

Tetrathiafulvalene-annulated [28]hexaphyrin(1.1.1.1.1.1): a multi-electron donor system subject to conformational control†

Cite this: *Chem. Commun.*, 2013, **49**, 8937

Received 2nd July 2013,
Accepted 13th August 2013

DOI: 10.1039/c3cc44934c

www.rsc.org/chemcomm

Atanu Jana,^a Masatoshi Ishida,^{ab} Kevin Cho,^a Sudip Kumar Ghosh,^a Kyuju Kwak,^a Kei Ohkubo,^c Young Mo Sung,^a Christina M. Davis,^d Vincent M. Lynch,^d Dongil Lee,^{*a} Shunichi Fukuzumi,^{*ce} Dongho Kim^{*a} and Jonathan L. Sessler^{*ad}

Tetrathiafulvalenes (TTF)-annulated [28]hexaphyrin affords an electron rich flexible π -conjugated system whose limiting conformations can be controlled through choice of solvents. The conformation-dependent intramolecular charge transfer character, as well as electron reserve capability of the hexakis-TTF annulated hexaphyrin, was analyzed.

Tetrathiafulvalene (TTF) is an electron rich molecule that can stabilize three different valence states, namely TTF⁰, TTF^{•+} and TTF²⁺ as the result of stepwise oxidations that take place at relatively low redox potentials.¹ This has made TTF and its derivatives attractive for use in a wide range of applications, including molecular-based electronics and optoelectronics.² As a result, TTF has been incorporated into a variety of molecular scaffolds and ensembles, which have been exploited *inter alia* as receptors for electron deficient guests,³ redox active ligands⁴ and molecular machines.⁵ Moreover, Misaki and coworkers⁶ suggested that grafting TTF subunits onto a π -conjugated platform could provide an approach to developing high charge storage capacitors and molecular batteries. While TTF-porphyrins are known,⁷ to date TTF has yet to be incorporated into so-called expanded porphyrins. One expanded porphyrin of particular interest is the *meso*-(pentafluorophenyl) substituted [28]hexaphyrin(1.1.1.1.1.1).⁸ This system possesses a flexible π -framework that is capable of dynamic inter-conversion between limiting Möbius aromatic and Hückel anti-aromatic conformations in solution. The use of this expanded

porphyrin as a tethering core-unit for annulated TTF subunits was thus expected to provide a system containing multiple redox centres whose interactions could be controlled through molecular motion. Depending on the nature of these interactions, limiting scenarios can be envisioned wherein the coupling between the individual TTF subunits is either strong or weak. This, in turn, would allow the redox features of the overall system to be perturbed through the application of “external stimuli”, such as solvent, which are known to affect the electronic and conformational features of the parent unfunctionalised system **3**. Of particular interest would be the weak coupling limit since in this case the TTF units would act independently allowing a large number of electrons to be transferred at or near the same potential thus providing a new type of “electron reservoir”.⁹

In order to test these hypotheses we have prepared and report here a new TTF-annulated *meso*-aryl [28]hexaphyrin (1.1.1.1.1.1) (**1**). As detailed below, the conformation, electronic, and redox properties, of this system may indeed be modulated through appropriate changes in solvent. In dichloromethane, **1** acts as an effective electron reservoir. This is not the case in acetonitrile.

The TTF-annulated [28]hexaphyrin (**1**) was prepared *via* a conventional one-pot condensation reaction. Briefly, the benzo-TTF pyrrole **2** and 2,3,4,5,6-pentafluorobenzaldehyde were subject to borontrifluoride etherate-catalysed condensation in dry CH₂Cl₂, followed by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) oxidation. This afforded a set of higher order polypyrrolic macrocyclic products, rather than the porphyrin derivative,^{7c} as determined by mass spectrometric analysis (Fig. S1 in ESI†).¹⁰ Purification of the crude mixture *via* chromatography over silica gel, followed by recycling preparative HPLC, then gave compound **1** in 6% yield. The purity of compound **1** was confirmed by elemental and high performance liquid chromatographic analyses (Fig. S2 and S3, ESI†).

Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of diethyl ether into a solution of **1** in CHCl₃. The resulting structure revealed that the core hexaphyrin adopts a “figure-eight” conformation, which is similar to that of β -tetraphenyl-substituted [28]hexaphyrin¹¹ (Fig. 1 and Fig. S4; cf. ESI†). Evidence for hydrogen bonding interactions between the

^a Department of Chemistry, Yonsei University, Seoul 120-749, Korea.

E-mail: dongho@yonsei.ac.kr, dongil@yonsei.ac.kr

^b Education Center for Global Leaders in Molecular Systems for Devices, Kyushu University, Fukuoka 819-0395, Japan

^c Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency, Suita, Osaka 565-0871, Japan. E-mail: fukuzumi@chem.eng.osaka-u.ac.jp

^d Department of Chemistry and Biochemistry, The University of Texas at Austin, Texas 78712-0156, USA. E-mail: sessler@cm.utexas.edu

^e Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea

† Electronic supplementary information (ESI) available: Synthetic experimental, details of spectroscopic, calculational and electrochemical analyses, and X-ray experimental. CCDC 946736. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc44934c

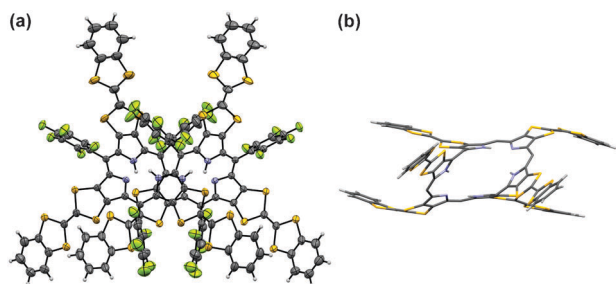


Fig. 1 Single crystal X-ray structure of **1**; (a) top view and (b) side view. *meso*-Pentafluorophenyl groups are omitted in the side view for clarity. The thermal ellipsoids are scaled to the 50% probability level.

pyrrolic NHs and the *N*-imines came from the short $N_{\text{amine}}-N_{\text{imine}}$ distances within the core (e.g., 2.689 and 2.730 Å, respectively). In addition, steric clashes between the β -peripheral TTF-moieties and the *meso*-aryl substituents are seen in the structure of **1**; these are thought to reflect the figure-eight geometry.¹²

The spectroscopic data for compound **1** are also consistent with the proposed structure. A high-resolution MALDI-TOF mass spectrum of **1** exhibited a parent peak at $m/z = 2817.5187$, which is consistent with the theoretical isotope patterns for $C_{114}H_{28}F_{30}N_6S_{24}$ formulated as a 28 π -electron species (Fig. S5 and S6, ESI†). The 1H NMR spectrum of **1** recorded in CD_2Cl_2 at room temperature exhibits two singlets at $\delta = 13.64$ and 16.58 ppm for the pyrrolic-NH protons (Fig. S7, ESI†). Overlapping signals were also observed in the aromatic region between 6.82 and 7.49 ppm that are assigned to be peripheral C-Hs of benzo-TTF subunits. These spectral signals provide support for the conclusion that in dichloromethane hexaphyrin **1** exists in the form of a weakly antiaromatic Hückel species with a figure-eight conformation (designated as **1-H** in Scheme 1). This is in agreement with what is observed for unfunctionalised [28]hexaphyrin derivatives.^{8,11}

The steady-state absorption spectrum of **1** recorded in CH_2Cl_2 exhibited a typical broad peak at 564 nm in the UV-vis spectral region, as well as a characteristic weak NIR band tailing to 1800 nm (Fig. 2). The latter band is attributed to a one-photon forbidden transition, which is expected for a $4n$ π -electron antiaromatic compound with a small HOMO–LUMO energy gap.⁸ In accord with the one-photon absorption spectra, the femtosecond transient absorption (fs-TA) spectrum of **1** in toluene (Fig. S8, ESI†) showed a broad excited state absorption (ESA) band between 650–850 nm

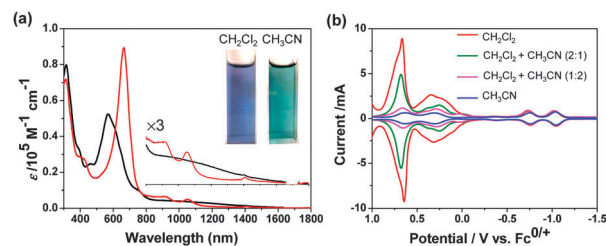


Fig. 2 (a) UV-vis-NIR absorption spectra of **1** recorded in CH_2Cl_2 (black) and CH_3CN (red). Inset: photos of solutions containing **1** showing the colour in CH_2Cl_2 and CH_3CN . (b) Square wave voltammograms of **1** recorded in varying mixtures consisting of CH_2Cl_2 and CH_3CN .

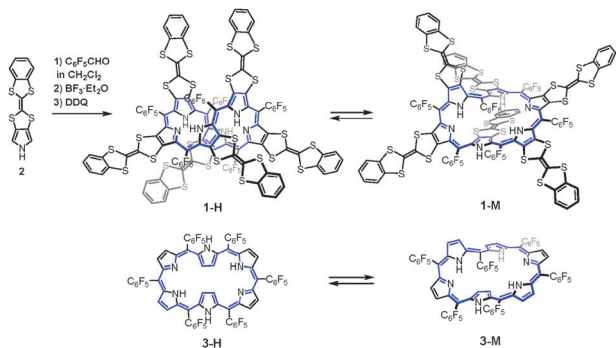
and the excited state decay of **1** is ultrafast (biexponential decay with time constants of 0.2 and 5.0 ps). These findings support the proposed figure-eight Hückel-type structure shown as structure **1-H** in Scheme 1.

Based on prior studies of unfunctionalised hexaphyrins (e.g., **3**),⁸ it was expected that the conformation features, and hence photo-physical and electrochemical properties, of **1** could be readily tuned. In particular, the use of more polar solvents or lower temperatures was expected to affect the switching of the figure-eight conformer, that is dominant in CH_2Cl_2 , to a twisted geometry (i.e., **1-M**, Scheme 1) with spectral features that resemble those seen for the Möbius aromatic form of unfunctionalised hexaphyrin (**3-M**; Scheme 1).¹³ In fact, when the temperature was lowered from 45 to -80 °C, the absorption spectrum of **1** recorded in tetrahydrofuran (THF) exhibited an intense Soret-like band that is red-shifted relative to what was seen at room temperature (from 642 nm to 679 nm). The appearance of a Q-like band around 1000 nm was also observed (Fig. S9, ESI†). These latter spectral features are identical to those found in the UV-vis spectrum of **1** in acetonitrile. The distinct solvatochromic behaviour of **1** can be followed easily by eye (Fig. 2). These observed changes, which occur in a monotonic fashion as the acetonitrile : CH_2Cl_2 ratio increases (Fig. S10, ESI†), are attributed to a conformation change of **1-H** to a somewhat more planar, twisted form (**1-M**) as observed in other [28]hexaphyrin systems.^{13,14}

On the basis of comparisons involving the steady-state absorption spectra of the benzo-TTF pyrrole (**2**) subunit and the Möbius [28]hexaphyrin (**3-M**), the extremely weak intense tailing band observed in the NIR region (~ 1800 nm) for **1-M** is attributed to intramolecular CT transitions between the TTF fragments and the hexaphyrin core.

Proton NMR spectroscopic studies of **1** in different solvents provide further support for the conclusion that the conformation of **1** changes with polarity of the solvents. For instance, upfield shifts for the pyrrole NH resonances are observed as the polarity of the solvent increases (Fig. S7 and S11–S14, ESI†); this is consistent with the proposed increased flattening of the still-twisted macrocycle.

To gain insight into the differences in the electronic properties of **1-H** and **1-M**, the DFT calculations (B3LYP/3-21G*) for two conformers were carried out. The resulting frontier molecular orbital (MO) maps demonstrated a clear difference in the distribution patterns in the electron occupied MOs (Fig. S15–S17, ESI†). Specifically, both the HOMO and LUMO of the Hückel form **1-H** are predominantly delocalised over the hexaphyrin π -circuit with a small contribution from the TTF subunits. In contrast, the HOMOs



Scheme 1 Synthesis and reversible interconversion between the limiting figure-eight (**1-H**) and twisted conformers (**1-M**). The chemical structure and its dynamic conversion of unfunctionalised hexaphyrin (**3**) are shown.

(up to HOMO – 6) of the twisted form, **1-M** is localised on the TTF fragment, with the LUMO mainly delocalised over hexaphyrin core. On this basis, we conclude that charge transfer interactions from the TTF-donor to the central hexaphyrin acceptor are controlled by the conformation of the 28 π -conjugated core. The broad CT band of **1-M** seen in the NIR region was also identified by the vertical transition stick spectra obtained by TD-DFT calculations (Fig. S18, ESI†).

Consistent with the proposed solvent driven changes in conformation and electronic structure as put forward above, the fs-TA spectrum of **1** recorded in the relatively polar solvent benzonitrile was found to be very different from that observed in toluene. A strong ground-state bleaching (GSB) band at 677 nm and weak ESA bands in the higher region (~ 500 nm) and far red to NIR region (~ 700 nm) were observed. The decay of the ESA band was used to estimate the excited state lifetime (Fig. S8, ESI†). The resulting value (11 ps) is, in fact, significantly shorter than that of the corresponding Möbius [28]hexaphyrin, **3-M** (e.g., $\tau_s = 260$ ps at 173 K).¹³ The short lifetime found for **1-M** reflects the intramolecular charge transfer pathway in the excited state as observed in TTF-substituted porphyrins.⁷ Support for this proposed photo-induced charge separation in the specific case of the twisted conformer (**1-M**) came from EPR spectroscopy (Fig. S19, ESI†). The EPR spectrum of **1** recorded in THF at 77 K exhibited a signal at $g = 2.0041$ after photoirradiation using a high pressure Hg lamp,¹⁵ whereas that of **1-H** was silent under these conditions.

The electrochemical properties of **1** were analysed by square wave voltammetry (SWV) in CH_2Cl_2 and CH_3CN solution. Assignments of the oxidation processes were made by comparison with hexaphyrin **3** and the benzo-TTF pyrrole **2** (Fig. S20 and Table S2, ESI†). A number of oxidation processes were seen within the solvent window for **1** (Fig. 2). Cleaner oxidation features were observed upon switching to dichloromethane from acetonitrile (Fig. 2). Specifically, a broad multi-electron oxidation wave centred at ca. 0.33 V (vs. Fc/Fc^+) was seen, with a second sharper oxidation wave at 0.65 V also being observed.

On the basis of control experiments involving hexaphyrin **3** and benzo-TTF pyrrole **2**, the first oxidation wave seen in CH_2Cl_2 was assigned to one-electron oxidations involving the TTF fragments present in **1**, as well as that of the hexaphyrin core. The asymmetric splitting feature observed for the first oxidation may indicate a small degree of intramolecular through-bond interaction between the TTF moieties. However, a relatively sharp wave was seen for the second TTF-based oxidation. The cleaner nature of the second electron transfer is ascribed in part to an electrostatic-induced partial flattening of **1** that occurs upon oxidation.¹⁶ This conformational change results in further inter-subunit separation and reduced electronic coupling between the TTF moieties. Overall 18 electrons, including contributions from the hexaphyrin core, are transferred during the oxidation processes as estimated from an integration of the current (Table S2, ESI†). On this basis, we conclude that in CH_2Cl_2 (but not CH_3CN) TTF-hexaphyrin **1** acts as an effective electron reservoir.

In summary, we have developed a conformationally controlled electron storage system (**1**) that combines a flexible π -electron conjugated macrocycle (hexaphyrin) with redox active TTF fragments.

The electronic, photophysical, and structural features of **1** may be varied *via* an appropriate choice of solvent and temperature. Moreover, these changes may be monitored *via* simple spectroscopic means. These topology-dependent features could make **1** and like systems useful for the development of molecular capacitors and switches.

This work was supported by the U.S. National Science Foundation (CHE-1057904 to J.L.S.), the Robert A. Welch Foundation (F-1018 to J.L.S.), the Japanese Society for the Promotion of Science (No. 20108010 to S.F.), the World Class University (WCU) program (R32-2012-000-10217-0 to D.K., R31-2008-000-10010-0 to S.F.) of the Ministry of Education, Science and Technology, and the National Research Foundation of Korea (20110029735 and 20110022975 to D.L.).

Notes and references

- J. L. Segura and N. Martín, *Angew. Chem., Int. Ed.*, 2001, **40**, 1372.
- (a) D. Canevet, M. Sallé, G. Zhang, D. Zhang and D. Zhu, *Chem. Commun.*, 2009, 2245; (b) T. Sugawara, H. Komatsu and K. Suzuki, *Chem. Soc. Rev.*, 2011, **40**, 3105; (c) H. Dong, C. Wang and W. Hu, *Chem. Commun.*, 2010, **46**, 5211.
- (a) N. Martín, L. Sánchez, M. Á. Herranz, B. Illescas and D. M. Guldi, *Acc. Chem. Res.*, 2007, **40**, 1015; (b) K. A. Nielsen, W.-S. Cho, J. O. Jeppesen, V. M. Lynch, J. Becher and J. L. Sessler, *J. Am. Chem. Soc.*, 2004, **126**, 16296.
- C. Beijer, Y.-H. Tian, B. J. Barker, K. S. Boland, B. L. Scott, E. R. Batista, S. A. Kozimor and J. L. Sessler, *Dalton Trans.*, 2013, **42**, 6716.
- (a) M. B. Nielsen, Z.-T. Li and J. Becher, *J. Mater. Chem.*, 1997, **7**, 1175; (b) J. M. Spruell, A. Coskun, D. C. Friedman, R. S. Forgan, A. A. Sarjeant, A. Trabolsi, A. C. Fahrenbach, G. Barin, W. F. Paxton, S. K. Dey, M. A. Olson, D. Benítez, E. Tkatchouk, M. T. Colvin, R. Carmielli, S. T. Caldwell, G. M. Rosair, V. M. Lynch, G. Hewage, F. Duclairoir, J. L. Seymour, A. M. Z. Slawin, W. A. Goddard III, M. R. Wasielewski, G. Cooke and J. F. Stoddart, *Nat. Chem.*, 2010, **2**, 870–879.
- Y. Inatomi, N. Hojo, T. Yamamoto, S. Watanabe and Y. Misaki, *ChemPlusChem*, 2012, **77**, 973.
- (a) H. Li, J. O. Jeppesen, E. Levillain and J. Becher, *Chem. Commun.*, 2003, 846; (b) K. A. Nielsen, E. Levillain, V. M. Lynch, J. L. Sessler and J. O. Jeppesen, *Chem.-Eur. J.*, 2009, **15**, 506; (c) A. Jana, M. Ishida, K. Kwak, Y. M. Sung, D. S. Kim, V. M. Lynch, D. Lee, D. Kim and J. L. Sessler, *Chem.-Eur. J.*, 2013, **19**, 338.
- (a) A. Osuka and S. Saito, *Chem. Commun.*, 2011, **47**, 4330; (b) S. Saito and A. Osuka, *Angew. Chem., Int. Ed.*, 2011, **50**, 4342.
- (a) D. Astruc, *Chem.-Asian J.*, 2011, **6**, 1679; (b) D. Astruc, *New J. Chem.*, 2009, **33**, 1191.
- The formation of side-products, including the hepta- and octa-pyrrolic analogues of **1**, is inferred on the basis of MALDI-TOF mass spectrometry and HPLC analysis. See ESI†.
- T. Koide, K. Youfu, S. Saito and A. Osuka, *Chem. Commun.*, 2009, 6047.
- M. Toganoh and H. Furuta, *J. Org. Chem.*, 2010, **75**, 8213.
- K. S. Kim, Z. S. Yoon, A. B. Ricks, J.-Y. Shin, S. Mori, J. Sankar, S. Saito, Y. M. Jung, M. R. Wasielewski, A. Osuka and D. Kim, *J. Phys. Chem. A*, 2009, **113**, 4498.
- Attempts to characterise the twisted conformer, **1-M** were precluded by the low solubility in polar solvents at low temperature. The ^1H NMR spectrum of **1** in CD_3CN (298 K) revealed an absence of NH signals and slight shifts in the aromatic CHs resonances, as expected for a fast equilibrium between the figure-eight and twisted forms.
- The radical cation and anion species cannot be distinguished due to their broad EPR signals. The g value of the benzo-TTF pyrrole radical cation is observed at 2.0079. See: S. Fukuzumi, K. Ohkubo, Y. Kawashima, D. S. Kim, J. S. Park, A. Jana, V. M. Lynch, D. Kim and J. L. Sessler, *J. Am. Chem. Soc.*, 2011, **133**, 15938.
- As inferred from titrations carried out using the chemical oxidant, tris(4-bromophenyl)aminium hexachloridoantimonate ("magic blue"), oxidation of **1** gives rise to changes in the spectral features that are consistent with a move to a more planar form (cf. Fig. S21, ESI†).