Electronic Supplementary Information

Metastable oxidation states of tetrathiafulvalenes on the surface of liposomes

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NMR and MS spectra for Chol-TTF 1

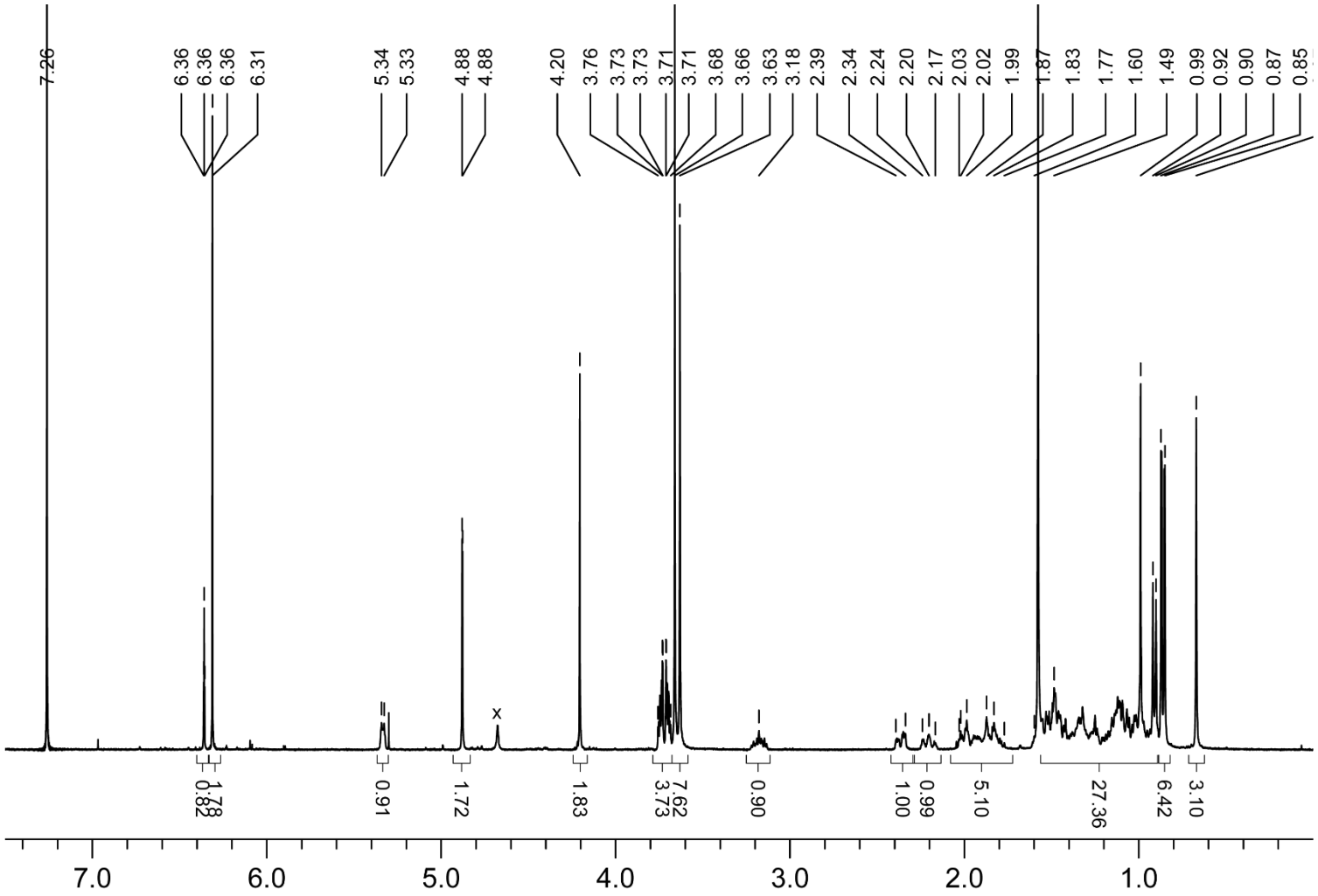

Figure S1. ^{1}H NMR spectrum of Chol-TTF **1** (360 MHz, $CDCl_3$).

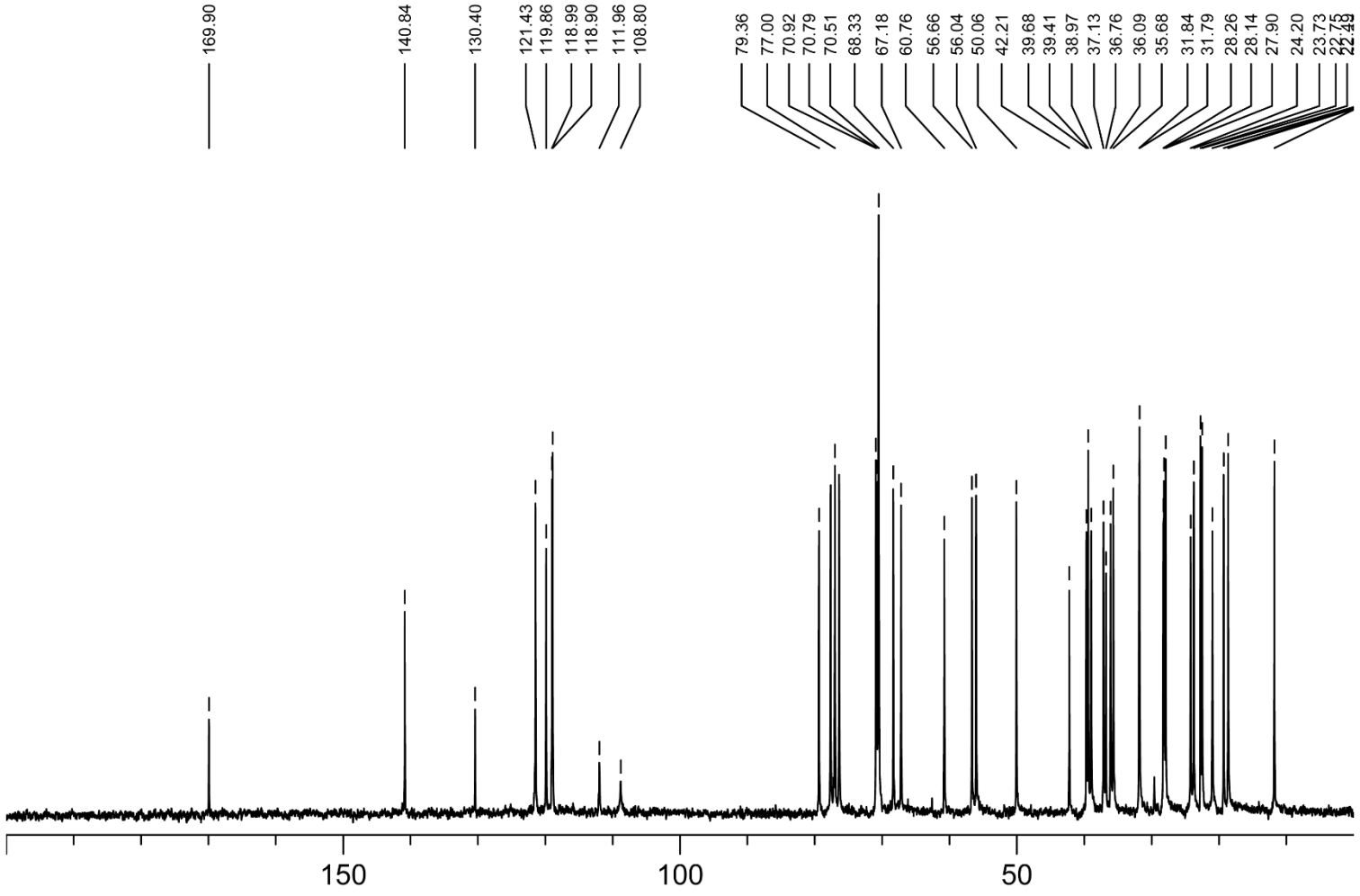

Figure S2. ^{13}C NMR spectrum of Chol-TTF **1** (50 MHz, $CDCl_3$).

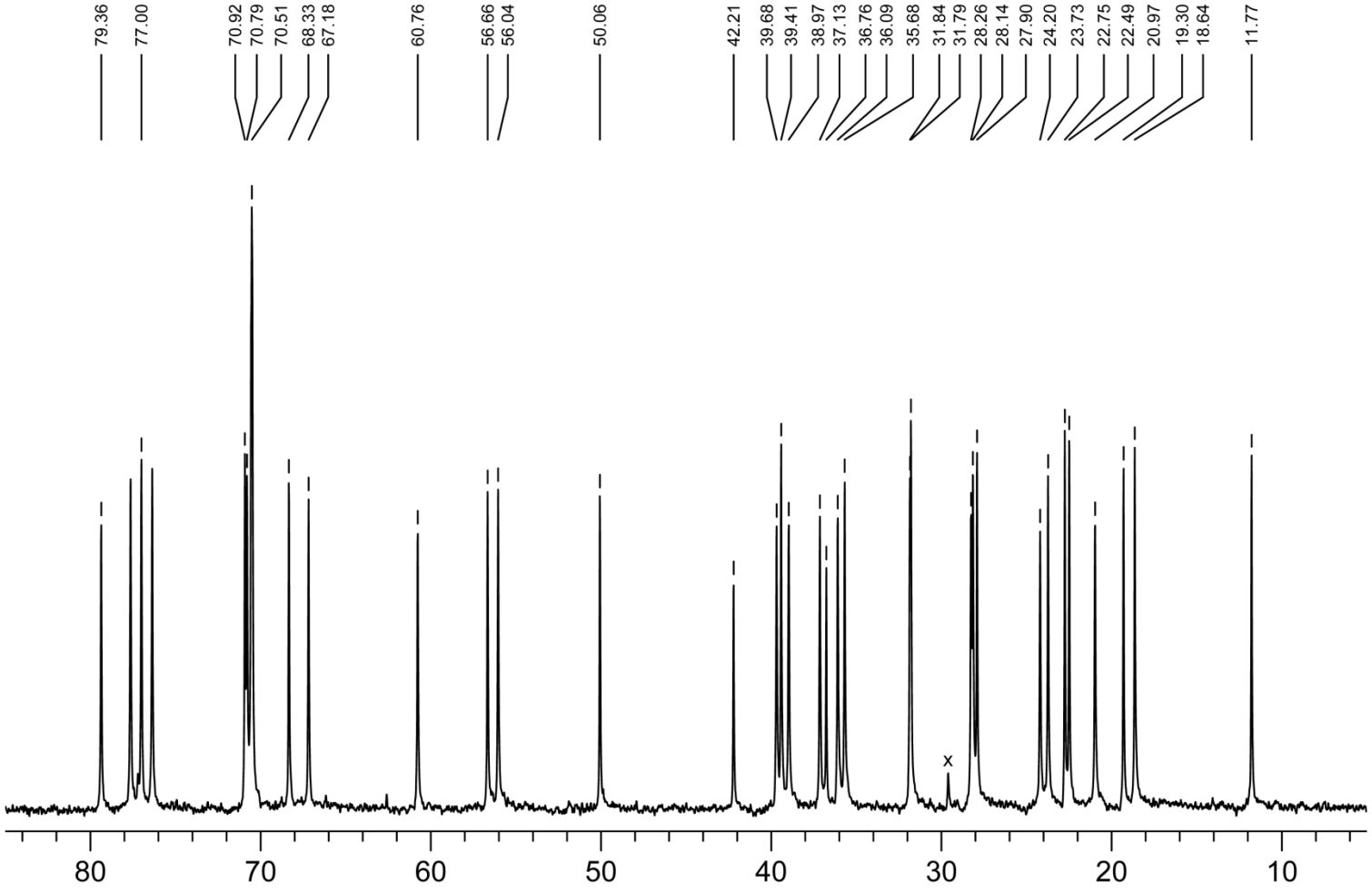

Figure S3. ^{13}C NMR spectrum of Chol-TTF **1** (50 MHz, $CDCl_3$), zoom on the aliphatic region.

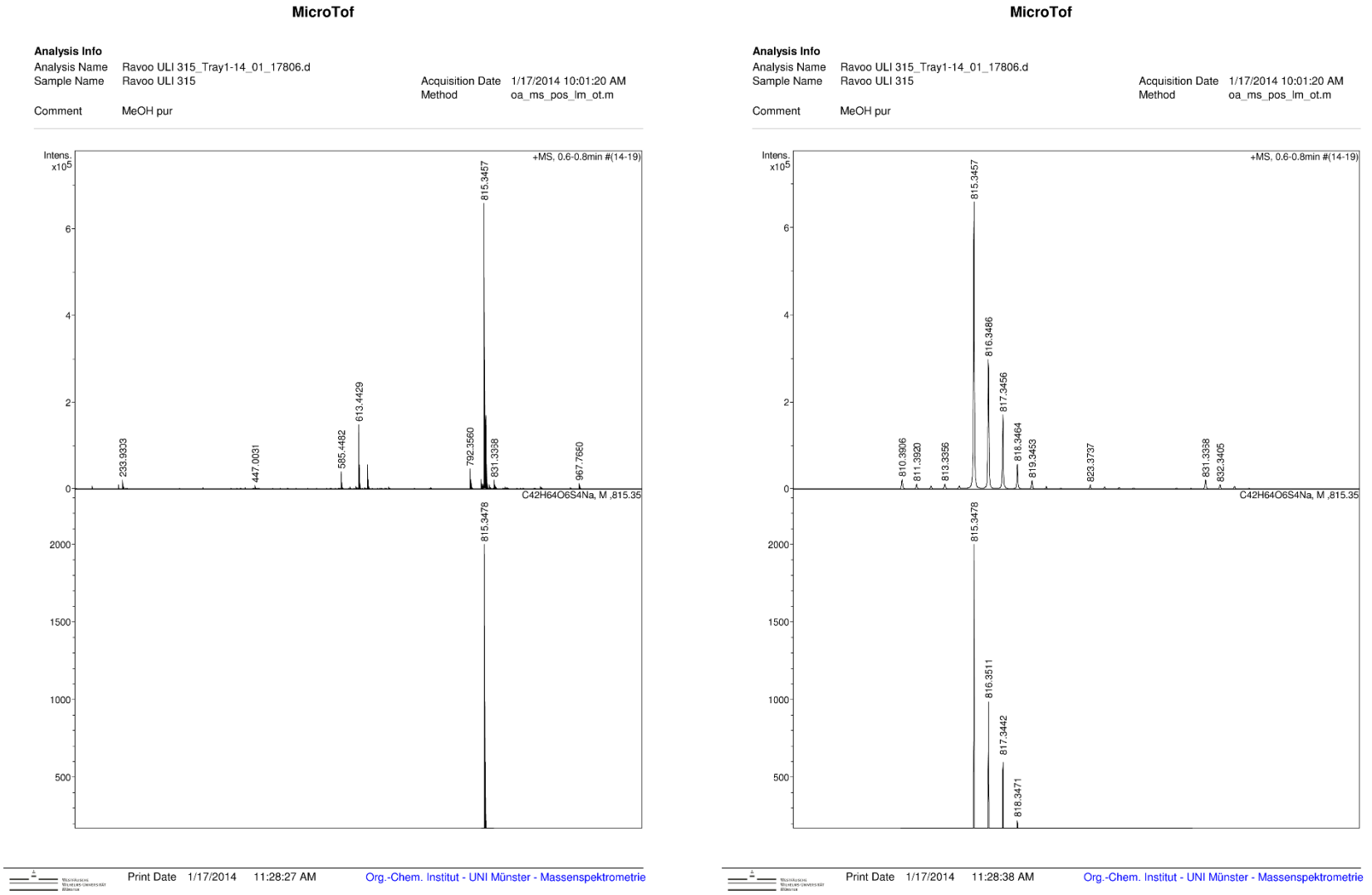

Figure S4. HRMS (ESI^+) spectrum of Chol-TTF **1** showing observed (above) and simulated (below) isotopic patterns.

CV for the oxidation of Chol-TTF 1 in acetonitrile

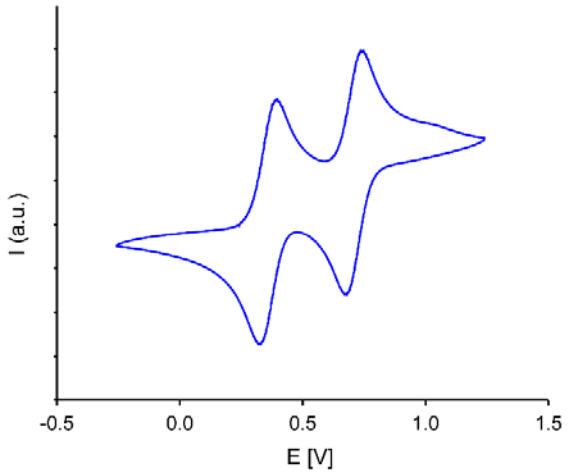

Figure S5. Cyclic voltammogram of Chol-TTF **1** (MeCN/0.1 M Bu_4NClO_4).

UV-vis spectra for the oxidation of Chol-TTF 1 in acetonitrile

Chol-TTF **1** in MeCN (0.06 mM) was titrated with $Fe(ClO_4)_3$ in MeCN. Non-oxidized **1** shows major absorption at 314 nm, as well as a shoulder at 360 nm (Fig. S6, black line). Upon addition of 1 eq. of $Fe(ClO_4)_3$ signals at 438 nm and 584 nm, assigned to TTF^{+}•, dominate (Fig. S6, red line), whereas no absorption at higher wavelengths, indicative of $(TTF^{+\bullet})_2$ dimers, is detected. Upon addition of an excess of $Fe(ClO_4)_3$, one strong absorption peak at 380 nm (Fig. S6, blue line). The spectra of TTF, TTF^{+}•, and TTF^{2+} species in MeCN are fully consistent with the previously reported ones.[1]

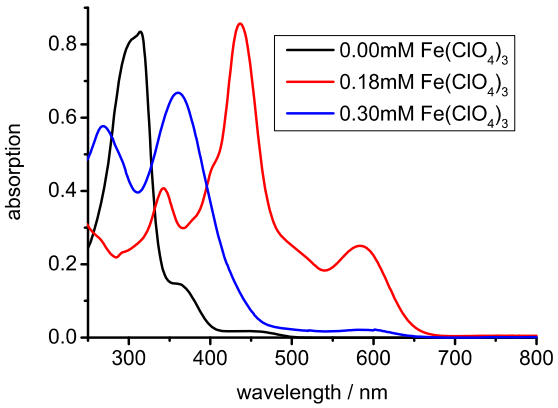

Figure S6. Oxidation of Chol-TTF **1** in MeCN upon addition of $Fe(ClO_4)_3$. [Chol-TTF **1**] = 0.06 mM; [$Fe(ClO_4)_3$)] = 0.00–0.30 mM.

DLS of non-oxidized and oxidized liposomes containing Chol-TTF 1

DLS data obtained from liposomes formed from DOPC and Chol-TTF **1** show constant liposome size before and after the addition of $Fe(ClO_4)_3$ implying that liposomes remain intact upon oxidation of TTF.

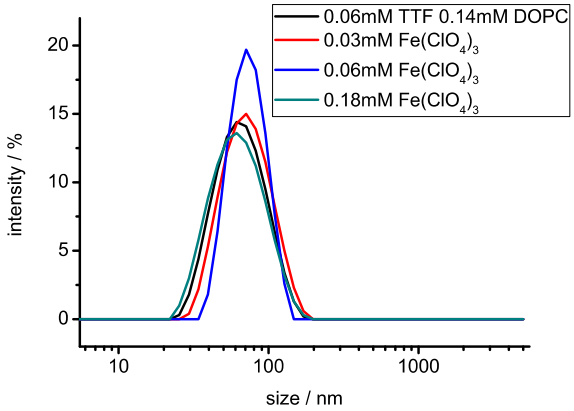

Figure S7. DLS measurements of liposomes before and after $Fe(ClO_4)_3$ addition. [DOPC] = 0.14 mM, [Chol-TTF **1**] = 0.06 mM, [$Fe(ClO_4)_3$] = 0.00–0.18 mM.

DLS data obtained upon oxidation of Chol-TTF-containing liposomes in the presence of CB[8] show that liposomes aggregate at intermediate $Fe(ClO_4)_3$ concentration, but not at higher $Fe(ClO_4)_3$ concentration (Fig. S8). It is reasonable to assume that aggregation is driven by the formation of *intervesicular* ternary inclusion complexes of $TTF^{+\bullet}$ and CB[8].

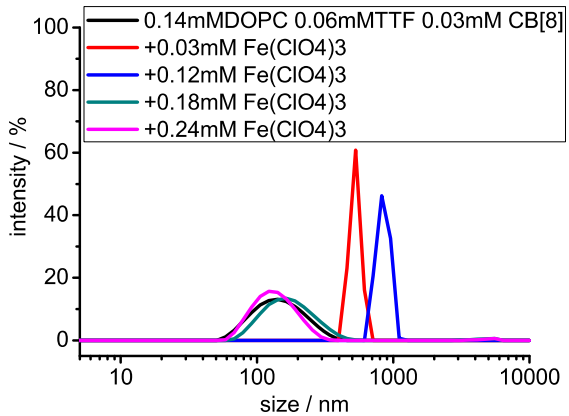

Figure S8. DLS measurements of liposomes before and after oxidation of Chol-TTF in the presence of CB[8]. [DOPC] = 0.14 mM, [Chol-TTF **1**] = 0.06 mM, [CB[8]] = 0.03mM, [$Fe(ClO_4)_3$] = 0.00–0.24 mM.

DLS data obtained for liposomes formed from DPPC and Chol-TTF **1** before and after stepwise addition of increasing amounts of $Fe(ClO_4)_3$ demonstrate that the liposome diameter remains constant and no aggregation is observed (Fig. S9).

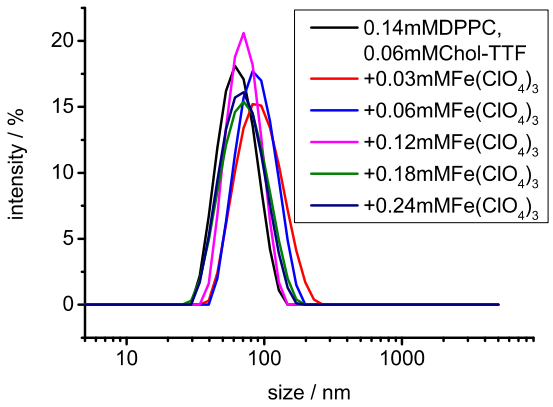

Figure S9. DLS measurements of DPPC liposomes before and after oxidation of Chol-TTF 1. [DPPC] = 0.14mM, [Chol-TTF **1**] = 0.06 mM, $[Fe(ClO_4)_3]$ = 0.00–0.24 mM.

Reversibility of oxidation

Reversibility of the TTF oxidation was demonstrated using ascorbic acid as a reducing reagent. Chol-TTF **1** in MeCN (0.06 mM) was oxidized via the addition of 0.3 mM $Fe(ClO_4)_3$ (see also S6). Upon addition of 1 eq. of ascorbic acid signals at 438 nm and 584 nm, assigned to $TTF^{+\bullet}$, dominate (Fig. S10, blue line), whereas no absorption at higher wavelengths, indicative of $(TTF^{+\bullet})_2$ dimers, is detected. Upon addition of an excess of ascorbic acid, the typical TTF absorption spectrum with one strong absorption peak at 314 nm as well as a shoulder at 360nm is obtained (Fig. S10, green line).

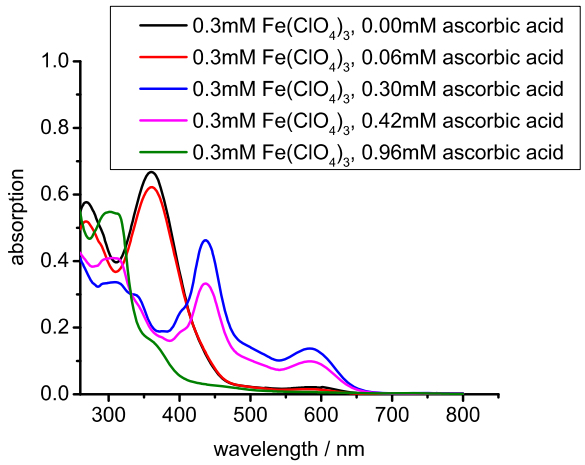

Figure S10. Reduction of Chol-TTF^{2+} in MeCN upon addition of ascorbic acid. [Chol-TTF **1**] = 0.06 mM; [$Fe(ClO_4)_3$)] = 0.30 mM, [ascorbic acid] = 0.00-0.96 mM.

Reversibility of the TTF oxidation was also observed on the surface of liposomes containing 0.14 mM DOPC and 0.06 mM Chol-TTF **1**. Addition of ascorbic acid to vesicles with fully oxidized TTF units led to gradual build up and disappearance of the same absorption bands ad 775 nm, indicating the reverse process, which included the reduction of doubly oxidized TTF to TTF$^{\bullet+}$ with dimer formation and then to neutral TTFs as follows: TTF^{2+} -> $(TTF^{\bullet+})_2$ -> TTF. (Fig. S10).

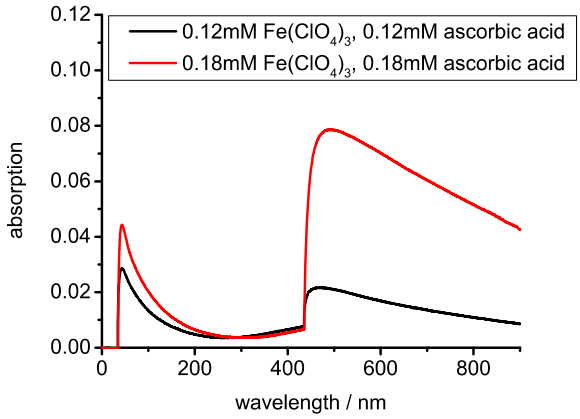

Figure S11. Oxidation (0–420min) and reduction (420–850min) of TTF on the surface of DOPC liposomes monitored at 775 nm. [DOPC] = 0.14 mM, [Chol-TTF **1**] = 0.06 mM, [$Fe(ClO_4)_3$] = 0.12 / 0.18 mM; [ascorbic acid] = 0.12 / 0.18 mM.

DLS data obtained for liposomes formed from DOPC and Chol-TTF **1** after oxidation via $Fe(ClO_4)_3$ and reduction via addition of ascorbic acid indicate that the average liposome diameter and size distribution remain constant. (Fig. S12).

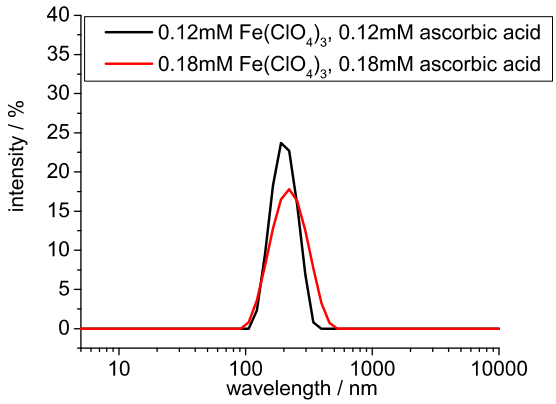

Figure S12. DLS measurements of liposomes after oxidation and reduction of Chol-TTF **1** in the presence of. [DOPC] = 0.14 mM, [Chol-TTF **1**] = 0.06 mM, $[Fe(ClO_4)_3]$ = 0.12 / 0.18 mM; [ascorbic acid] = 0.12 / 0.18mM.

Reference

1. P. R. Ashton, V. Balzani, J. Becher, A. Credi, M. C. T. Fyfe, G. Mattersteig, S. Menzer, M. B. Nielsen, F. M. Raymo, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 3951–3957.