Supporting Information

Study of a bifuran *vs*. bithiophene unit for the rational design of π -conjugated systems. What have we learned?

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General

¹H and ¹³C NMR spectra were recorded in solution on 300 MHz and 500 MHz spectrometers (Brücker) using ²H-chloroform as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are expressed in δ units. High resolution mass spectra were measured on a Waters Micromass GCT Premier Mass Spectrometer using field desorption (FD) ionization. Differential scanning calorimetry (DSC) measurements were performed on a TA Q200 DSC instrument. Melting points were determined using DSC by taking the peak maximum at a scan rate of 10 deg/min. UV-vis absorption measurements were recorded on a Cary-50 spectrometer (Varian). Steady state fluorescence measurements in solution were performed on a Cary Eclipse fluorometer (Varian) with the excitation/emission geometries at right angles. Fluorescence quantum yields (Φ_f) were determined using a standard procedure,¹ and coumarine 30 in acetonitrile ($\lambda_{abs} = 403$ nm, $\lambda_{em} = 480$ nm, $\Phi_f = 0.67$) was used as a reference.² Quantum yield measurements were made using four excitation wavelengths, the quantum yields were averaged over 20 measurements, and the errors were estimated to be less than 5%. The solid state fluorescence quantum yields were measured with a Hamamatsu Quantaurus-QY C11347 spectrometer using an absolute photoluminescence quantum yield technique.

Fluorescence lifetime measurements were performed by the time correlated single photon counting technique using FluoroCube (HORIBA Jobin Yvon) station equipped with TBX-04 detection module of less than 180 ps typical timing jitter and less than 100 ps overall time resolution. The instrument response function was obtained by measuring scattering from a standard sample (Ludox) with the monochromator set for detection at or close to the excitation source wavelength and remaining all other parameters unchanged. Samples were excited using a laser diode (NanoLED 406 L) that generated 200 ps pulses of 406 nm light. The samples were excited with 1 MHz repetition rate and 10 000 counts in the peak channel were collected. Lifetime decays were deconvoluted and fitted using Das6 decay analysis software. In all cases, a single exponential function was fitted to the decay curves to obtain the value for the fluorescence lifetimes.

For electrochemical measurements, 1,2-dichloroethane (DCE), acetonitrile (MeCN), or propylene carbonate (PC) were used as the solvent, and 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) or 0.1 M tetra-*n*-butylammonium trifluoromethanesulfonate (TBACF₃SO₃) were used as the electrolyte. Ag/AgCl wire was used as a pseudo-reference electrode. A ferrocene/ferrocenium redox couple (Fc/Fc⁺ = 0.40 V vs. saturated calomel electrode (SCE) in DCE,^{3a} and 0.34 V vs. SCE in PC and MeCN^{3b}) was used as an internal reference for all measurements.

FTTF was polymerized on indium tin oxide (ITO) (5–15 Ω/\Box , Delta Technologies, Stillwater) coated glass as a working electrode by applying a constant potential of 0.65 V vs. SCE for 450 s, in MeCN solution containing 0.1 M TBASO₂CF₃ (attempts to electropolymerize **TFFT** did not result in stable film). For spectroelectrochemistry measurements, spectra were measured in a UV-vis-NIR quartz optical cell (100-QS, Hellma) with a JASCO V-570 UV-VIS-NIR spectrophotometer.

4T and 2-(tributylstannyl)furan were purchased from Sigma-Aldrich. $Pd(PPh_3)_4$ was purchased from Strem Chemicals. The synthesis of 5,5'-dibromo-2,2'-bifuran,⁴ **4F**⁵, and **FTTF**⁶ were described elsewhere. Dry anhydrous DCE, MeCN, PC, and TBACF₃SO₃ were purchased from Sigma-Aldrich and used as is. TBABF₄ (Fluka) was dried under vacuum. Ag/AgCl wire was prepared by dipping silver wire in a solution of FeCl₃ and HCl.

All calculations were carried out using the Gaussian 09 program.⁷ Molecules were fully optimized without symmetry constraints using a hybrid density functional⁸ of Becke's threeparameter exchange functional combined with the LYP correlation functional (B3LYP)⁹ and with the 6-31G(d) basis set (B3LYP/6-31G(d)). Some results for oligofurans and oligothiophenes were taken from ref. 10. Currently, the B3LYP/6-31G(d) level is widely used to study organic electronic materials and conducting polymers because it predicts geometries very reliably and provides good estimates for optical bandgaps.^{10,11} Calculations of the twisting energies were performed by twisting interring bonds spirally relative to neighbouring rings. The geometry at each given twisted dihedral angle was optimized at the B3LYP/6-31G(d) level of theory, while keeping the interring dihedral angles constant. The dihedral angle between the four external carbons of the two external rings was also constrained by setting the value to the sum of the internal dihedral angles. For more details as to the methodology used to calculate twisting potentials, see ref. 12. The calculations for polymers were performed using the periodic boundary conditions (PBC) approximation as implemented in Gaussian 09¹³ at the PBC/B3LYP/6-31G(d) level. Mulliken population analysis¹⁴ was used to calculate the charges (summarized for furan and thiophene rings) of the oligomer cations radicals at the B3LYP/6-31G(d) level. TD-DFT calculations¹⁵ were performed at the B3LYP/6-31G(d) level in order to estimate UV-vis and fluorescence spectra. Geometry optimizations at the TD/B3LYP/6-31G(d) level were performed to calculate the first excited states of oligofurans and oligothiophenes. These geometries were used for calculations of fluorescence spectra.

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Synthesis



Scheme S1. Synthetic route to TFFT.

TFFT. 2,5'-Dibromobifuran⁴ (363 mg, 1.24 mmol), 2-tributylstannylthiophene (0.9 mL, 0.97 g, 2.73 mmol), Pd(PPh₃)₄ (77 mg, 0.07 mmol, 2.7% mol), and toluene (30 mL) were placed in a two necked flask containing a reflux condenser and refluxed under N₂ overnight. The cooled solution was separated with saturated NaHCO₃, dried (MgSO₄), evaporated, and then purified over a silica column using a hexane/ethyl acetate mixture to yield the product as a bright yellow powder. Recrystallization from ethanol gave the pure product as bright yellow crystals (300 mg, 81% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.28 (dd, *J* = 3.6, 1.0 Hz, 2H), 7.23–7.18 (m, *J* = 5.0, 1.7 Hz, 2H), 7.02 (dd, *J* = 5.0, 3.6 Hz, 2H), 6.63 (d, *J* = 3.5 Hz, 2H), 6.54 (d, *J* = 3.5 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 148.9, 145.3, 133.4, 127.7, 124.35, 122.8, 107.5, 107.1 ppm. HRMS (FD): m/z calcd for C₁₆H₁₀O₂S₂: 298.0122; found: 298.0113.



Figure S1. Differential scanning calorimetry (DSC) of **TFFT**, **FTTF**, **4T** and **4F** under N_2 , scan rate: 10°C/min.

X-ray structural analyses

X-ray structural analysis of TFFT *Crystal data:* $C_{16}H_{10}O_2S_2$, colorless plate, $0.30 \times 0.30 \times 0.08 \text{ mm}^3$, monoclinic P2(1)/c, a = 15.8370(17) Å, b = 5.4707(6) Å, c = 7.9739(8) Å, $\beta = 102.726(3)^{\circ}$ from 11783 reflections, T = 100(2)K, V = 673.88(12) Å³, Z = 2, Fw = 298.36, Dc = 1.470 Mg m⁻³, $\mu = 0.392 \text{ mm}^{-1}$. *Data collection and processing:* Bruker KappaApexII CCD diffractometer, MoK α (λ =0.71073Å), graphite monochromator, $-22 \le h \le 22$, $-7 \le k \le 7$, $-11 \le 1 \le 11$, 2θmax = 61.5°, frame scan width = 0.5°, scan speed 1.0° per 40 sec, typical peak mosaicity 0.67°, 11783 reflections collected, 2077 independent reflections (R-int =0.034). The data were processed with BrukerApex2. *Solution and refinement:* The structure was solved with Bruker AutoStructure. Full matrix least-squares refinement based on F² with SHELXL-97 on 99 parameters with no restraints gave final R₁= 0.0339 (based on F²) for data with I > 2\sigma(I) and, R₁ = 0.0438 on 2077 reflections, goodness-of-fit on F² = 1.073, largest electron density peak 0.367 e Å⁻³. Largest hole = -0.248 e Å⁻³.

X-ray structural analysis of FTTF *Crystal data:* $C_{16}H_{10}O_2S_2$, yellow, $0.25 \times 0.09 \times 0.02$ mm³, Orthorhombic, Pbca, a = 7.4341(7) Å, b = 7.5723(6) Å, c = 23.450(2) Å, from 20 degrees of data, T = 100(2) K, V = 1320.1(2) Å³, Z=2, Fw = 298.36 g/mol, Dc =1 .501 Mg.m⁻³, $\mu = 0.400$ mm⁻¹. *Data collection and processing:* Bruker KappaApexII CCD diffractometer, MoKa (λ =0.71073Å), graphite monochromator, 11141 reflections collected, $-9 \le h \le 9$, $-9 \le k \le 9$, $-29 \le 1 \le 30$, 20max = 54.98°, frame scan width = 0.5°, scan speed 1.0° per 80 sec, typical peak mosaicity 0.64°, 1503 independent reflections (R-int = 0.0470). The data were processed with BrukerApex2. *Solution and refinement:* Structure solved by direct methods with SHELXS. Full matrix least-squares refinement based on F² with SHELXL-97. 91 parameters with 0 restraints, final R₁= 0.0397 (based on F²) for data with I > 2\sigma(I) and R₁ = 0.0540 on 1503 reflections, goodness-of-fit on F² = 1.092, largest electron density peak = 0.424 e/Å⁻³, deepest hole = -0.589 e/Å⁻³.



Figure S2. Crystal packing of (a) TFFT and (b) FTTF.



Figure S3. Space-filling model of (a) **TFFT** and (b) **FTTF**.

Solid state fluorescence



Figure S4. Normalized fluorescence spectra of crystalline samples of **4F**, **TFFT**, **FTTF**, and **4T**.

Chemical oxidation

For the absorption measurements, the compounds were dissolved in CH_2Cl_2 solution (1–4 × 10⁻⁴ M). To this solution, an oxidant (FeCl₃) in DCM was added (0.2–1.0 equivalents), the resulting solution was quickly mixed and immediately subjected to UV-Vis-NIR measurements. The compounds were then reduced to the neutral state using hydrazine, in order to check the reversibility of the oxidation process (Fig. S5).



Figure S5. Absorption spectra of (a) \mathbf{TFFT}^+ and (b) \mathbf{FTTF}^+ in dichloromethane formed upon chemical oxidation with FeCl₃, and subsequent reduction with hydrazine.

Electrochemistry



Figure S6. Cyclic voltammograms of **4F**, **TFFT**, **FTTF** and **4T** *vs.* SCE in propylene carbonate (PC) and 0.1 M TBABF₄ on a Pt disk as the working electrode, scan rate is 50 mV/s. The reference electrode is Ag/AgCl wire, potential was referenced to $Fc/Fc^+ = 0.34$ V *vs.* SCE^{3b} with PC as the solvent.

We subjected both **TFFT** and **FTTF** to polymerization by repetitive cyclic voltammetry (CV) and note that polymerization of both oligomers should result in polymers with the same chemical structure (poly(TFFT) = poly(FTTF)). This should allow a direct comparison between structurally-identical polymers obtained from different oligomers. Repetitive CV of **FTTF** results in smooth polymer film growth, indicative of a conductive polymer forming on the surface of the working electrode (Fig. S7a). Upon applying constant bias, FTTF electropolymerizes on ITO to form a stable film (poly(FTTF)) that exhibits well defined spectroelectrochemical response properties (Fig. S8). Oxidation of the polymeric film results in a decrease in the π - π^* transition at around 420–450 nm, and an increase in new transitions first around 800 nm and then around 650 nm and in the NIR region at around 1300 nm. The subsequent reduction of the polymeric film back to 0.0 V vs. SCE results in reversible formation of the neutral polymer, so indicating its stability (Fig. S8, orange line). The bandgap of the polymeric film (assigned as the onset of the π - π^* transition) is 2.0 eV, which is in good agreement with the calculated (PBC/B3LYP/6-31G(d)) value for poly(FTTF) of 2.18 eV. The experimental values reported for polythiophene¹⁶ and polyfuran¹⁷ are 2.0 and 2.3 eV respectively. The calculated bandgap for poly(FTTF) of 2.18 eV is midway between the calculated value for polyfuran (2.42 eV) and polythiophene (2.06 eV).¹⁰

Repeated CV of **TFFT** produces a film on the Pt working electrode (Fig. S7b). Electropolymerization of **TFFT** on ITO was attempted with various solvents (MeCN, DCM and DCE) and electrolytes (TBABF₄ and TBASO₂CF₃) using CV and potentiostatic depositions, but failed to produce a good quality polymer film. Hucke and Cava previously noted that oligomer **TFTFT** shows a reversible oxidation peak while **FTFTF** oxidation is not

reversible,⁶ which is in line with our current finding.



Figure S7. Repetitive CV scans of (a) **FTTF** and (b) **TFFT** (first cycle is shown in red) in 1,2-dichloroethane (DCE) with 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) on a Pt disk as the working electrode. In all experiments, the scan rate is 50 mV/s, the reference electrode is Ag/AgCl wire. Potential was referenced to $Fc/Fc^+ = 0.40$ V vs. SCE with DCE as solvent.¹⁸



Figure S8. Spectroelectrochemistry of poly(**FTTF**) on an ITO electrode at different potentials, in MeCN and 0.1 M TBASO₂CF₃. The reference electrode is Ag/AgCl wire, potential was referenced to $Fc/Fc^+ = 0.34 \text{ V} \text{ vs. SCE}^{3b}$ with MeCN as solvent.

Calculations

Structure	Energy (HF)
FTTF	-1562.49114817
TFFT	-1562.49848135
\mathbf{FTTF}^+	-1562.26814883
\mathbf{TFFT}^+	-1562.27633819
4F	-916.54057697
$4\mathbf{F}^+$	-916.31982252
4 T	-2208.44696248
4T ⁺	-2208.22174676

Table S1. Absolute energies (Hartrees) for **FTTF**, **TFFT**, **4F**, **4T**, and their cation radicals, calculated at B3LYP/6-31G(d).

Table S2. Calculated (at TD-B3LYP/6-31G(d) level of theory) first absorption and emission transitions for **FTTF**, **TFFT**, **4F** and **4T**.

		Absorption	Emission		
	$\lambda_{ m abs}$	Oscillator strength	λ_{flu}	Oscillator strength	
4F	383	1.21	431	1.29	
TFFT	405	1.20	454	1.30	
FTTF	419	1.18	478	1.25	
4 T	436	1.22	497	1.29	

Table S3. Twisting energy (absolute energies, Hartrees) of **FTTF** and **TFFT** calculated at B3LYP/6-31G(d).

Twist angle (degrees)	FTTF	TFFT
0	-1562.49111852	-1562.49848119
5	-1562.49106285	-1562.49832854
10	-1562.49077885	-1562.49788097
15	-1562.49030842	-1562.49713810
20	-1562.48962162	-1562.49608245
25	-1562.48864810	-1562.49470453
30	-1562.48743037	-1562.49301783
40	-1562.48423557	-1562.48885118

Table S4. Calculated (B3LYP/6-31G(d)) Mulliken charges and spin densities at the two terminal rings (term) and the two central rings (core) for $4F^+$, $TFFT^+$, $FTTF^+$, and $4T^+$.

	$4\mathbf{F}^+$		\mathbf{TFFT}^+		FTTF⁺		4T ⁺	
	term	core	term	core	term	core	term	core
Mulliken charges	0.50	0.50	0.41	0.59	0.61	0.39	0.52	0.48
Spin densities	0.40	0.60	0.38	0.62	0.42	0.58	0.40	0.60

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Figure S9. Calculated (B3LYP/6-31G(d)) shapes of HOMO and LUMO for **TFFT** and **FTTF**. Isovalue of 0.02 has been used for all orbitals.



Figure S10. (a) Calculated (B3LYP/6-31G(d)) and (b) experimental (taken from X-ray data) bond length alternation (BLA) for **TFFT** and **FTTF**. For the experimental BLA, the values for bond numbers 2, 3, 13 and 15 for **TFFT** are omitted since the outer thiophene rings of are disordered.

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 - ¹ J. R. Lakowicz, *Principles of Fluorescence spectroscopy*. 2nd ed., Kluwer Academic/Plenum: New York, 1999.
 - ² G. Jones, W. R. Jackson, C. Choi and W. R. Bergmark, J. Phys. Chem., 1985, **89**, 294-300.
 - ³ (a) N. Eugster, D. J. Fermin and H. H. Girault, *J. Phys. Chem. B*, 2002, **106**, 3428-3433. (b) N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910.
 - ⁴ H. Ishida, K. Yui, Y. Aso, T. Otsubo, and F. Ogura, *Bull. Chem. Soc. Jpn.* 1990, **63**, 2828-2835.
 - ⁵ O. Gidron, Y. Diskin-Posner and M. Bendikov J. Am. Chem. Soc. **2010**, 132, 2148-2150.

⁶ Hucke and M. P. Cava, J. Org. Chem., 1998, **63**, 7413-7417.

⁷ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.

⁸ (a) R. G. Parr and W. Yang, *Density-functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989. (b) W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, New York, 2000.

⁹ (a) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789. (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.

¹⁰ S. S. Zade and M. Bendikov, *Org. Lett.*, 2006, **8**, 5243-5246.

¹¹ (a) S. S. Zade, N. Zamoshchik and M. Bendikov, *Acc. Chem. Res.*, 2010, **44**, 14-24. (b) S. Yang, P. Olishevski and M. Kertesz, *Synth. Met.*, 2004, **141**, 171-177. (c) R. Stowasser and R. Hoffmann *J. Am. Chem. Soc.*, 1999, **121**, 3414-3420.

¹² S. S. Zade and M. Bendikov, *Chem. Eur. J.* 2007, **13**, 3688–3700.

¹³ (a) K. N. Kudin and G. E. Scuseria, *Chem. Phys. Lett.*, 1998, **289**, 611-616. (b) K. N. Kudin and G. E. Scuseria, *Phys. Rev. B*, 2000, **61**, 16440-16453.

- ¹⁴ R. S. Mulliken, J. Chem. Phys., 1955, 23, 1833-1840.
- ¹⁵ R. E. Stratmann, G. E. Scuseria and M. J. Frisch, J. Chem. Phys., 1998, **109**, 8218-8224.
- ¹⁶ M. Kobayashi, J. Chen, T. C. Chung, F. Moraes, A. J. Heeger and F. Wudl, *Synth. Met.*, 1984, **9**, 77-86.

¹⁷ (a) S. Glenis, M. Benz, E. Legoff, J. L. Schindler, C. R. Kannewurf and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 1993, **115**, 12519-12525. (b) M. J. González-Tejera, E. S. de la Blanca and I. Carrillo, *Synth. Met.*, 2008, **158**, 165-189. (c) D. Sheberla, M. Bendikov, *unpublished*

results.

¹⁸ N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910.