Supporting Information

A self-assembled tetrathiafulvalene box

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Chemicals and instrumentation

Chemicals

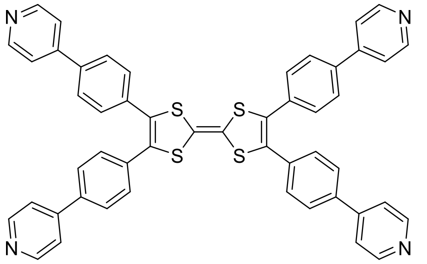
Compound 4-(4-bromophenyl)pyridine[1] and complex **RuNaph**[2] were synthesized using procedure described in the literature. All reagents were commercial reagent grade and were used without further purification. For synthesis and crystallization, analytical grade solvents were used.

Instrumentation

Characterizations and NMR experiments were carried out on an NMR Bruker Avance III 300 spectrometer at room temperature or 298 K (^{1}H NMR DOSY), using perdeuterated solvents. Chemical shifts are reported in ppm relative to the solvent residual value. ^{1}H DOSY NMR spectra were analyzed with MestReNova software. ESI-FTICR spectra were performed on an IonSpec (Agilent), 9.4 T hybride ESI q-Q-q in CH_3CN ($C = 10^{-3}$ M). Cyclic voltammetry experiments were carried out on a BioLogic SP-150 potentiostat, Pt counter electrode and $Ag/AgNO_3$ (0.1 M $n$$Bu_4NPF_6$ in CH_3CN) reference electrode. Spectrophotometric measurements were carried out in direct reflexing mode on the working electrode (i.e. Pt) with a homemade bench composed of different Princeton Instruments modules (light sources, fibers, monochromators, spectroscopy camera, and software). The connection between the light source, the cell, and the spectrophotometer is ensured through a “Y-shaped” optical fiber bundle.

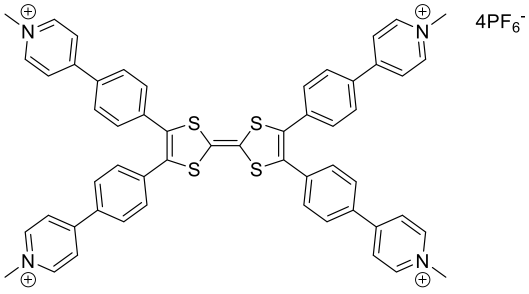
Experimental procedures and characterizations

TTF(PhPyr)$_4$



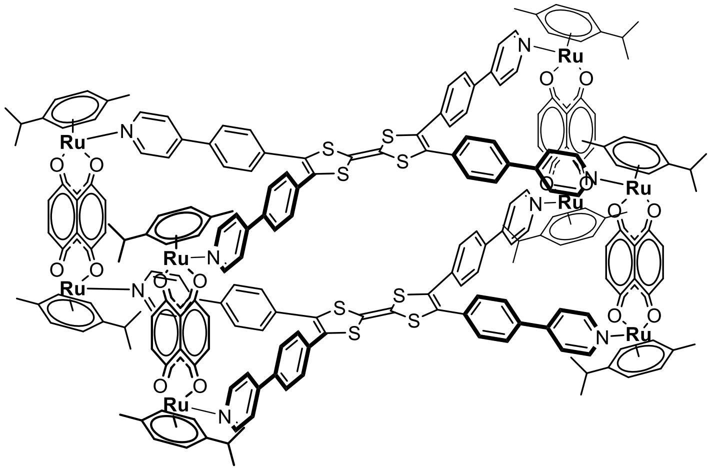
To a suspension of palladium acetate (32 mg, 0.14 mmol), tri-tert-butylphosphonium tetrafluoroborate (104 mg, 0.36 mmol) and cesium carbonate (812 mg, 2.49 mmol) in distilled and argon degassed dioxane (3 mL), was added *via* cannula an argon degassed solution of TTF (100 mg, 0.489 mmol) and 4-(4-bromophenyl)pyridine (420 mg, 1.790 mmol) in distilled dioxane (3 mL). The mixture was stirred at 110°C for 48h. The solvent was evaporated and dichloromethane (20 mL) was added. The resulting suspension was filtered and the filtrate was washed three times with water (20 mL). The organic phase was dried on magnesium sulfate and filtered on cotton. The solvent was evaporated and a chromatography column on silica gel was realized using a gradient of eluent: from dichloromethane/methanol (99/1) to dichloromethane/methanol (92/8) with a constant portion of triethylamine of 0.5%. Compound **TTF(PhPyr)$_4$** was isolated as a red powder (251 mg, 86%). ^{1}H NMR (300MHz, $CDCl_3$): 8.66 (HαPy, d, $J =$ 5.7 Hz, 8H), 7.56 (HPh, d, $J =$ 8.4 Hz, 8H), 7.48 (HβPy, d, $J =$ 5.7 Hz, 8H), 7.39 (HPh, d, $J =$ 8.4 Hz, 8H). ^{13}C NMR (76 MHz, $CDCl_3$): 150.41, 147.14, 138.22, 133.31, 129.89, 129.24, 127.35, 121.34, 108.55. FAB-HRMS: found: 816.1522, calculated: 816.1510. Melting point 360 ^{0}C.

TTF(PhPyrMe)$_4$



To a suspension of **TTF(PhPy)$_4$**(40 mg, 0.049 mmol) in 4 ml dry DMF was added iodomethane (120 uL, 278 mg, 1.96 mmol, d = 2.28). The mixture was stirred overnight until formation of clear intense red solution. Et$_2$O was added until precipitation of a dark powder. The solid was filtered, washed with Et$_2$O and dried under vaccum. The solid was dissolved in minimum amount of water and anion exchange was performed by adding a saturated solution of potassium hexafluorophosphate. The resulting precipitate was centrifuged, washed with minimum amount of methanol, Et$_2$O and dried under vacuum to give **TTF(PhPy-Me)$_4$** as a dark powder (25 mg, 35 %). ^{1}H NMR (300 MHz, Acetonitrile-d$_3$): 8.60 (HαPy, d, J = 6.9 Hz, 8H), 8.19 (HβPy d, J = 7.0 Hz, 8H), 7.85 (HPh d, J = 8.6 Hz, 8H), 7.53 (HPh, d, J = 8.5 Hz, 8H), 4.27 (Me, s, 12H). ^{13}C NMR (76 MHz, CD$_3$CN): 155.63, 146.27, 136.57, 135.11, 131.33, 130.66, 129.56, 125.71, 108.52, 48.53. HRMS-ESI-FTICR m/z for [TTF(PhPyrMe)$_4$$^{4+}$(PF$_6$)$_4$$^-$ – 2(PF$_6$$^-$)]$^{2+}$ found 583.0842, calculated 583,0860, for [TTF(PhPyrMe)$_4$$^{4+}$(PF$_6$$^-$)$_4$ – 3(PF$_6$$^-$)]$^{3+}$ found 340.4006, calculated 340,4024. Melting point 250 ^{0}C (decomp).

TTF-box



Ruthenium complex **RuNaph** (10.63 mg, 11 µmol) and **TTF(PhPyr)$_4$** (4.51 mg, 5.5 µmol) were dissolved in deuterated acetone (0.5 mL) and the solution was stirred at 50°C overnight. After cooling the solution to room temperature, Et$_2$O was added. The precipitate was centrifuged; washed with Et$_2$O and dried under vacuum to afford 13 mg of **TTF-box** (86%). ^{1}H NMR (300 MHz, Acetone-d$_6$): 8.50 (d, *J* = 6.7 Hz, 16H), 7.69 (d, *J* = 6.7 Hz, 16H), 7.58 (d, *J* = 8.5 Hz, 16H), 7.34 (s, 8H), 7.25 (s, 8H), 7.15 (d, *J* = 8.5 Hz, 16H), 6.00 (m, 16H), 5.78 (d, *J* = 6.0 Hz, 16H), 2.94 (m, 8H), 2.19 (s, 24H), 1.37 (m, 48H). ^{1}H DOSY NMR (Acetone-d$_6$): D = 4.74 10^{-10} m^{2}s^{-1}. HRMS-ESI-FTICR: *m/z* calculated: [(**TTF-box**) - 3OTf$^-$]$^{3+}$: 1671.4091; [(**TTF-box**) **-** 4OTf$^-$]$^{4+}$ 1216.3187; *m/z* found: [(**TTF-box**) **-** 3OTf$^-$]$^{3+}$: 1671.4093, [(**TTF-box**) **-** 4OTf$^-$]$^{4+}$: 1216.3185.

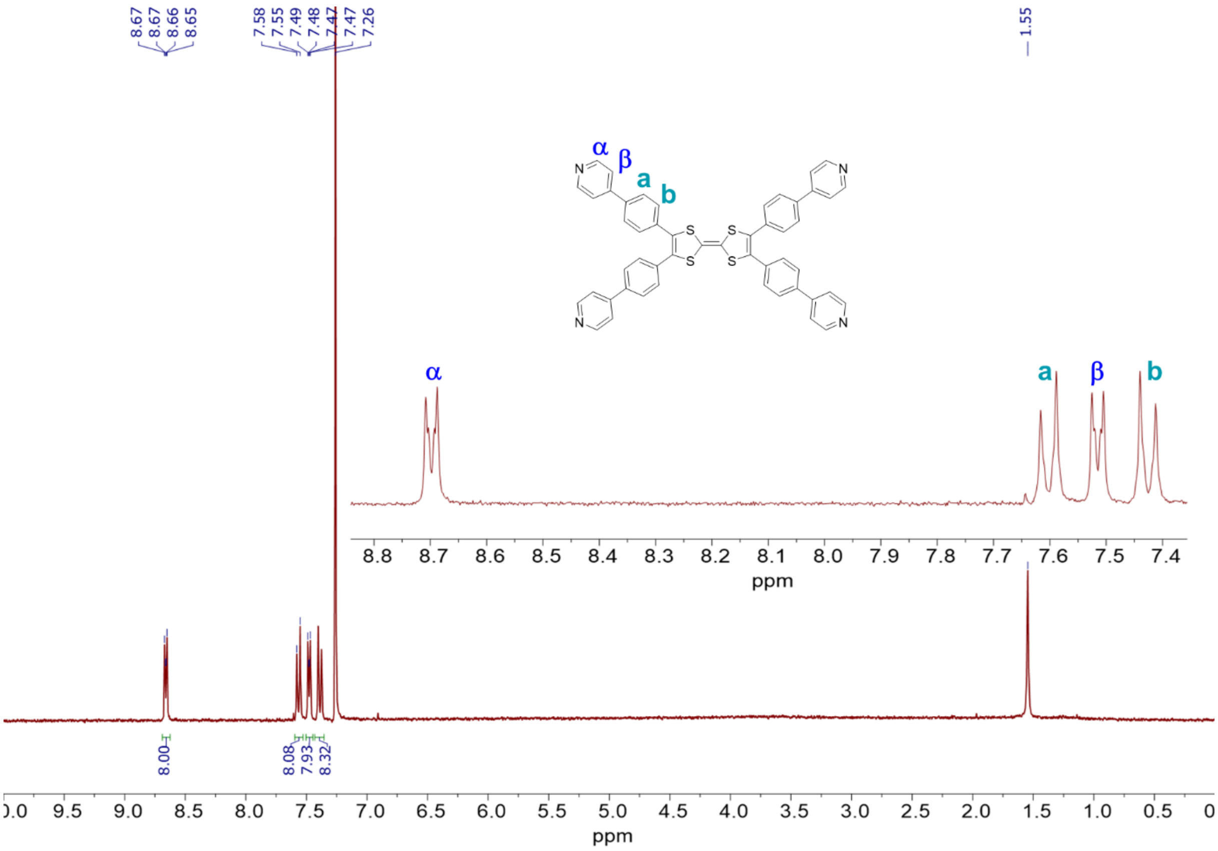


Figure S1. ^{1}H NMR spectrum of TTF(PhPyr)$_4$ in CDCl$_3$.

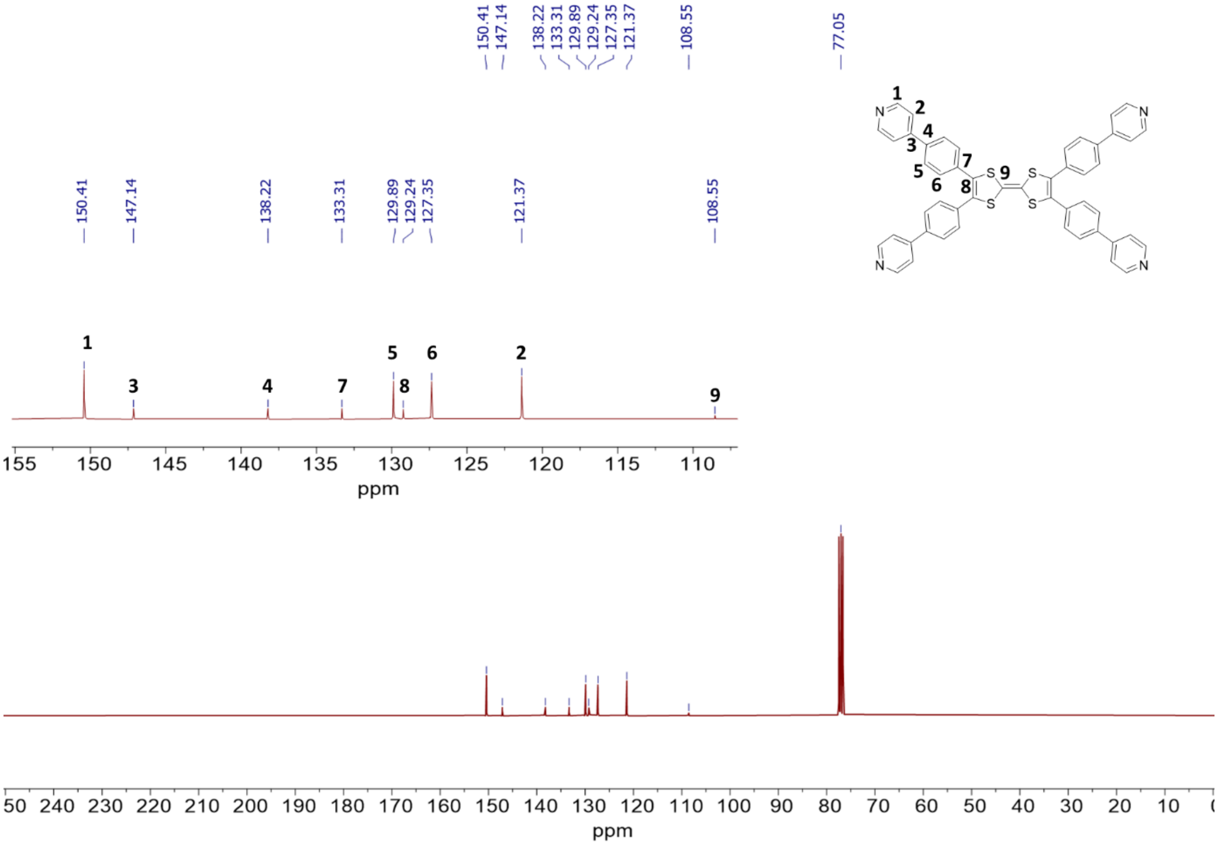


Figure S2. ^{13}C NMR spectrum of TTF(PhPyr)$_4$ in CDCl$_3$.

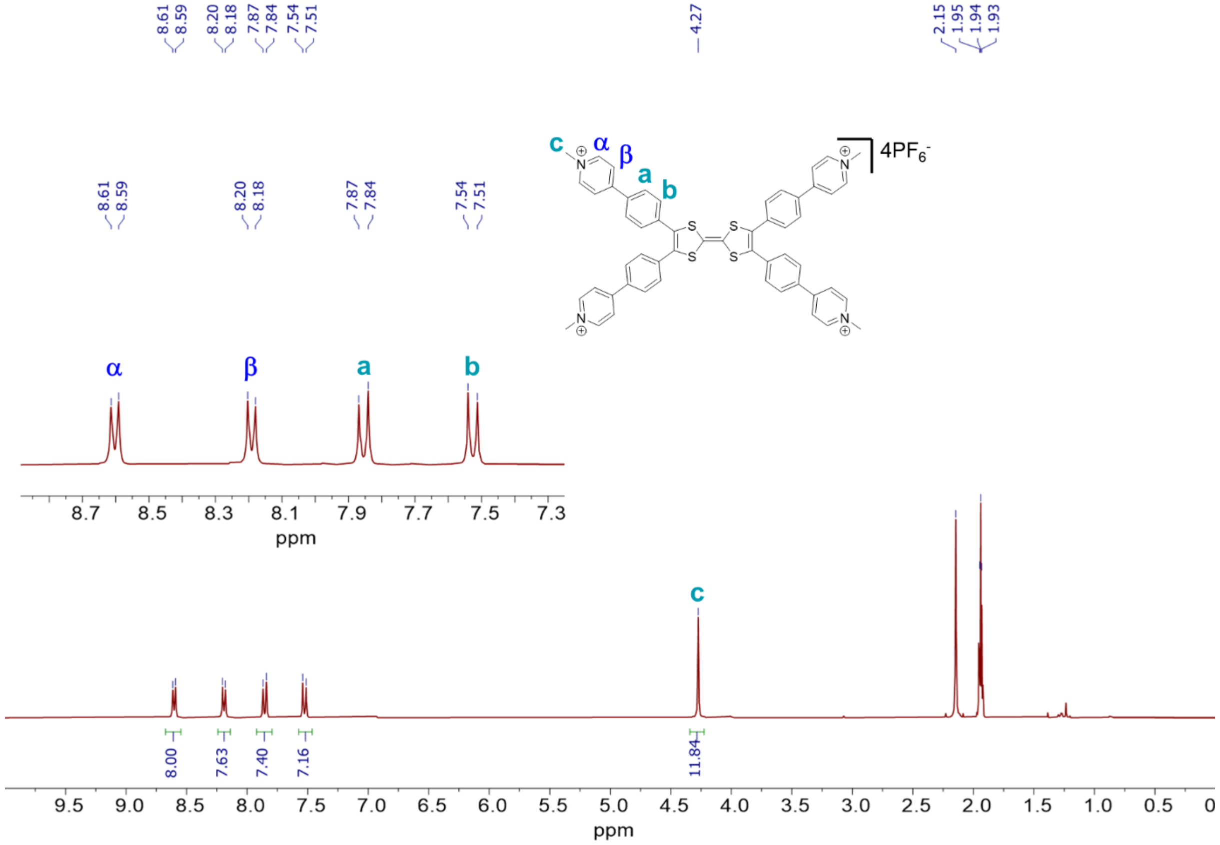


Figure S3. ^{1}H NMR spectrum of TTF(PhPyrMe)$_4$ in CD$_3$CN.

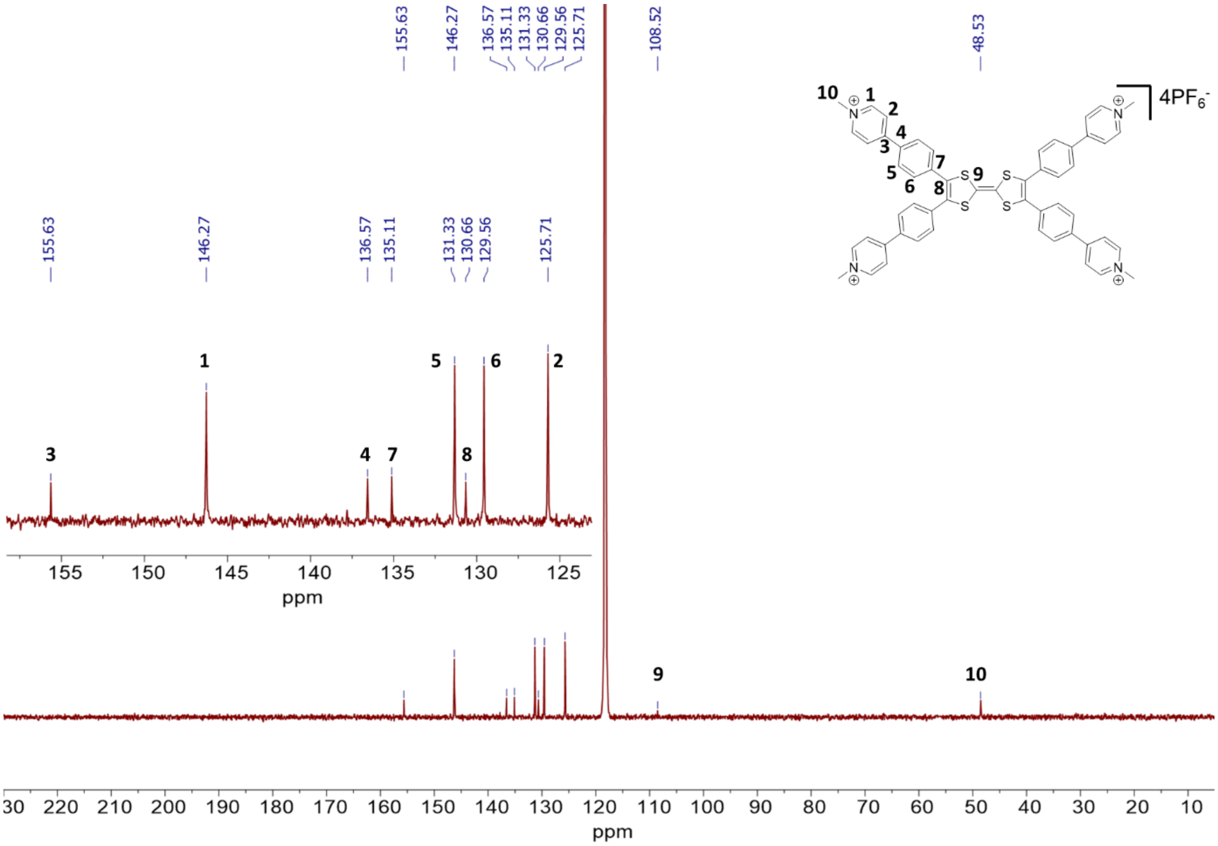


Figure S4. ^{13}C NMR spectrum of TTF(PhPyrMe)$_4$ in CD$_3$CN.

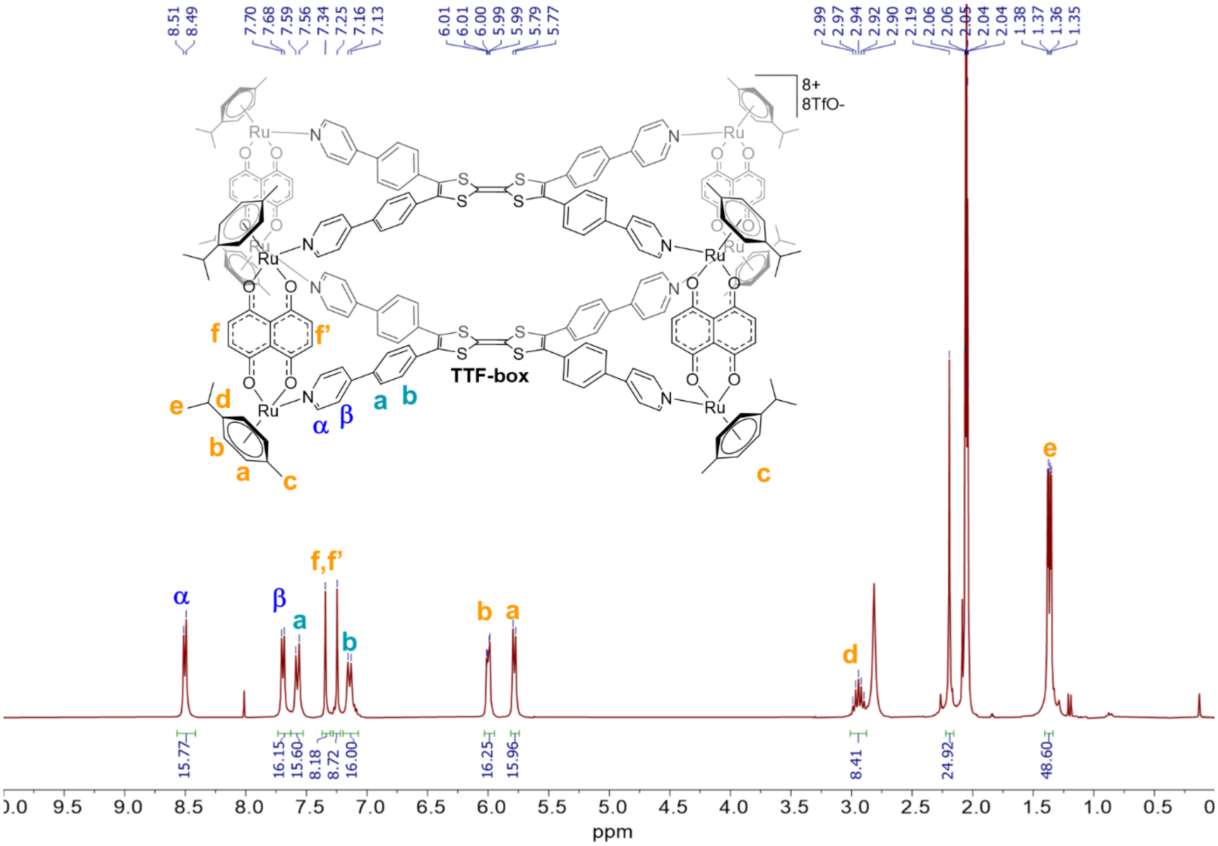


Figure S5. ^{1}H NMR spectrum of TTF-box in Acetone-d$_6$.

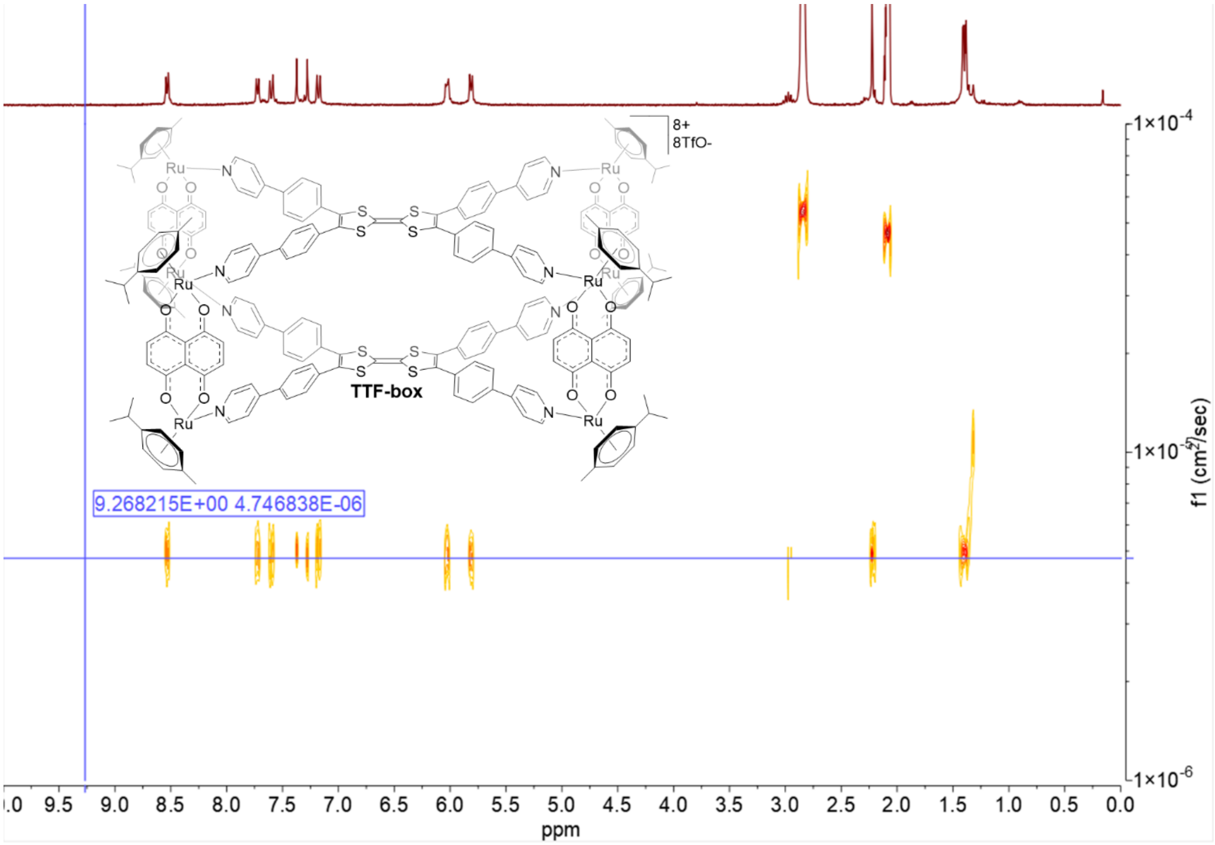


Figure S6. ^{1}H DOSY NMR spectrum of TTF-box in Acetone-d$_6$ at 298K (C = 10^{-3} M).

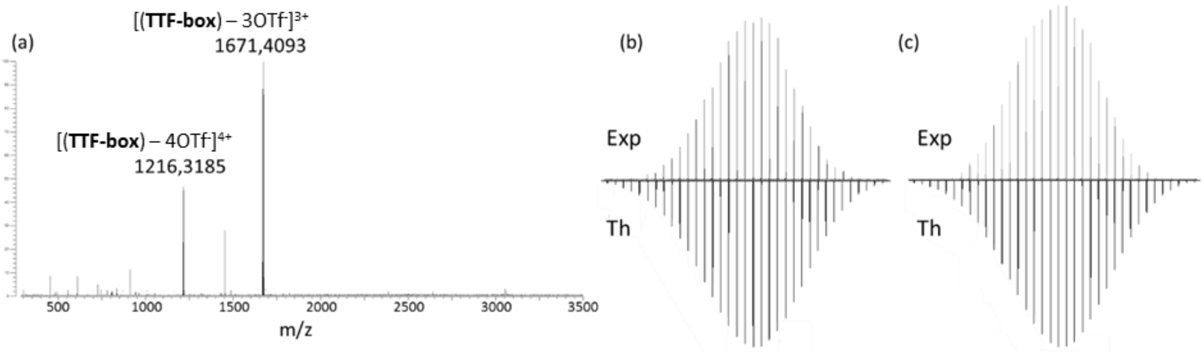


Figure S7. ESI-FTICR spectrum of TTF-box recorded in MeOH at C = 10^{-3} M (a) and comparison between experimental and theoretical isotopic patterns of [(TTF-box) – 4OTf$^-$]$^{4+}$ (b) and [(TTF-box) – 3OTf$^-$]$^{3+}$ (c).

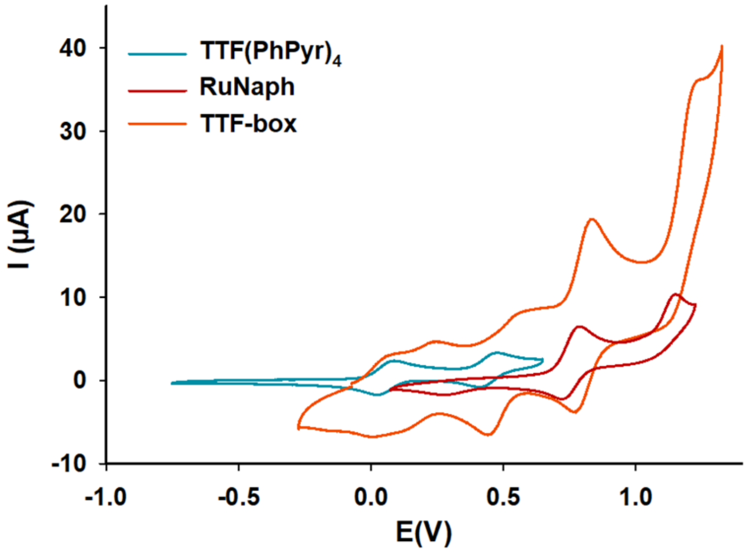


Figure S8. Cyclic voltammetry in CH_3CN/CH_2Cl_2 1/1 (C = 1 mM, nBu_4NPF_6 (0,1 M)), 100 mV.s^{-1}, glassy carbon, vs Fc/Fc$^+$) of TTF-box, compared to the starting ligand TTF(PhPyr)$_4$ and the bis-Ruthenium complex RuNaph.

X-ray diffraction

X-ray single-crystal diffraction data for **TTF-box** were collected at 150 K on a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Atlas CCD detector and micro-focus Cu-K$_\alpha$ radiation (λ = 1.54184 Å). Crystal data for **TTF(PhPyr)$_4$** were collected at 200K on a BRUKER KappaCCD diffractometer, equipped with a graphite monochromator utilizing MoKα radiation (λ = 0.71073Å). The two structures were solved by direct methods, expanded and refined on F^2 by full matrix least-squares techniques using SHELX programs (G. M. Sheldrick 2013-2016, SHELXS 2013/1 and SHELXL 2016/4). All non-H atoms were refined anisotropically and the H atoms were placed at calculated positions and refined using a riding model. Multiscan empirical absorption was corrected using CrysAlisPro program (CrysAlisPro, Rigaku Oxford Diffraction, V1.171.38.41r, 2015) for **TTF-box** and SADABS program (Sheldrick, Bruker, 2008) for **TTF(PhPyr)$_4$**.

The two structures refinements showed disordered electron density which could not be reliably modeled and the program PLATON/SQUEEZE was used to remove the corresponding scattering contribution from the intensity data. This electron density can be attributed to solvent molecules (methanol) and missing atoms (CF_3SO_3 anions and some C atoms on p-cymene cycles) for **TTF-box**. The assumed solvent composition was used in the calculation of the empirical formula, formula weight, density, linear absorption coefficient, and F(000). For **TTF(PhPyr)$_4$**, a statistical disorder on the first phenyl rings was applied to lead to occupation rate of 0.70/0.30 and 0.55/0.45.

Crystallographic data for **TTF(PhPyr)$_4$**: $C_{54}H_{48}N_4O_4S_4$, M = 945.20, red prism, 0.30 x 0.25 x 0.13 mm^3, monoclinic, space group P $2_1/c$, a = 20.340(5) Å, b = 5.3607(6) Å, c = 21.704(4) Å, β = 113.09(2)°, V = 2176.9(8) Å^3, Z = 2, ρ_{calc} = 1.442 g/cm^3, μ = 0.274 mm^{-1}, F(000) = 992, θ_{min} = 2.177°, θ_{max} = 26.608 °, 29529 reflections collected, 4372 unique (R_{int} = 0.0611), parameters / restraints = 336 / 0, R1 = 0.0746 and wR2 = 0.1952 using 2511 reflections with $I>2\sigma(I)$, R1 = 0.1309 and wR2 = 0.2513 using all data, GOF = 1.051, $-0.322 < \Delta\rho < 0.401$ e.Å^{-3}. CCDC 1971368.

Crystallographic data for **TTF-box**: $C_{234}H_{216}F_{24}N_8O_{46}Ru_8S_{16}$, M = 5653.66, black needle, 0.352 x 0.094 x 0.044 mm^3, triclinic, space group P -1, a = 20.403(2) Å, b = 25.576(1) Å, c = 26.264(1) Å, α = 77.017(5)°, β = 69.854(7)°, γ = 77.969(6)°, V = 12409(2) $Å^3$, Z = 2, ρ_{calc} = 1.513 g/cm^3, μ = 5.867 mm^{-1}, F(000) = 5736, θ_{min} = 2.729°, θ_{max} = 74.887°, 90731 reflections collected, 46941 unique (R_{int} = 0.187), parameters / restraints = 2044 / 273, R1 = 0.1619 and wR2 = 0.4111 using 14116 reflections with $I>2\sigma(I)$, R1 = 0.2716 and wR2 = 0.4889 using all data, GOF = 1.033, $-1.489 < \Delta\rho < 1.895$ e.$Å^{-3}$. CCDC 1971370.

References

1. Y. Wang, D. L. Frattarelli, A. Facchetti, E. Cariati, E. Tordin, R. Ugo, C. Zuccaccia, A. Macchioni, S. L. Wegener, C. L. Stern, M. A. Ratner and T. J. Marks, Twisted π-Electron System Electrooptic Chromophores. Structural and Electronic Consequences of Relaxing Twist-Inducing Nonbonded Repulsions, *J. Phys. Chem. C*, 2008, **112**, 8005.
2. N. P. E. Barry, J. Furrer and B. Therrien, In- and Out-of-Cavity Interactions by Modulating the Size of Ruthenium Metallarectangles, *Helv. Chim. Acta*, 2010, **93**, 1313.