

An Unprecedented Self-Assembled Porous Framework Constructed by Intermolecular S⋯S Contacts

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Received April 30, 2012, Accepted May 8, 2012

Key Words : ET, Ferrocene, Self-assembly, Porous framework, Intermolecular S⋯S contact

In contrast to the polar hydrogen bond donor-acceptor pairs, thiol-containing moieties are not regarded as good hydrogen bond tectons due to their insufficient polarity.¹ On the other hand, although it is not directional, the intermolecular S⋯S interaction can be used in forming functional molecular assemblies as exemplified in the sulfur-rich molecular complexes of 4,5-bis(ethylenedithio)tetrathiafulvalene (ET) and metal-bisdithiolene complexes.² These intermolecular charge transfer complexes need close contacts in solid states to exhibit electrical conductivity or magnetic properties, and the S⋯S interactions provide favorable interactions among the molecular components. The significant strength of this intermolecular interaction originates from a complementary electrophile-nucleophile interaction, or can be explained by a polar flattening model.^{3,4} It is envisioned that S⋯S interactions will lead to more examples showing molecular assemblies in the solid state. Herein, we report the synthesis and crystal structures of the asymmetrical FcVET compound (Fc = ferrocenyl; VET = (4,5-vinylenedithio-4',5'-ethylenedithio)tetrathiafulvalene) which has a unique integrated structure linked by intermolecular S⋯S interactions.

We previously reported the synthesis and properties of a symmetrical diferrocenyl-VT compound (VT = 4,5-bis(vinylenedithio)tetrathiafulvalene), which is a sort of modified ET-donor with additional Fe(II)/Fe(III) redox properties.^{5,6} As the electron donating property of VT is affected by Fc, we introduced a ferrocenyl moiety asymmetrically to a VET backbone to make the asymmetrical ferrocenyl-ET compound (FcVET). The typical phosphite-based cross-coupling reaction (Scheme 1) provided the FcVET donor molecule with a moderate yield, and the final product was fully characterized.⁷

The red-orange single crystals of FcVET were grown in a mixed CH₂Cl₂/MeOH solvent pair by a slow diffusion

method. The single crystals with lengths of 3-10 mm have a hexagonal-rod morphology (Figure 1), implying the directional packing of the molecules in the crystal lattice. The single crystal X-ray analysis shows that the unit cell belongs to a trigonal system defined as a hexagonal unit cell setting with very long *a*- and *b*- axes and a short *c*-axis.⁸

The asymmetric unit is composed of an FcVET molecule and occluded solvent molecules: FcVET·(CH₂Cl₂)_{1/6}(CH₃OH)_{1/3}. The molecular structure of FcVET has two kinked sulfides (S3 and S4) bridging two ethenyl groups in the six-membered 1,4-dithiin ring and almost flat sulfides (S7 and S8). As the four sulfides in the middle of the molecule (S1, S2, S5 and S6) are slightly kinked, the overall conformation of the VET moiety is curved (Figure 2).

In the crystal lattice, two enantiomeric FcVET molecules form a pair in head-to-tail mode with inversion symmetry, which is stabilized by two intra-dimer S1⋯S2^{*} (3.579(5) Å;

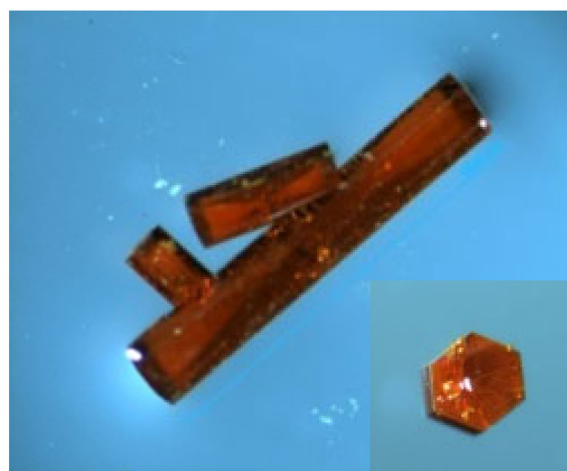
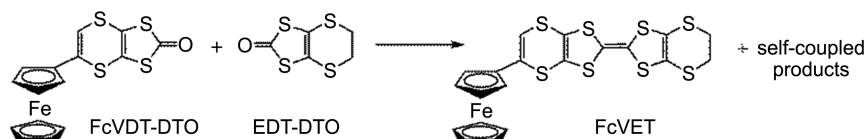


Figure 1. Photograph of FcVET(solv)_x single crystals. The inset shows a clear-cut hexagonal side view.



Scheme 1. Synthesis of FcVET.

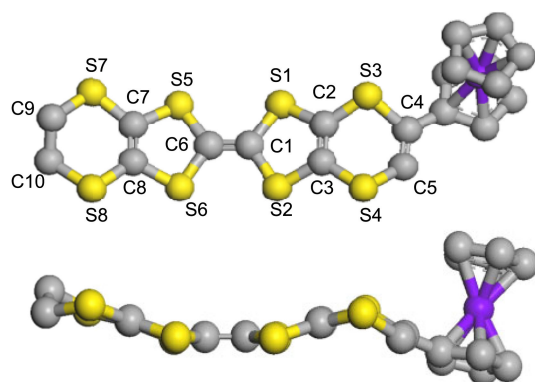


Figure 2. The top view of the molecular structure of FcVET with the selected numbering scheme (above) and its side view (below). The hydrogen atoms are omitted for the sake of clarity.

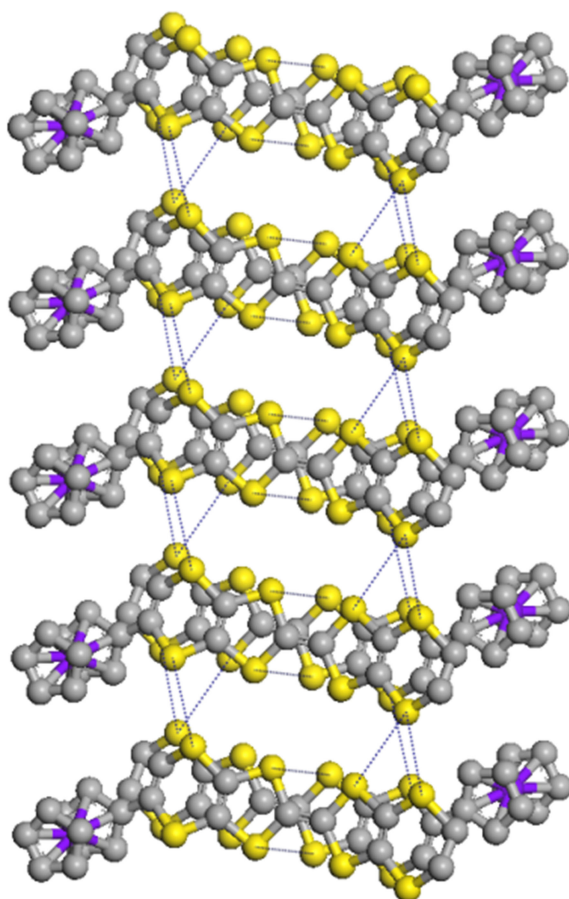


Figure 3. A strip of FcVET dimer expanded along the c -axis. One dimer is composed of two isomers overlapped in head-to-tail mode. The inter- and intra-dimer $S\cdots S$ contacts are denoted by the dotted lines. The hydrogen atoms are omitted for the sake of clarity. $S1\cdots S2^*$ 3.579(5) $S3\cdots S4^\#$ 3.582(6) $S7\cdots S6^\#$ 3.320(5) $S7\cdots S8^\#$ 3.441(6) Å for FcVET·(solv) $_x$ and $S1\cdots S2^*$ 3.568(3) $S3\cdots S4^\#$ 3.572(4) $S7\cdots S6^\#$ 3.310(4) $S7\cdots S8^\#$ 3.437(4) Å for FcVET (*: $x-2/3, y-1/3, z-4/3$; #: $x, y, z+1$).

* $x-2/3, y-1/3, z-4/3$) close contacts (Figure 3) shorter than the sum of the *van der Waals* radii (3.6 Å).⁹ These dimers are arranged along the c -axis in a side-by-side fashion, in which they are inter-connected by the inter-dimer $S\cdots S$ contacts to

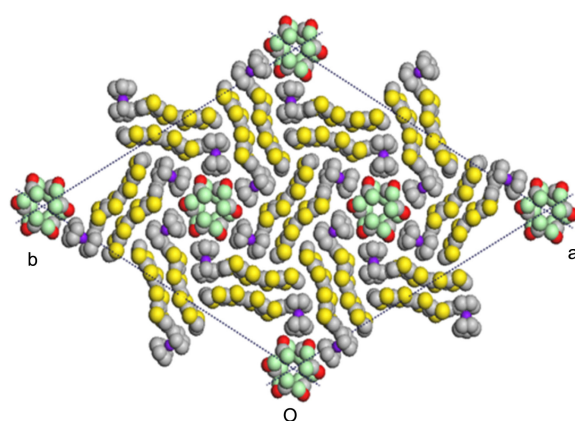


Figure 4. The closed-packing diagram of FcVET·(solv) $_x$ viewed normal to the (001) plane. The hydrogen atoms are omitted for clarity.

form a strip of dimers. The intermolecular short interactions within the strip are supported by the short contacts among $S(3)\cdots S(4)^\#$, $S(7)\cdots S(6)^\#$ and $S(7)\cdots S(8)^\#$ (#: $x, y, z+1$). These dimer strips are in turn arranged to form trigonal columns around each crystallographic three-fold rotoinversion axis in the ab -plane, as shown in Figure 4. These spatial arrangements mean that the six ferrocenyl groups of the FcVET molecules define the wall of the hexagonal 1-dimensional channels along the c -axis. No interactions between the nearest neighboring ferrocenyl groups in this hexagonal ring can be found, as the distance between the carbon atoms in the nearest ferrocenyl groups is much longer than the sum of their *van der Waals* radii (3.4 Å).⁹

Similar hexagonal arrangements of discrete or extended compounds have been reported in some crystals,^{10,11} among which the benzo-annulated TTF derivative with the nitronyl nitroxide radical group (ETBN) constitutes the most similar case to FcVET.¹⁰ The conformational differences in the seemingly similar compounds, ETBN and FcVET, originate from the fact that the molecular plane of the TTF-derivative moiety in ETBN is almost flat due to the presence of the peripheral phenyl group. In addition, the functional group attached to the fused TTF derivative is a five-membered ring containing a nitronyl nitroxide radical group and four methyl groups in ETBN, while the ferrocenyl group, which is known as a better donor, is present in FcVET. These structural and electronic differences may affect the molecular interactions in the crystal. After all, the contacts of the ETBN molecules are the *van der Waals* interactions among the carbon atoms rather than the $S\cdots S$ contacts, as shown in FcVET which has a hexagonal channel filled with solvent molecules. The diameter of the channel (ϕ) is about 7.5 Å considering the *van der Waals* radii of the carbon atoms in the two opposite ferrocenyl groups.

Thermogravimetric analysis (TGA) indicates that the gradual weight loss of the FcVET·(solv) $_x$ crystals from 29.0 °C to 160.5 °C is 4.2% (1/6(CH₂Cl₂) and 1/3(CH₃OH) molecules per one FcVET), which is attributed to the evaporation of the solvent molecules in the channel. The weight loss continues up to 210 °C, and after that the

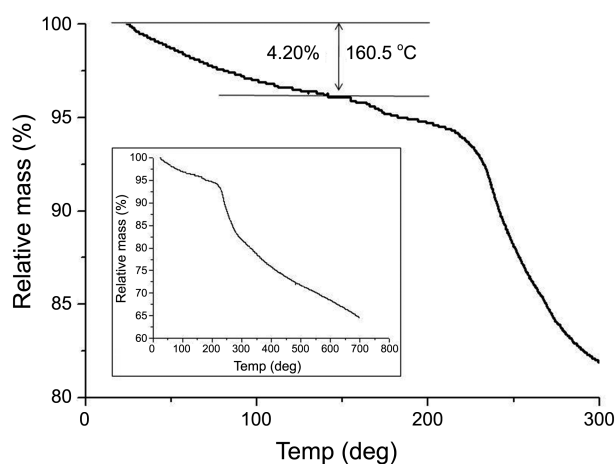


Figure 5. TGA diagram of FcVET·(solvent)_x. The weight loss of 4.20% from 29.0 °C to 160.5 °C corresponds to that of the solvated molecules. Inset shows the diagram within the full temperature range from 29 °C to 700 °C.

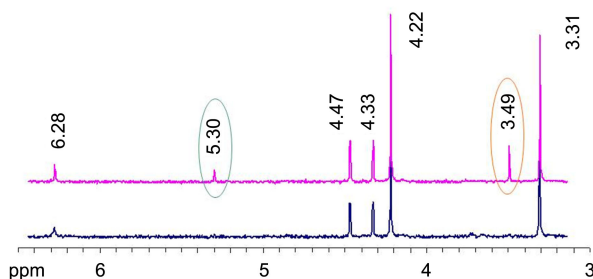


Figure 6. ¹H NMR spectra of FcVET·(CH₂Cl₂)_{1/6}·(CH₃OH)_{1/3} (above) and FcVET obtained after the evacuation of the solvated molecules in the 1D-channel (below). The peaks highlighted at 5.30 and 3.49 ppm correspond to the protons from the solvated CH₂Cl₂ and CH₃OH, respectively.

decomposition of the FcVET molecules begins (Figure 5). In order to quantify the contents of the included solvents, the ¹H NMR spectra were measured in CDCl₃ and compared for FcVET·(solvent)_x and FcVET in Figure 6.¹² Before dissolution, the as-prepared FcVET crystals were evacuated to remove their guest molecules. The ¹H NMR spectrum for FcVET·(solvent)_x showed several resonance peaks, among which the peaks observed at 3.31, 4.22, 4.33, 4.47 and 6.28 ppm belong to the FcVET molecule. The peaks at 5.30 and 3.49 ppm could be assigned to methylene chloride and methanol, respectively. These two peaks are not found in the spectrum for FcVET. Based on the analysis of the integrated peaks, the molecular ratios of methylene chloride and methanol to FcVET were approximately 1:6 and 1:3, respectively, which is in good agreement with the results obtained from the X-ray structure analyses and TGA result.

After careful evacuation of the FcVET·(solvent)_x crystals, the de-solvated crystals were stable without any loss of their crystallinity, which made it possible to examine the crystal structure of the evacuated crystal (FcVET).⁸ The crystal structure of FcVET was almost the same as that of FcVET·(solvent)_x except for the presence of the solvents (Figure 7). The distances of the intermolecular S··S contacts

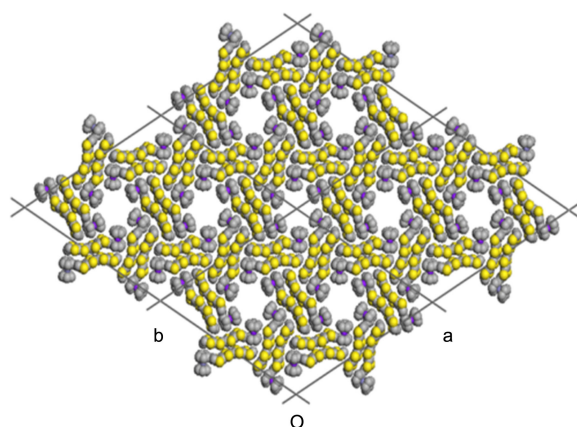


Figure 7. The porous structure of FcVET viewed normal to the (001) plane. The hexagonal 1D-channels are constructed by the ferrocenyl groups around the crystallographic three-fold rotoinversion axis.

are slightly shortened by 0.004–0.011 Å (Figure 3). The crystal parameters of the porous structure FcVET are consequently changed compared to those of FcVET·(solvent)_x: slight contractions along the *a*- and *b*-directions ($\Delta a = \Delta b = 0.043$ Å) with no change along the *c*-direction were found within the error range.⁸ This indicates that the hexagonal framework made of FcVET molecules is rigid, mainly due to the many intermolecular S··S contacts, and sufficient to maintain the void space at 7.8% of the crystal volume.¹³ Considering the fact that this compound is mostly composed of organic moieties and that the molecules in a crystal structure are generally packed as closely as possible in order to maximize the attractive intermolecular interactions,^{14,15} it is not usual for such a stable molecular crystal with a porous framework to be obtained, which in this case is constructed mainly by intermolecular S··S contacts, as shown in FcVET.

When the FcVET·(solvent)_x crystals were put in mixed solvents such as CH₃Cl/MeOH and CH₃Cl/*n*-hexane for several weeks, it was found that no solvent exchange occurred. This result is supported by the observation that the FcVET·(solvent)_x crystals were not formed in these solvent pairs. This strongly points to the solvent specificity in the formation of the crystals.

In summary, an unprecedented self-assembled porous framework is constructed with a multi-sulfur donor molecule with ferrocenyl group (FcVET). The solvent-specific framework maintained by intermolecular S··S contacts forms one-dimensional hexagonal channels ($\phi \approx 7.5$ Å) filled with the solvated molecules. A careful evacuation of the solvated FcVET crystals leaves solvent-free FcVET crystals in which the identical framework structure with the same intermolecular S··S contacts is maintained.

Acknowledgments. This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2010-0011478) and NRF-2003-070-C00029. K. I. Son is grateful for the

financial support by the Seoul Science Fellowship.

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- A mixture of FcVDT-DTO (390 mg, 1 mmol) and EDT-DTO (208 mg, 1 mmol) in freshly distilled P(OEt)₃ (8 mL) was refluxed for 3 h with stirring. The dark brown solution was cooled to room temperature and the orange precipitate was filtered and washed with methanol. The crude product was purified by column chromatography on a silica gel support loaded with CS₂ using ethyl acetate/*n*-hexane (1:2) as the eluent and recrystallized from methylene chloride/methanol. The spectroscopic analyses were carried out on the FcVET crystals dried in *vacuo*. Yield 44%. HR-EIMS (*m/z*) Calcd. for C₂₀H₁₄S₈Fe: 565.8211. Found: 565.8207. ¹H NMR (300 MHz, CDCl₃) δ 3.29 (4H, CH₂, d, *J* = 2.25 Hz), 4.22 (5H, C₅H₅, s), 4.33 (2H, C₅H₄, s), 4.47 (2H, C₅H₄, s), 6.27 (1H, CH, d, *J* = 1 Hz). FT-IR (KBr, cm⁻¹): 3034 (Cp C-H), 2917 (CH₂), 1409 (Cp C=C), 1285 (CH₂ wag), 1253, 1104 (Cp C=C), 1049, 1027, 1000 (asym. ip. ring), 908, 822, 767 (Cp C-H), 489 (Fe-C). UV-vis (MeCN, nm): 210 st, 222 sh, 314 m, 338 sh, 448 w.
- (a) Crystal data for FcVET·(CH₂Cl)_{1/6}·(CH₃OH)_{1/3}·C_{20.50}H_{15.67}-Cl_{0.33}FeO_{0.33}S₈, *M_w* = 591.48, trigonal, space group R-3 (No. 148), *a* = 44.313(8) Å, *c* = 6.514(3) Å, *V* = 11077(6) Å³, *Z* = 18, *T* = 293(2) K, λ = 0.71073 Å, *D_c* = 1.596 g m⁻³, μ = 1.337 mm⁻¹, *R* = 0.0654 [*I* > 2σ(*I*)]. (b) Crystal data for FcVET: C₂₀H₁₄FeS₈, *M_w* = 566.64, trigonal, space group R-3 (No. 148), *a* = 44.270(5) Å, *c* = 6.519(2) Å, *V* = 11064(4) Å³, *Z* = 18, *T* = 293(2) K, λ = 0.71073 Å, *D_c* = 1.531 g/m³, μ = 1.299 mm⁻¹, *R* = 0.0606 [*I* > 2σ(*I*)]. (c) The X-ray crystallographic data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by the direct method and refined by full-matrix least-squares analysis on *F*² using anisotropic thermal parameters for the non-hydrogen atoms with the SHELXL-97 program [16]. Crystallographic data for FcVET and FcVET·(solv)_x have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 878650 and 878651, respectively.
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