

A mono-TTF-annulated porphyrin as a fluorescence switch†

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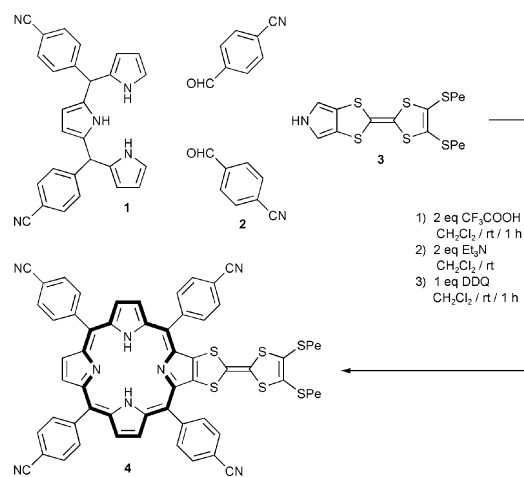
Annulation of one TTF unit directly to the porphyrin chromophore produces an almost nonfluorescent species which can be transformed into a fluorescent species by oxidation of the TTF unit.

Porphyrins¹ play a central role in biological systems and the development of modified porphyrins continues to provide a challenge for synthetic chemists. Modified porphyrins are useful for the understanding of fundamental functions of the photosynthetic reaction centres, such as the antenna function, the stabilisation of charge separation and sequential electron transfer processes.² In addition, porphyrins find their expanding applications in materials science,³ reaction catalysis,⁴ molecular recognition,⁵ and as diagnostic/therapeutic agents⁶ and sensors.⁷ The redox-active tetrathiafulvalene⁸ (TTF) unit is synonymous with the preparation of molecular organic metals and organic superconductivity⁹ which continues to be an active research field. However, during the past few years TTF and its derivatives have been incorporated into elaborate molecular and supramolecular systems such as chemical sensors,¹⁰ charge-separating ligands,¹¹ shuttles¹² and switches. The covalent association of the porphyrin ring system with a TTF unit could produce a donor–porphyrin dyad system which is expected to show electron transfer rather than energy transfer from the TTF donor to the porphyrin ring system.

Recently, we described^{13,14} the first examples of single molecules in which the intriguing optical and metal-ion binding properties of the porphyrin ring system have been coupled with the favourable redox properties of the TTF unit. However, these molecules in which the porphyrin ring system is directly annulated with four TTF units at the periphery consist of a mixture of the neutral porphyrin and its corresponding radical cation porphyrin in a ratio of approximately 4:1. As a consequence of the presence of radicals in the isolated compounds, the ¹H NMR spectroscopic and photophysical characterisation of these tetrakis-TTF porphyrins were rendered almost impossible. To further elucidate the effect of annulating a TTF unit directly to the porphyrin ring system, we decided to prepare the mono-TTF-porphyrin **4**.

Here, we present the synthesis and characterisation of the TTF-porphyrin dyad **4**, together with our preliminary electrochemical and photophysical investigations of this novel TTF-porphyrin dyad **4**.

The synthetic approach to the mono-TTF-porphyrin **4** is outlined in Scheme 1. The tripyrromethane **1** was obtained in 25% yield by the condensation of *p*-cyanobenzaldehyde (**2**) with 5 equiv. pyrrole. To obtain **4**, a cyclisation reaction was carried out in CH₂Cl₂ at room temperature by addition of 2 equiv. of trifluoroacetic acid to equimolar quantities of the tripyrromethane **1** and the monopyrrolo-TTF¹⁵ **3** and 2 equiv. of *p*-cyanobenzaldehyde (**2**). The cyclisation reaction was stopped after 1 h by addition of 2 equiv. of Et₃N, whereupon the resulting red mixture was oxidised (porphyrinogen → porphyrin) with 1 equiv. of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in a one-pot reaction to afford the porphyrin **4**



Scheme 1

as a dark purple solid in 7% yield after purification by means of column chromatography.†

A high-resolution MALDI-MS of **4** showed the exact mass m/z 1095.2184, corresponding to MH^+ • (calcd mass MH^+ • 1095.2242). The ¹H NMR spectrum (300 MHz) of the mono-TTF-porphyrin **4**, recorded in CDCl₃ at 298 K, showed sharp peaks indicating that **4** does not contain any radicals. This is in deep contrast with our previously studied tetrakis-TTF-porphyrins which contained 19% radicals. The β-pyrrolic part of the ¹H NMR spectrum of **4** featured a 2H singlet resonating at δ 8.68 and a 4H AB system ($J = 4.9$ Hz) resonating at δ 8.69 and 8.85, which can be assigned to the resonances for the H_{12,13} and H_{7,18/8,17} protons, respectively. The resonances for the two inner-ring NH protons are observed as a broad 2H singlet resonating at δ –3.00.

The electrochemical characterisation of the mono-TTF-porphyrin **4** was carried out using cyclic voltammetry (CV). As model compounds for **4**, we have also investigated the electrochemical behaviour of the monopyrrolo-TTF derivative **3** and *meso*-tetra(*p*-cyanophenyl)porphyrin¹⁶ (TCPP, **5**) under similar conditions. The deconvoluted voltammogram (Fig. 1a) of **4** revealed four reversible redox processes and the redox potentials are listed in Table 1, together with those for the model compounds **3** and TCPP **5**. The processes at –1.385 and –1.650 V can be associated with the first and second reduction of the porphyrin ring system. They are both anodic shifted as compared to the first (–1.505 V) and second (–1.825 V) reduction processes in the model compound TCPP **5**, indicating that the LUMO orbital of **4** is located at lower energy than the LUMO orbital of **5**. It is reasonable to assume that, the processes at +0.040 and +0.405 V can be associated with the first and second oxidation of the TTF unit, since they take place at potentials which are close to the first (–0.010 V) and second (+0.445) oxidation processes observed in the monopyrrolo-TTF model compound **3**. The first oxidation process associated with the TTF unit in **4** takes place at a potential that is more positive (+50 mV) than that observed for the model compound **3**, an observation which can be accounted for by the presence of an

† Electronic supplementary information (ESI) available: data for **4**. See <http://www.rsc.org/suppdata/cc/b2/b212456d/>

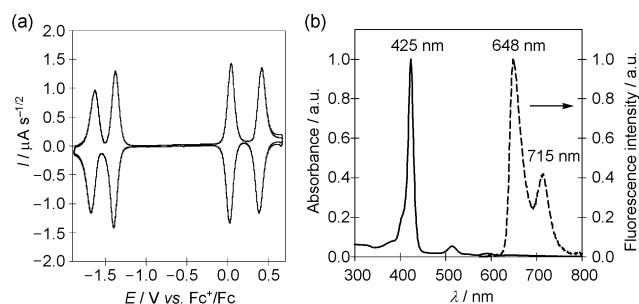


Fig. 1 (a) Deconvoluted voltammogram (vs. Fc^+/Fc) recorded on a solution of the mono-TTF-porphyrin **4** (0.5 mM) in $\text{CH}_2\text{Cl}_2/n\text{-Bu}_4\text{NPF}_6$ (0.1 M) on platinum electrode with a scan rate of 0.1 V s^{-1} . (b) Absorption (THF, 298 K, full line) and emission (THF, 298 K, dotted line) spectra of the mono-TTF-porphyrin **4**. Excitation was performed at 425 nm (Soret band). Note that the fluorescence intensity is very weak.

Table 1 Electrochemical data^a for the mono-TTF-porphyrin **4** and the model compounds **3** and **5** determined by cyclic voltammetry in CH_2Cl_2

Compound	Porphyrin ^b		TTF ^b	
	E_{red}^2 (V) ^c	E_{red}^1 (V) ^c	E_{ox}^1 (V) ^c	E_{ox}^2 (V) ^c
3			-0.010	+0.445
4	-1.650	-1.385	+0.040	+0.405
5	-1.825	-1.505		

^a 298 K, $n\text{-Bu}_4\text{PF}_6$ (0.1 M) as supporting electrolyte, potentials in V vs. the Fc^+/Fc couple. ^b Units involved in the observed processes. ^c Reversible and monoelectronic processes.

electron withdrawing 18 π -electron porphyrin ring system. Since the TTF unit in **4** show the electrochemical characteristics expected for a normal TTF unit, it can be concluded that **4** exists as the tautomer in which the pyrrole *c*-bond in the TTF unit is not included in the delocalisation pathway (shown in bold in Scheme 1) for the 18-annulene system. The electrochemical investigations of **4** show that the TTF unit and the porphyrin ring system can display their individual electrochemical characteristics and that there are only weak interactions between the two components.

The absorption spectrum (Fig. 1b) of the mono-TTF-porphyrin **4** is quite similar to the sum of the spectra of their model compounds **3** and **5**. It showed a strong Soret band at 425 nm and at longer wavelength four weak Q bands at 514, 548, 590 and 647 nm, respectively. These five bands are all associated with the porphyrin ring system, whereas the TTF unit is responsible for weak absorption bands in the 250–350 nm region. These results indicate that in the mono-TTF-porphyrin **4** there are no significant electronic interactions among its chromophoric units in the ground state. However, this is not the case in the excited state. A comparison of the emission spectra (Fig. 1b and 2a) of the mono-TTF-porphyrin **4** and the model compound **5** revealed that the porphyrin fluorescence of **4** is quenched by 98% relative to the model compound **5** lacking the

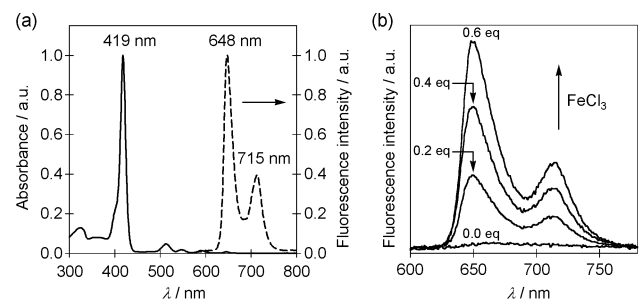


Fig. 2 (a) Absorption (THF, 298 K, full line) and emission (THF, 298 K, dotted line) spectra of the model porphyrin **5**. Excitation was performed at 419 nm (Soret band). (b) Emission (THF, 298 K) spectra of the mono-TTF-porphyrin **4** upon addition of increasing amounts of the oxidant FeCl_3 . Excitation was performed at 425 nm (Soret band).

TTF unit.¹⁷ This observation clearly indicates that substantial electron transfer, from the TTF donor to the porphyrin chromophore, occurs in the emitting excited state of **4**. Removal of one electron from the TTF unit ($\text{TTF} \rightarrow \text{TTF}^{+\bullet}$) in the mono-TTF-porphyrin **4** would prevent the TTF unit from acting as an electron donor and quenching the porphyrin emission. The outcome would be a fluorescence switch comprising of the nonfluorescent mono-TTF-porphyrin and fluorescent mono-TTF⁺•-porphyrin species and activated by oxidation of the TTF unit. A preliminary experiment was carried out to test the potential of the mono-TTF-porphyrin **4** as a fluorescence switch by adding increasing amounts of the chemical oxidant FeCl_3 to a solution of **4**. Absorption spectra recorded on this solution displayed the characteristic band ($\sim 810 \text{ nm}$) of a TTF radical cation and the emission spectra (Fig. 2b) showed that the fluorescence intensity increased upon addition of increasing amounts of FeCl_3 , clearly indicating that **4** has the potential to act as a fluorescence switch.

Preliminary experiments have shown that treatment of **4** with $\text{Zn}(\text{OAc})_2$ afford the zinc complex of **4** in 83% yield.

In summary, a novel mono-TTF-annulated porphyrin **4** has been synthesised and characterised. The electrochemical and photophysical investigations of **4** showed that there are no significant interactions among its chromophoric units in the ground state. However, substantial electron transfer from the TTF donor to the porphyrin chromophore, occurs in the emitting excited state of **4** and preliminary experiments have shown that the emission intensity can be controlled by the oxidation state of the TTF unit. The unique properties of this mono-TTF-annulated porphyrin **4** make it an attractive candidate for incorporation into optical sensors and devices.

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