdong Zeng, and Jun Ding

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# Conformationally Flexible Bis(9-fluorenylidene)porphyrin Diradicaloids

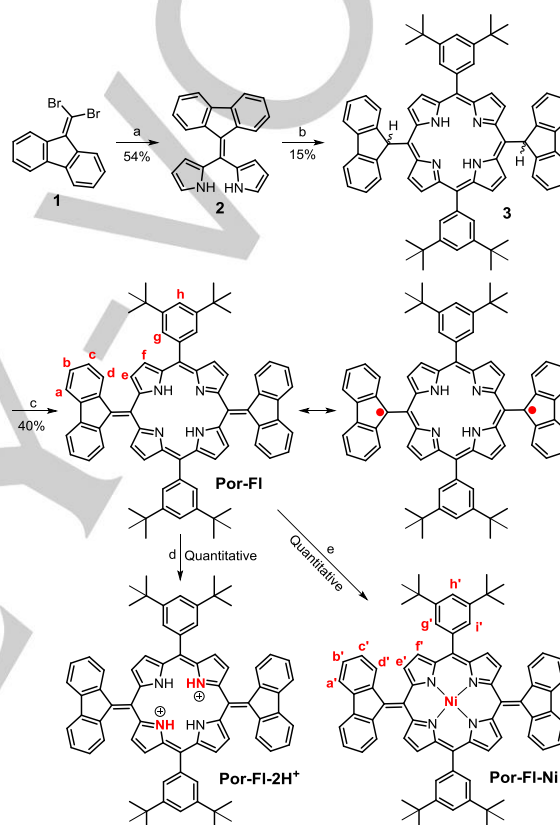
Hejian Zhang,<sup>[a]</sup> Hoa Phan,<sup>[a]</sup> Tun Seng Heng,<sup>[b]</sup> Tullimilli Y. Gopalakrishna,<sup>[a]</sup> Wangdong Zeng,<sup>[a]</sup> Jun Ding,<sup>[b]</sup> and Jishan Wu<sup>[a]\*</sup>

**Abstract:** A stable 5,10-bis(9-fluorenylidene)porphyrin (**Por-FI**) diradicaloid was synthesized. It shows a quinoidal, saddle-shaped geometry in single crystal but can be thermally populated to triplet diradical both in solution and in solid state. Coordination with Ni<sup>2+</sup> ion (**Por-FI-Ni**) does not significantly change the contorted conformation but reduces the singlet-triplet gap. Heat-induced geometric change can explain the observed paramagnetic properties as well as unusual hysteresis in SQUID measurements. On the other hand, protonation (**Por-FI-2H<sup>+</sup>**) dramatically changes the conformation while maintains the closed-shell electronic structure. Our studies demonstrate how heat, coordination and protonation affect the geometry, diradical character and physical properties of conformationally flexible open-shell singlet diradicaloids.

Recent studies demonstrated that open-shell singlet diradicaloids normally showed narrow band gap, redox amphotericity, large two-photon absorption and thermally activated paramagnetism, and thus they have potential applications for organic electronics, photonics and spintronics.<sup>1</sup> So far, most reported diradicaloids have a rigid conformation and the thermal population from singlet ground state to triplet excited state usually does not induce significant geometric change.<sup>2</sup> However, there are indeed a few examples where the singlet-to-triplet conversion involves dramatic conformational change, such as the overcrowded tetra-substituted ethylene (C=C)<sup>3</sup> and Si=Si.<sup>4</sup> Herein, we report a new quinoidal bis(9-fluorenylidene)porphyrin diradicaloid (**Por-FI**, Scheme 1), which has a saddle-shaped geometry in the closed-shell singlet ground state, but can be thermally populated to the paramagnetic triplet excited state accompanying a geometric change. The process was monitored by variable-temperature (VT) NMR in solution and SQUID in solid state. Moreover, it was found that coordination of metal ion or protonation also significantly changed the geometry, singlet-triplet gap and diradical character.

We are particularly interested in porphyrin-based diradicaloids because spin delocalization over the large  $\pi$ -conjugated network can effectively stabilize the radicals.<sup>5</sup> Our design is based on quinoidal porphyrins,<sup>6</sup> which have irresistible wish to become diradical by recovering the aromaticity of non-aromatic quinoidal porphyrin unit. Previously, we synthesized a tetrakis(4-*tert*-butylphenyl)-substituted porphyrinquinodimethane, which however only exhibits a closed-shell quinoidal structure.<sup>7</sup> To enhance the diradical character, we expected that a 5,15-

bis(9-fluorenylidene)porphyrin (**Por-FI**) could work better as the steric hindrance between the  $\beta$ -H of porphyrin core and the rigid fluorenyl unit becomes even more severe, which can drive the molecule to become flexible diradical (Scheme 1). Coordination or protonation of the free-base porphyrin may further tune its geometry and diradical character. To validate the hypothesis, compound **Por-FI** was synthesized according to Scheme 1.



**Scheme 1.** Synthetic routes of **Por-FI**, **Por-FI-Ni** and **Por-FI-2H<sup>+</sup>**. Reagents and conditions: (a) *N*-Boc-2-pyrroleboronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, Cs<sub>2</sub>CO<sub>3</sub>, toluene, MeOH, 120 °C, overnight; (b) 3,5-di-*tert*-butylbenzaldehyde, dry DCM, TFA, DDQ, rt; (c) DDQ, toluene, reflux for 5h; (d) TFA, DCM; (e) Ni(CH<sub>3</sub>COO)<sub>2</sub>•4H<sub>2</sub>O, toluene, reflux for 5h.

Suzuki coupling between 9-(dibromomethylene)-9H-fluorene (1) and *N*-Boc-2-pyrroleboronic acid followed by *in situ* deprotection of the Boc group gave the dipyrrole 2 in 54% yield. Trifluoroacetic acid (TFA) mediated [2+2] condensation between 2 with 3,5-di-*tert*-butylbenzaldehyde and subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded the 5,15-bis(9-fluorenyl)-10,20-di(4-*tert*-butylphenyl)porphyrin 3 in 15% yield. Oxidative dehydrogenation of 3 with DDQ in refluxing toluene finally provided the target compound **Por-FI** in 40% yield, which could be purified by silica gel column chromatography. Coordination of **Por-FI** with Ni(OAc)<sub>2</sub>•4H<sub>2</sub>O gave the Ni(II)-complex **Por-FI-Ni** in nearly quantitative yield. However, the more electron-rich Zn(II) complex was unstable and could not be isolated in pure form. Protonation with 2 equiv TFA in dichloromethane (DCM) generated the doubly protonated porphyrin **Por-FI-2H<sup>+</sup>** quantitatively.

H. Zhang, Dr. H. Phan, Dr T. Y. Gopalakrishna, Dr. W. Zeng, Prof. J. Wu  
Department of Chemistry, National University of Singapore  
3 Science Drive 3, 117543, Singapore  
Fax: (+65) 6779 1691  
E-mail: [chmwuj@nus.edu.sg](mailto:chmwuj@nus.edu.sg)

Dr. T. S. Heng, Prof. J. Ding  
Department of Materials Science and Engineering, National University of Singapore, 119260, Singapore

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