HETEROCYCLES, Vol. 71, No. 3, 2007, pp. 549 - 555. © The Japan Institute of Heterocyclic Chemistry
Received, 21st November, 2006, Accepted, 12th January, 2007, Published online, 15rh January, 2007. COM-06-10954

SYNTHESIS AND AGGREGATION OF TETRATHIAFULVALENE-ANNULATED PORPHYRAZINES

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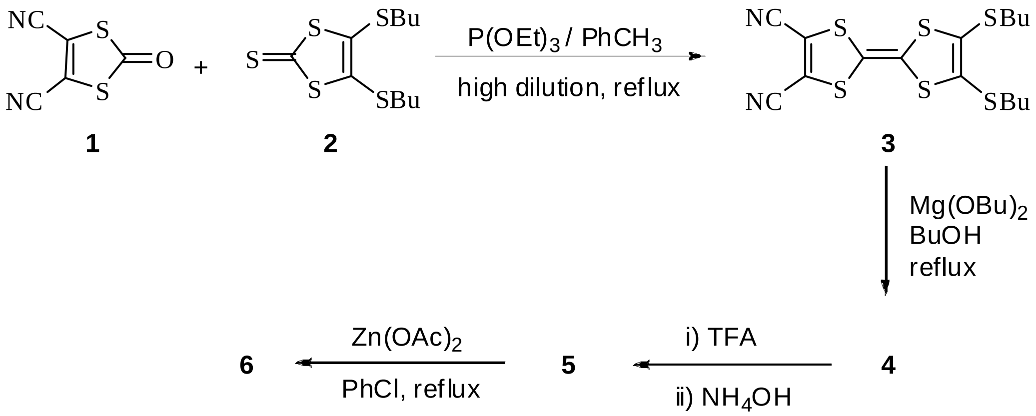
Abstract – Magnesium(II)-porphyrazine (**4**) was prepared *via* a Mg-butoxide templated macrocyclization of 2,3-dicyano-6,7-dibutylthiotetrathiafulvalene in buthanol, and then **4** was converted to metal-free porphyrazine (**5**) by treatment with trifluoroacetic acid in the dark. **5** reacted with excess zinc acetate to give zinc(II)-porphyrazine (**6**) in the chlorobenzene. Their structure has been characterized by ^{1}H NMR, MALDI-TOF-MASS, UV-VIS, ESR and EA, and self-assembly behavior of **4** was studied with the help of TEM and DLS data. **4** self-assembled to spherical aggregates in toluene.

INTRODUCTION

Phthalocyanines(Pcs) and their macrocyclic analogues are currently in focus for application in supramolecular and materials chemistry due to that they show a rich and diverse chemistry as well as specific electronic, optical, structural, and coordination properties,[1] for which phthalocyanine chromophore has been extensively modified to enhance their desired properties. A significant modificaton of the Pcs system is introducing one, two, four, or eight tetrathiafulvalenes(TTFs) units to the ring periphery, in which TTFs units covalently linked by a space group.[2] It is worthy of note that tetrakis(tetrathiafulvalene-crown-ether)-substituted metal-free and copper Pc self–assembled to helical tapes with nanometers wide and micrometers long, which show potentially novel electronic and structural properties.[3] Very recently, four tetrathiafulvalene unit direct annulated metal-free and metallophthalocyanine have been reported for their synthesis and electrochemical and photophysical properties.[4] Their solution electrochemical data show two reversible four-electron oxidation waves, indicating that these fused system are strong π-electron donors, which give rise to tetra- or octaradical cation species and that tetrathiafulvalene unit acts as an efficient reductive electron-transfer quencher for the Pc emission ,but on its oxidation, an intense luminescence is switched on. On the other hand, it is surprising that TTF-derived porphyrazine was scarcely studied even though it is an analogue of phthalocyanine which having same nitrogen-contaning 18-π elecrton conjugated system besides only one report about TTF-derived pyrazinoporphyrazine.[5]

In here, we report the first examples of tetrakis-TTF-annulated Pz molecules, specifically their preparation, characterization as well as aggregation.

RESULTS AND DISCUSSION



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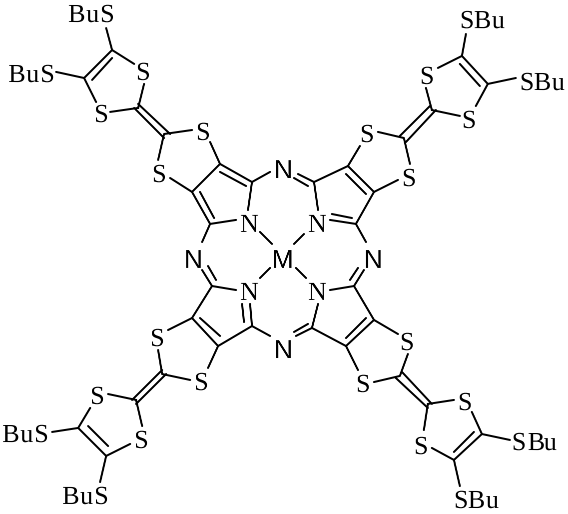
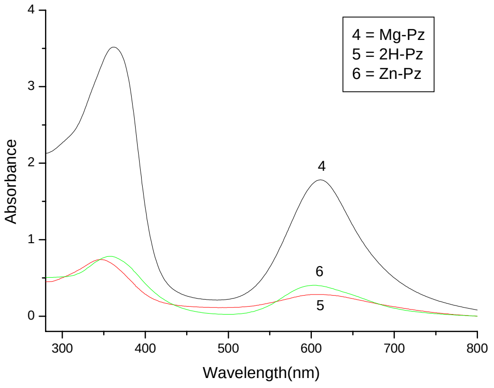


4 M=Mg
5 M=2H
6 M=Zn

Previously, we have been reported that the parent 2,3-dicyano-6,7-butylthiotetrathiafulvalene(**3**) was prepared by cross-coupling reaction of 4,5-dicyano-1,3-dithiol-2-one with 4,5-dubutylthio-1,3-dithiol-2-

thione in the triethyl phosphite under high dilution condition.[6] With this building block, we synthesized the targeted compounds(**4**-**6**) as show in Scheme 1. Mg-porphyrazine **4** was prepared by a Mg-butoxide templated self-tetramerization of 2,3-dicyano-6,7-dibutylthiotetrathiafulvalene(**3**) in Butanol in 35% yield. Demetalation of **4** with trifluoroacetic acid gave metal-free porphyrazine(**5**) in 63% yield. Upon acting of zinc acetete, **5** was converted to Zn-porphyrazine **6** in 73% yield. The MALDI-TOF-MS spectrum of **4** showed peaks at *m/z* 1747.62 which corresponds with the M^+ (1747.18) of **4**. Furthermore, small peak at *m/z* 3496.55 corresponding with the MM^+(3494.36) of **4** were founded, indicating the aggregation is occurred. The MALDI-TOF-MS spectra of **5** and **6** featured the peaks at 1726.50 and 1788.50, respectively, corresponding to M^++1(1725.89) of **5** and M^+(1788.26) of **6**. The ^{1}H NMR spectra of **4**-**6** recorded in $CDCl_3$ featured only very broad signals, which could be attributed to the presence of radical cation of tetrathiafluvalene units or slow tumbing resulting from aggregation in solution.[7] It is noticeable that the UV-VIS absorption spectra of these compounds(**4**-**6**) no appeared the sharp peak(about 700nm) of Q-band arising from monomer as distinct from tetrathiafulvalene-annulated phthalocyanene.[4] The Q-band and B-band(or soret band) of these compounds appeared at 611nm and 363nm for **4**, 608nm and 346nm for **5**, and 603nm and 358nm for **6** without any split, respectively (Figure 1). The broadening and blue shifting of Q-band should be attributable to aggregation of monomers through the strong intermolecular Pz-Pz, Pz-TTF and TTF-TTF $\pi-\pi$ interaction.[3]



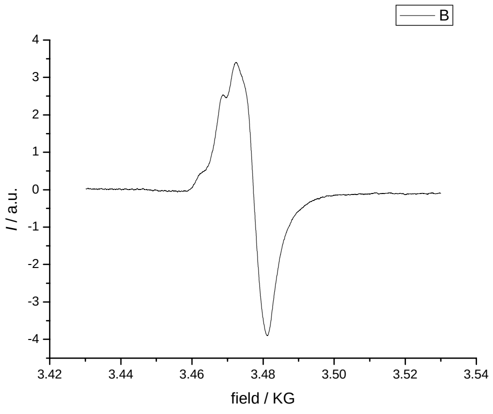


Figure 1. Absorption spectra of compounds **4**,**5** and **6** in $CHCl_3$(c=5 x 10^{-5}M)

Figure 2. ESR spectrum of **4** in solid state

Electron paramagnetic resonance(EPR) spectroscopy of **4** showed strong broad signal arising from radical cation with several shoulder signal at g=2.0059 in solid, which is consistent with the TTF radical cation.[8] In order to identify several shoulder signals, growth character test of microwave power have been carried out at 0.2mW and 100mW. The results revealed that the ratio of signal 1, 2 and 3 at 0.2mW are 7.7:5.7:1, whereas at 100mW the ratio change to 6.6:6.6:1, indicating the several shoulder signals are attributable to overlape of several radicals, and that not from hyperfine structure(Figure 3).

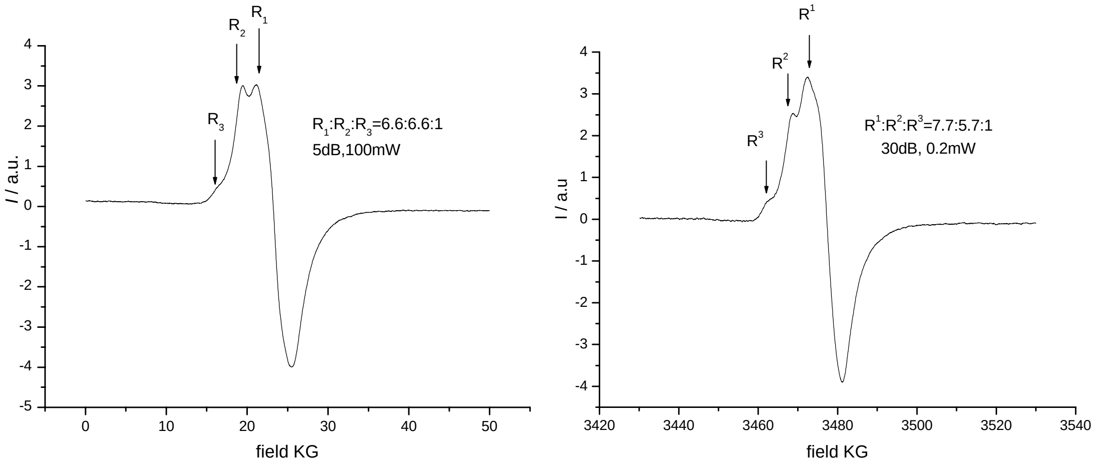


Figure 3. ESR spectra of **4** in solid state at different power

In order to characterize futher the structure of Tetrakis-TTF-Pzs, the electrochemical sduty of compounds **3** and **4** was carried out by using cyclic voltammetry in benzonitrile. The cyclic voltammogram of compound **3** shows two oxidation waves. Each oxidation wave wan assigned to a one-electron process. The TTF unit is oxidized to the radical cation at a potential of 1.05V vs Ag/AgCI. The second oxidation potential corresponding to the formation of the dication is located at 1.32V. In comparison to the TTF molecule, both oxidation steps are shifted to higher oxidation potential duo to the electron-withdrawing effect of the cyano groups. The cyclic voltammogram of compound **4** reveal that the TTF moieties are

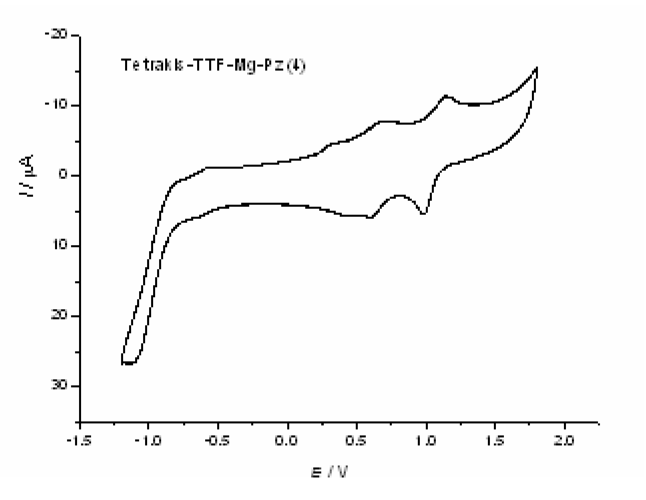


Figure 4. Cyclic voltammogram of 4, in 0.1M tetrabutylammonium hexafluorophosphate in CH_2Cl_2/CH_3CN(5/1,v/v) at $0.1Vs^{-1}$, Pt electrode.

oxidized in two reversible steps involving two four-electron processes at 0.67V and 1.04V, respectively (Figure 4). Noteworthy, the first oxidation potential is splitted to two broaded waves, which is characteristic of a molecular system in which the donor moieties interact through conjugation and/or through space.[9] In the our system it is caused by the annulation of the four TTF units to the porphyrazine core, which results in a high degree of aggregation and also a stabilization of the monoradical cation. A reversible one-electron wave was found at -0.58V vs Ag/AgCI, which can be assigned to a reduction of the porphyrazine core. These behavior very similar to the tetrathiafulvalene-annulated phthalocyanine[4].

Dynamic light scattering (DLS) measurements for the toluene solution of Mg-Pz (**4**) showed that the molecules self-assembled into aggregates of uniform size (see Figure 4). The average diameter of aggregates was observed to be approximately 205 nm, whose diameter is larger than the molecule stretching length 2.3 nm by far, suggesting that the **4** organized to spherical aggregates in toluene. Further evidence for the formation of these aggregates was confirmed by TEM experiments. As shown in Figure 5, the images also revealed spherical aggregates that are about 200nm in diameter and are thus consistent with the results obtained from DLS measurement.

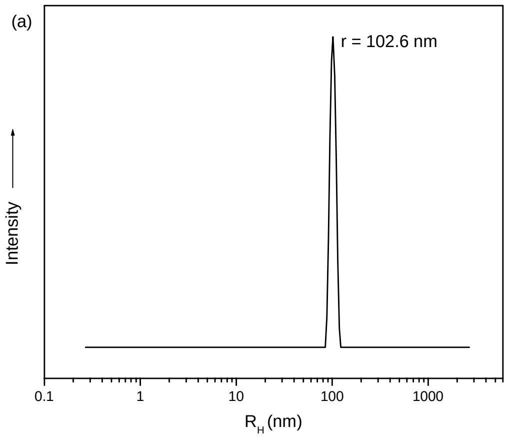


Figure 4. Dynamic laser light scattering study

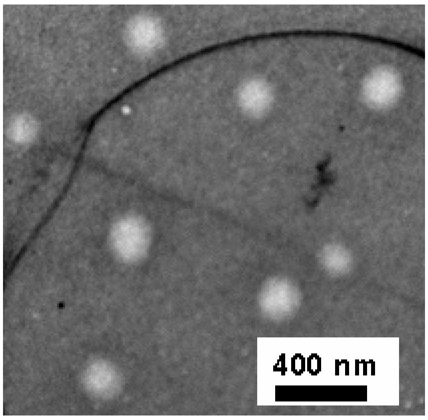


Figure 5. Transmission electron micrograph of 4 in toluene.

In summary, we have synthesized the tetrakis-TTF-annulated Pz molecules(**4**,**5** and **6**) for the first time and studied the aggregartion behavior of Magnesium complex **4**, which self-organises into spherical aggregates.

Further study on complete physical characterization and structural confirmation of the spherical aggregates, functionalization and generation of mono-, bis-,and tris-(tetrathiofulvale)-annulated porphyrazines and TTFs convalently linked porphyrazines are in progress.

EXPERIMENTAL

The ^{1}H NMR spetra were recorded with a Bruker AV-300 spetrometer(300MHz). The UV-VIS spectra were taken on a Hitachi U-3010 spectrophotometer. The MALDI-TOF-MS were obtained by a Shimadzu AXIMA-CFR^{TM} *plus* spectrometer .The ESR spectra were recorded using a Bruker ER200D spectrometer. Cyclic voltammetry was carried out on a Potentiostat/Galvanostat 273A instrucment employing 0.1M Bu4PF6 as the supporting electrode in benzonitrile, with sweep speed of 100mv/s. The dynamic light scattering study was carried out by a Malvem CGS-3 instrument. The trasmission electron micrograph was taken using a JEOL JEM-2010 microscopy. Starting materials 1,2 and 3 were prepared according to reference.[6]

Tetrakis-TTF-Mg-Pz (**4**)

Magnesium (273 mg, 11.4 mmol) and dry *n*-BuOH (30 mL) was heated to reflux under Argon. At reflux, a small chip of iodine was added to facilitate the formation of magnesium butoxide. After 12 h at reflux, the compound **3** (15 mg, 0.35 mmol) was added to the butoxide mixture , the solution turned a dark blue from purplish red. After 3 h the reaction was stopped and the reaction mixture was cooled to rt. The precipitate was collected by suction and washed with dilute hydrochloric acid. The dark blue solid was dissolved in $CHCl_3$, filtered and washed successively with $CHCl_3$ until the filtrate turned to colorless. The dark blue filtrate was rotarily evaporated and the residue was chromatographed (silica gel , CH_2Cl_2/MeOH, 40/1) to give **4** as a dark blue solid(53. 6mg, 35.2%); mp >250 ℃; ^{1}H NMR($CDCl_3$): δ 0.99(brm, 24H), 1.58(brm, 32H), 2.96(brm, 16H); MALDI-TOF-MS(1,8,9-anthracenetriol) *m/z* 1747.62. Anal. Calcd for $C_{64}H_{72}MgN_8S_{24}$: C, 44.00; H, 4.15; N, 6.41. Found: C, 43.40; H, 4.35; N, 6.09.[10]

Tetrakis-TTF-2H-Pz (5)

Porphyrazine derivatives **4** (40 mg, 0.023 mmol) was dissolved in trifluoroacetic acid (5 mL). In the dark, the solution was stirried for 20 min and stored in the dark for 24 h, then the reaction mixture was poured onto crushed ice and neutralized with concentrated NH_4OH resulting in a deep blue solid which was collected by filtration and washed thoroughly with water, and MeOH. The solid was recrystallized from CH_2Cl_2-MeOH to give deep blue powder (25 mg, 61.3%); mp >250 ℃; ^{1}H NMR($CDCl_3$): δ 0.60-1.30(brm, 24H), 1.30-2.00(brm, 32H), 2.60-3.50(brm, 16H); MALDI-TOF-MS(1,8,9-anthracenetriol) *m/z* 1726.50. Anal. Calcd for $C_{64}H_{74}N_8S_{24}$: C, 44.32; H, 4.25; N, 6.19. Found: C, 44.56; H, 4.32; N, 6.50.

Tetrakis-TTF-Zn-Pz (6)

Metal-free Pz (**5**) (20 mg, 0.01 2mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (excess) were dissolved in chlorobenzene (5mL) and heated to reflux for 5 h under argon. The reaction mixture was brought slowly back to rt, and the resulting precipitate was filtered and washed with dilute hydrochloric acid and water. The solid was dried under vacuum to give dark blue powder (15.12 mg, 72.9%); mp >250 ℃; ^{1}H NMR($CDCl_3$): δ

0.70-1.30(brm, 24H), 1.30-2.10(brm, 32H), 2.60-3.40(brm, 16H); MALDI-TOF-MS(1,8,9-anthracenetriol) *m/z* 1788.50. Anal. Calcd for $C_{64}H_{74}N_8S_{24}$: C, 43.42; H, 4.21; N, 6.11. Found: C, 42.99; H, 4.06; N, 6.27.

ACKNOWLEDGEMENTS

We gratefully acknowledge the National Science Foundation of China for the financial support (No. 20462001 and No.20662010).

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