Supplementary Material (ESI) for PCCP

Bis(Tetrathiafulvalenes) with Aromatic Bridges: Electron Delocalization in the Oxidized Species through EPR and Theoretical Studies

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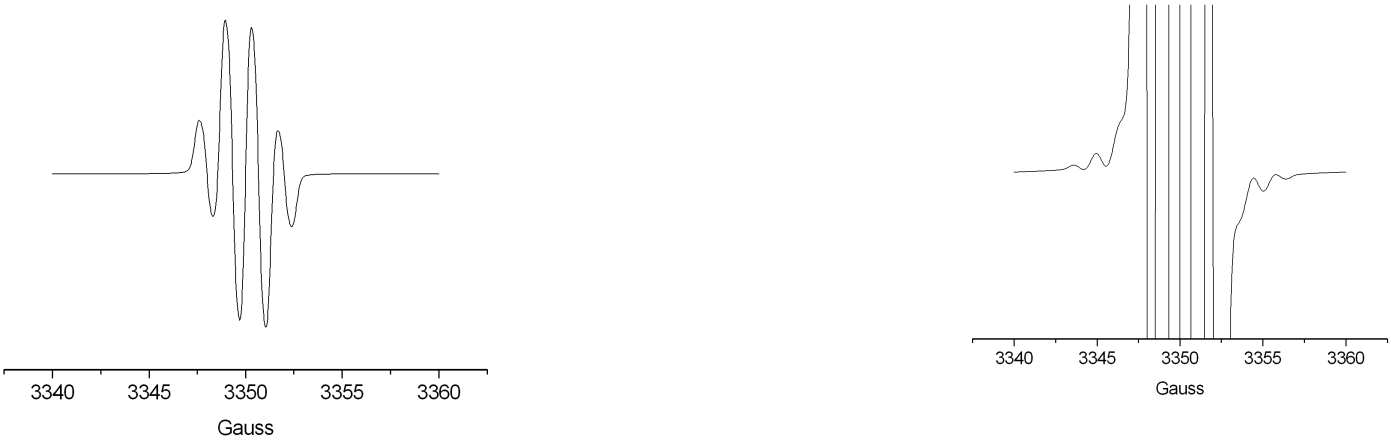
Supplementary Material

Fig. S1. EPR spectrum simulated for $(Pyr\text{-}TTF)^{\cdot+}$ by using the coupling constants obtained from DFT calculations.



spectrum a **spectrum b**

spectrum b has been simulated with an expansion of the y-scale in order to show the satellite lines due to ^{33}S.

Fig. S2. EPR spectrum simulated for $(Bz\text{-}TTF)^{\cdot+}$ by using the coupling constants obtained from DFT calculations

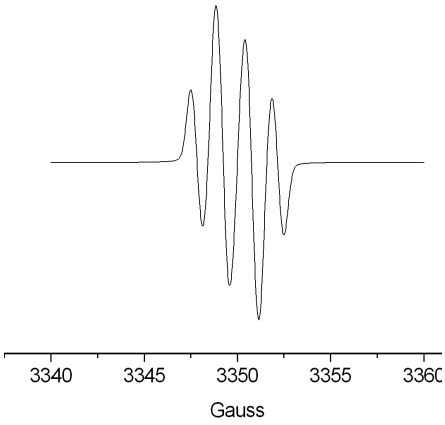


Fig. S3. EPR spectrum simulated for **(TTF-Pyr-TTF)**$^{\cdot+}$ by using the coupling constants obtained from DFT calculations

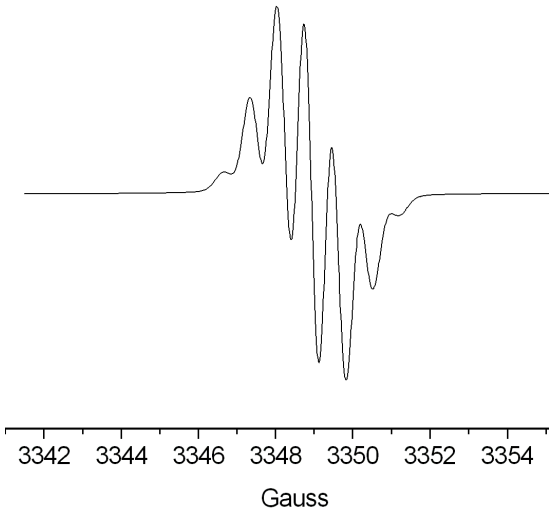


Fig. S4. Experimental EPR spectra obtained after oxidation of **(TTF-Bz-TTF)$_{meta}$.**

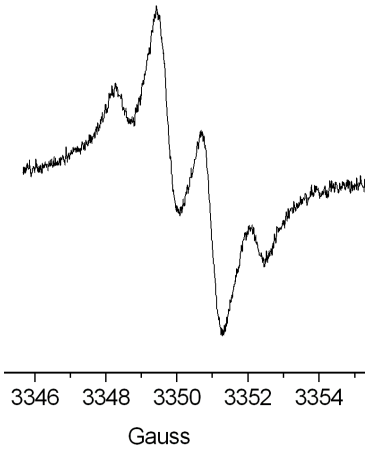


Fig. S4a.

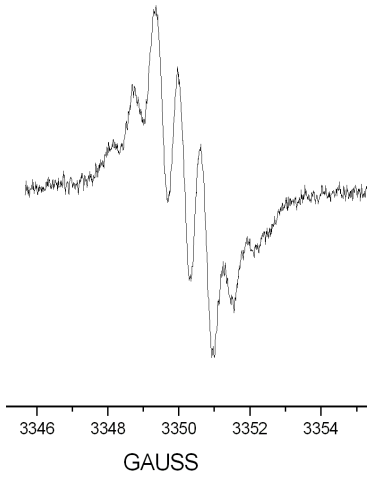


Fig. S4b

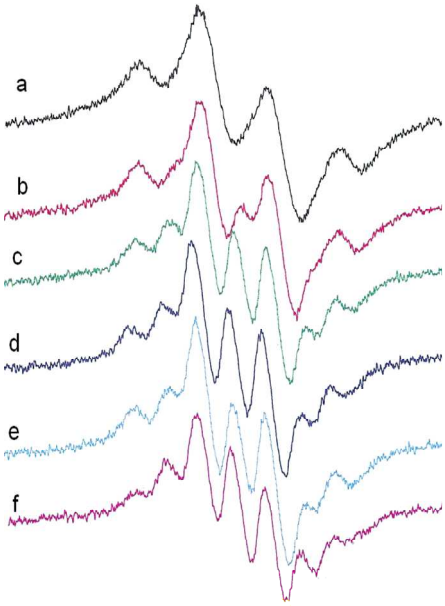


Fig. S4c

Fig. S4a: ***Oxidation of TTF-Bz-TTF with 20 equivalents of ferricinium PF_6***
Fig. S4b: ***Oxidation of TTF-Bz-TTF with 0.01 equivalents of ferricinium PF_6***
Fig. S4c: ***variation of the hyperfine pattern with the amount of ferricinium PF_6 (in equivalents). a: 20 equiv., b: 2 equiv., c: 1.5 equiv., d: 1 equiv., e: 0.5 equiv., f: 0.1 equiv.***

Fig. S5. EPR spectrum simulated for **(TTF-Bz-TTF)**$_{meta}^{\cdot+}$ by using the coupling constants obtained from DFT calculations.

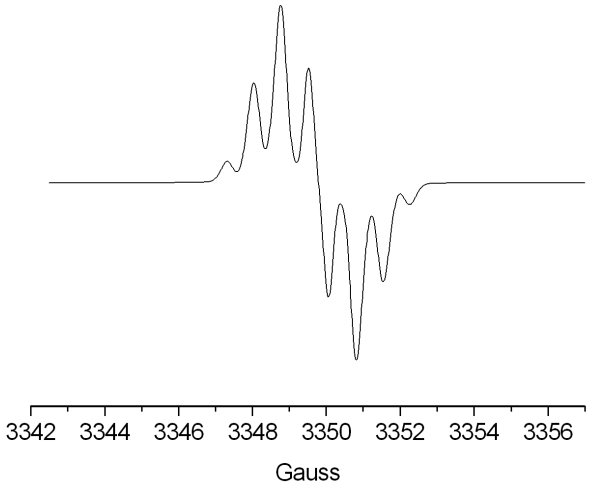
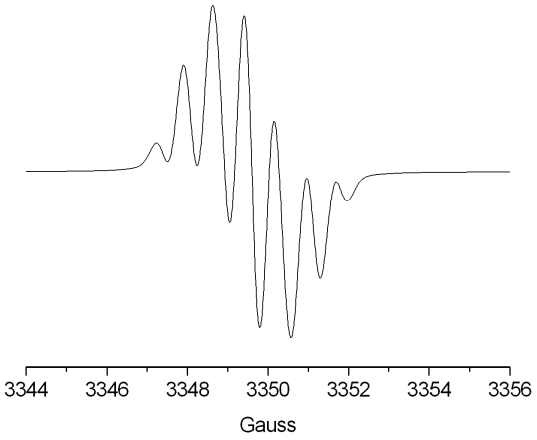
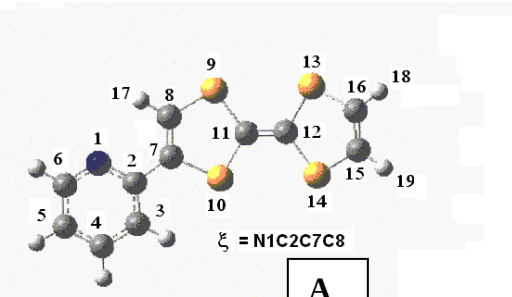


Fig. S6. EPR spectrum simulated for **(TTF-Bz-TTF)**$_{para}^{\cdot+}$.



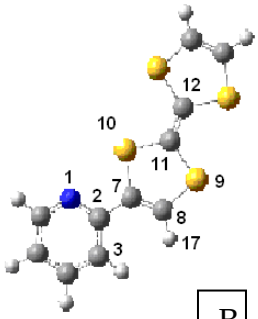
Simulation was performed by using the following coupling constants: -0.90 G (with two protons), -0.65G (with two protons), -0.63 (with two protons).
The DFT coupling constants are very slightly different: -1.51 (for H17, H17'), -0.64 (for H18, H18'), -0.59 (for H19,H19'), for H1, H1', H3, H3' coupling are less than 0.09G).

Table S1a. Solvent and conformation dependences of the ^{1}H and ^{14}N coupling constants $(Pyr\text{-}TTF)^{\cdot+}$



A

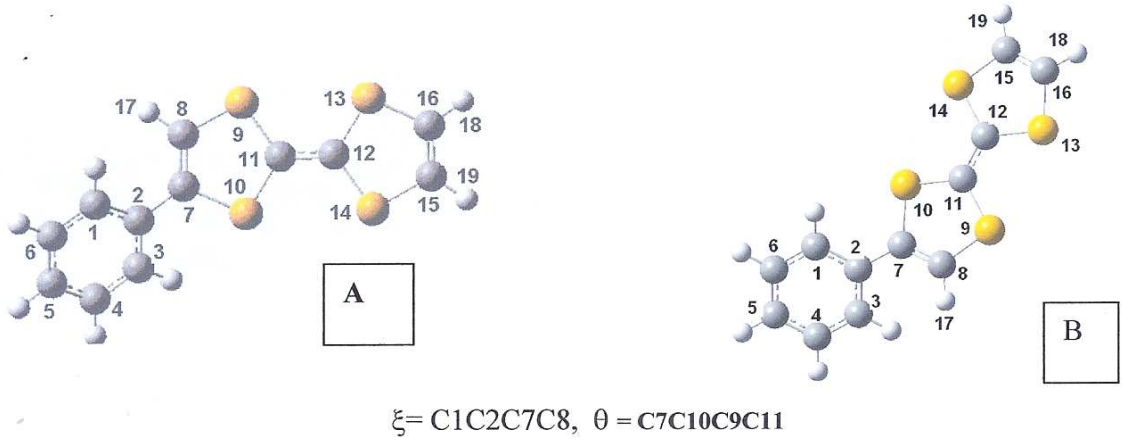
θ = C7C10C9C11



B

	H17	H18	H19	H-C3	H-C4	H-C5	H-C6	N1
$(Pyr\text{-}TTF)^{\cdot+}$ conformation A ξ= 0°, θ =180°								
No solvent	-1.626	-1.212	-1.237	-0.394	0.130	-0.465	0.163	0.188
THF	-1.412	-1.309	-1.338	-0.355	0.122	-0.450	0.115	0.120
CH_2Cl_2	-1.390	-1.313	-1.342	-0.355	0.121	-0.443	0.115	0.120
H_2O	-1.628	-1.337	-1.364	-0.348	0.115	-0.405	0.115	0.117
conformation B ξ= 180°, θ =180°								
No solvent	-1.578	-1.263	-1.263	-0.098	0.003	-0.281	-0.211	-0.141
THF	-1.273	-1.345	-1.351	-0.199	0.011	-0.276	-0.076	-0.046
CH_2Cl_2	-1.249	-1.347	-1.355	-0.198	0.008	-0.274	-0.071	-0.043
H_2O	-1.126	-1.356	-1.377	-0.194	0.003	-0.266	-0.05	-0.030

Table S1b. Solvent and conformation dependences of the ^{1}H coupling constants for $(Bz\text{-}TTF)^{\cdot+}$

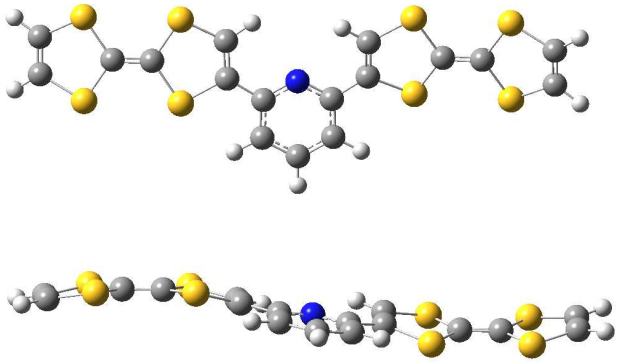


ξ= C1C2C7C8, θ = C7C10C9C11

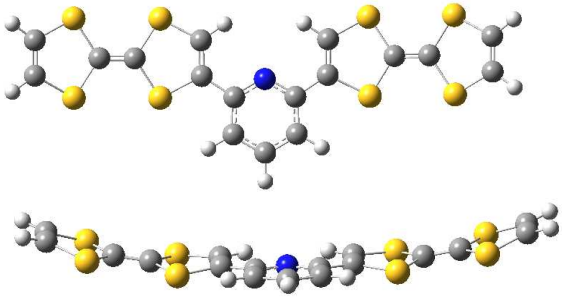
	H17	H18	H19	H-C3	H-C4	H-C5	H-C6	H-C1
$(Bz\text{-}TTF)^{\cdot+}$ **conformation A** ξ= -33.1°, θ =-177.5 °								
No solvent	-2.003	-1.227	-1.233	-0.106	0.130	-0.338	0.061	-0.140
THF	-1.726	-1.306	-1.296	-0.124	0.124	-0.315	0.134	-0.200
CH_2Cl_2	-1.712	-1.308	-1.298	-0.130	0.128	-0.310	0-133	-0.200
H_2O	-1.623	-1.312	-1.310	-0.155	0.135	-0.319	0.126	-0.206
conformation B ξ= 146.5 °, θ =-177.5 °								
No solvent	-2.003	-1.227	-1.233	-0.140	0.061	-0.338	0.130	-0.106
THF	-1.726	-1.306	-1.296	-0.200	0.134	-0.315	0.124	-0.124
CH_2Cl_2	-1.712	-1.308	-1.298	-0.200	0-133	-0.310	0.128	-0.130
H_2O	-1.623	-1.312	-1.310	-0.206	0.126	-0.319	0.135	-0.155

Table S2. Equilibrium conformations calculated for neutral TTF-Pyr-TTF

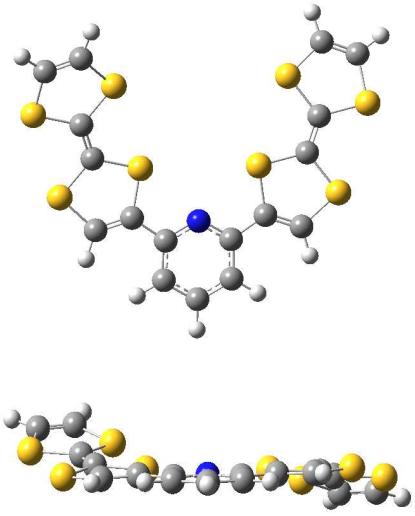
Min 1 C2 **AA (C2 sym)** E= -3893.38347 h, ξ_1 =+7.8° θ_1=+165.6°, ξ_2= +7.8° θ_2=+165.6°



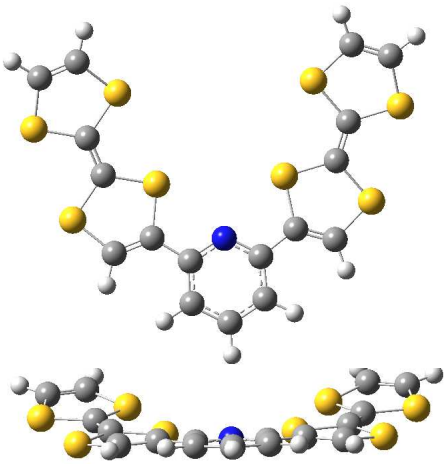
Min 1 CS **AA(Cs sym)** E= -3893.38341 h, ξ_1 =-4.04° θ_1=-165.9°,ξ_2= +4.04° θ_2=165.9°



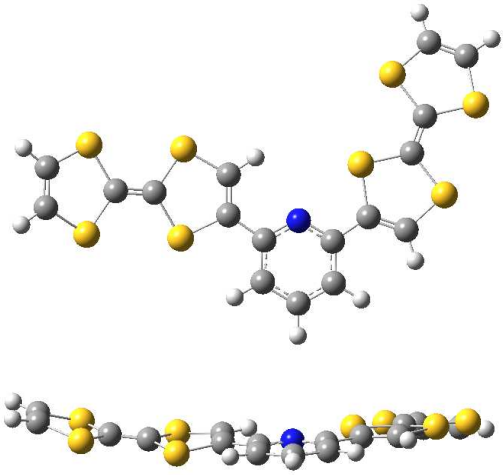
Min 2 C2 **BB(C2 sym)** E= -3893.38394 h, ξ_1 =176.8° θ_1=169.3°, ξ_2= 176.8° θ_2= 169.3°



Min 2 Cs **BB(Cs sym)** E= -893.38391 h, ξ_1 =176.1° θ_1=168.8°,ξ_2= -176.1° θ_2=-168.8°



Min 3 C1a **AB (conform a)** E= -893.38467 h ξ_1 =-3.4°,θ_1=166.6°, ξ_2= 177.7°, θ_2=170.8°



Min 3 C1b **AB (conform b)** E= -893.38471 h, ξ_1 = 4.6° θ_1=166.1° ξ_2=178.1 ° θ_2=169.7°

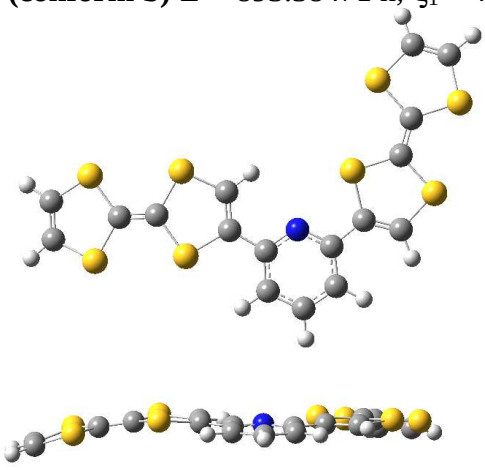
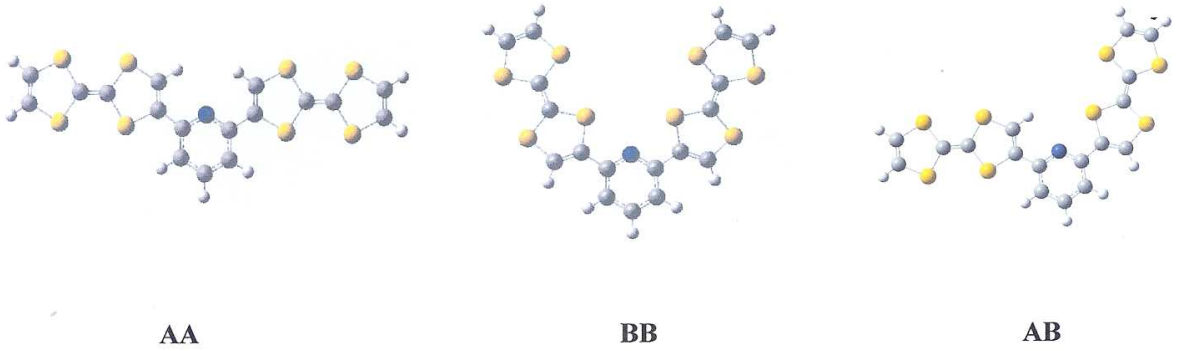


Table S3. Conformation dependence of the isotropic coupling constants[a] in (TTF-Pyr-TTF)$^{\cdot+}$ (the calculations take the solvent effects (THF) into account)



AA BB AB

	H17	H18	H19	H17'	H18'	H19'	H-C3	H-C3'	H-C4	N1
(TTF-Pyr-TTF)$^{\cdot+}$										
Conformation AA ξ_1= 0°, θ_1= 180° ξ_2= 0°, θ_2= 180° E= -3893.17543 a.u. (ΔE = 3.5 kcal. mol$^{-1)}$	-0.74	-0.67	-0.69	-0.73	-0.67	-0.69	0.0	0.0	0.10	0.28
Conformation BB ξ_1= 180°, θ_1= 180° ξ_2= 180°, θ_2= 180° E=-3893.18107 a.u. (ΔE = 0.0 kcal. mol$^{-1)}$	-1.0	-0.66	-0.63	-1.0	-0.66	-0.63	-0.62	-0.62	0.25	-0.22
Conformation AB ξ_1= 0° θ_1= 180° ξ_2= 180° θ_2= 180° E= -3893.17806 a.u. (ΔE = 1.89 kcal. mol$^{-1)}$	-0.13	-0.53	-0.56	-0.79	-0.89	-0.85	0.15	-0.02	0.13	0.21
Conformation BA ξ_1= 180°, θ_1= 180° ξ_2= 0°, θ_2= 180°	-0.79	-0.89	-0.85	-0.13	-0.53	-0.56	0.13	-0.02	0.15	0.21

Table S4. Conformations of neutral $(TTF\text{-}Bz\text{-}TTF)_{meta}$

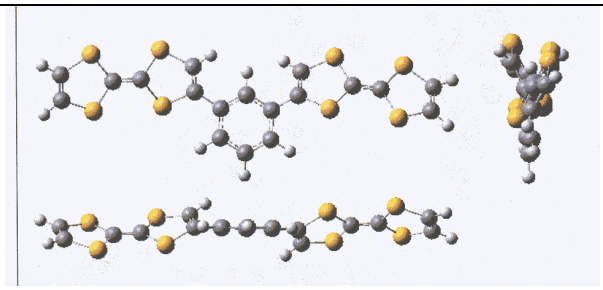
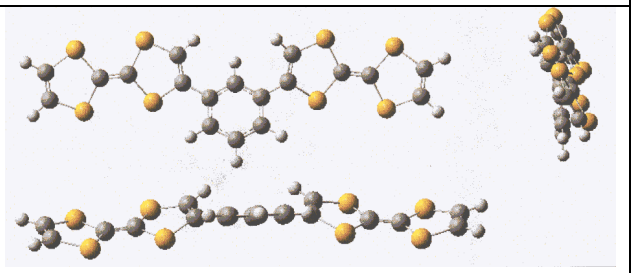
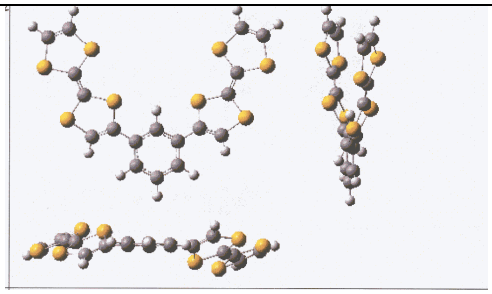
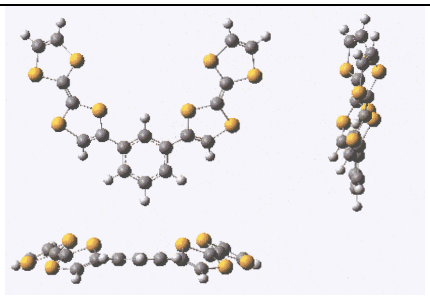
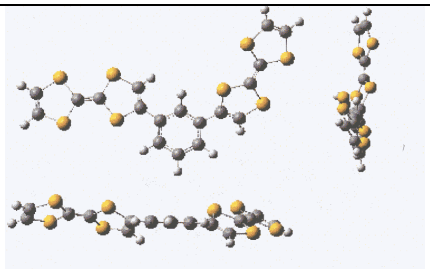
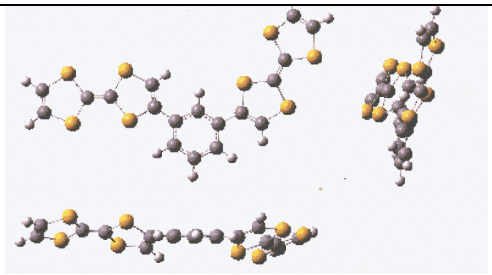
AA sym C2 (min1) **E = -3877.34014 h ΔE=0.08 kcal.mol^{-1}** **ξ_1= -32.8° θ_1=-164.2°** **ξ_2= -32.8° θ_2= -164.2°**	
AA sym Cs (min1) **E = -3877.33998 h ΔE=0.18 kcal.mol^{-1}** **ξ_1= -33.3° θ_1= -164.3°** **ξ_2= +33.3° θ_2= +164.3°**	
BB sym C2 (min2) **E = -3877.33972 h ΔE= 0.35 kcal.mol^{-1}** **ξ_1= 148.4° θ_1= -163.8°** **ξ_2= 148.4° θ_2=-163.8°**	
AA sym Cs (min2) **E = -3877.33982 h ΔE= 0.28 kcal.mol^{-1}** **ξ_1= 148.1° θ_1= -164.0°** **ξ_2= -148.1° θ_2= +164.0°**	
AB sym C1 (min3, a) **E = -3877.34021 h ΔE= 0.04 kcal.mol^{-1}** **ξ_1= +34.4° θ_1=+164.0°** **ξ_2= -148.9° θ_2=+163.9°**	
AB sym C2 (min3,b) **E = -3877.34027 h ΔE= 0.0 kcal.mol^{-1}** **ξ_1= -31.37° θ_1=-164.0°** **ξ_2= -148.6° θ_2=+163.3°**	

Table S5. Optimized conformations for $(TTF\text{-}Bz\text{-}TTF)^{\cdot+}$

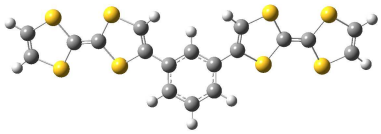
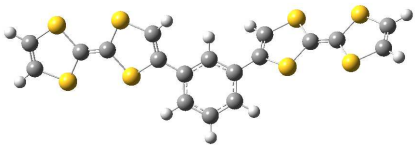
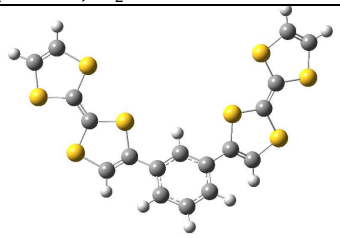
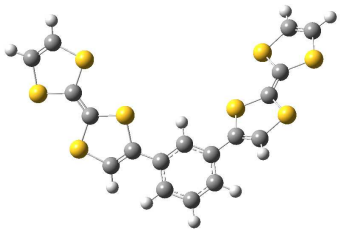
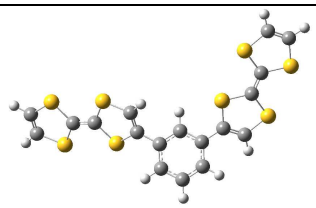
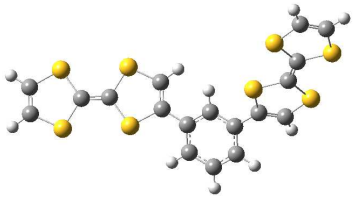
AA **Min1 Cs** E= -3877.13219 a.u. (ΔE = 0.55 kcal. mol^{-1}) **Min1 C2** E=-3877.13250 a.u. (ΔE = 0.36 kcal. mol^{-1})	 **Min1 Cs** ξ_1= -33.4°, θ_1 = -176.7° ξ_2= 33.4°, θ_2 = 176.7°	 **Min1 C2** ξ_1= -33.5°, θ_1 = -176.7° ξ_2= -33.5°, θ_2 = -176.7°
BB **Min2 Cs E**=-3877.13307 a.u. (ΔE = 0 kcal. mol^{-1}) **Min2 C2** E=-3877.13292 a.u. (ΔE = 0.09 kcal. mol^{-1})	 **Min2 Cs** ξ_1= 148.7°, θ_1 = -176.9° ξ_2= -148.7°, θ_2 = 176.9°	 **Min2 C2** ξ_1= 148.8°, θ_1 = -176.9° ξ_2= 148.8°, θ_2 = -176.9°
AB **Min3 C1** E=-3877.13272 a.u. (ΔE = 0.22 kcal. mol^{-1}) **Min3 asym** E=-3877.13253a.u (ΔE = 0.34 kcal. mol^{-1})	 **Min3 C1** ξ_1= -39.5°, θ_1 = -177.0° ξ_2=-148.1°, θ_2 = 176.3°	 **Min3 asym** ξ_1= 34.39°,θ_1 = 177.5° ξ_2= -141.6°, θ_2 = 176.8°

Table S6. Isotropic coupling constants[a] for the various conformations of $(TTF\text{-}Bz\text{-}TTF)^{\cdot+}_{meta}$

$(TTF\text{-}Bz\text{-}TTF)^{\cdot+}$	H17	H18	H19	H17'	H18'	H19'	H-C3	H-C3'	H-C4	H-C1
Min1 (Cs) AA ξ_1= -33.4°, θ_1 = -176.7° ξ_2= 33.4°, θ_2 = 176.7°	-0.82	-0.68	-0.68	-0.79	-0.68	-0.68	-0.28	-0.02	-0.03	0.19
Min1 pseudo C2 AA ξ_1= -33.5°, θ_1 = -176.7° ξ_2= -33.5°, θ_2 = -176.7°	-0.81	-0.68	-0.67	-0.80	-0.68	-0.67	-0.54	0.19	0.19	-0.05
Min 2 pseudo Cs BB ξ_1= 148.7°, θ_1 = -176.9° ξ_2= -148.7°, θ_2 = 176.9°	-0.74	-0.70	-0.69	-0.76	-0.69	-0.68	-0.34	-0.03	-0.03	0.11
Min2 (C2) BB ξ_1= 148.8°, θ_1 = -176.9° ξ_2= 148.8°, θ_2 = -176.9°	-0.77	-0.70	-0.68	-0.77	-0.70	-0.68	-0.38	0.08	0.08	0.05
Min3 C1 (AB) ξ_1= -39.5°, θ_1 = -177.0° ξ_2=-148.1°, θ_2 = 176.3°	-0.81	-0.89	-0.89	-0.61	-0.49	-0.48	-0.35	0.07	0.0	0.15
Min3 C1 (BA) ξ_1= °, θ_1 = ° ξ_2= °, θ_2 = °	-0.61	-0.49	-0.48	-0.81	-0.89	-0.89	-0.35	0.0	0.07	0.15
Min3 asym AB ξ_1= 34.39°,θ_1 = 177.5° ξ_2= -141.6°, θ_2 = 176.8°	-0.79	-0.71	-0.71	-0.84	-0.65	-0.64	-0.24	-0.02	-0.06	0.08
Min3 asym BA ξ_1=141.6°, θ_1 = 176.8 ° ξ_2= 34.3°, θ_2 = 177.6 °	-0.84	-0.65	-0.64	-0.79	-0.71	-0.71	-0.24	-0.06	-0.02	0.08

Table S7. Spin-spin exchange parameters calculated for $(TTF\text{-}Bz\text{-}TTF)^{2+}_{meta}$

	Isomer AA				Isomer BB				Isomer AB	
	J_N (cm^{-1})		J_Y (cm^{-1})		J_N (cm^{-1})		J_Y(cm^{-1})		J_N (cm^{-1})	J_Y(cm^{-1})
BP	C2	Cs	C2	Cs	C2	Cs	C2	Cs	C1	C1
TZV	1.4	0.8	1.2	0.8	0.6	0.0	0.6	0.0	1.5	1.5
Aug-cc-pVDZ	1.2	0.7	1.4	0.7	0.8	-0.1	0.8	-0.1	1.3	1.3
IGLO-III	1.2	0.8	1.2	0.8	0.8	0.0	0.8	0.0	1.3	1.3
B3lyp	C2		C2							
TZV	1.2		1.2							
Aug-cc-pVDZ	1.1		1.1							
IGLO-III	1.1		1.1							

[a] values calculated at the geometry optimized with Gaussian G03 using B3lyp/6-31G

Table S8. Optimized structures for neutral $(TTF\text{-}Bz\text{-}TTF)_{para}$

ξ_1= C1C2C7C8, θ_1 = C7C10C9C11, ξ_2= C1'C2'C7'C8', θ_2 = C7C10C9C11

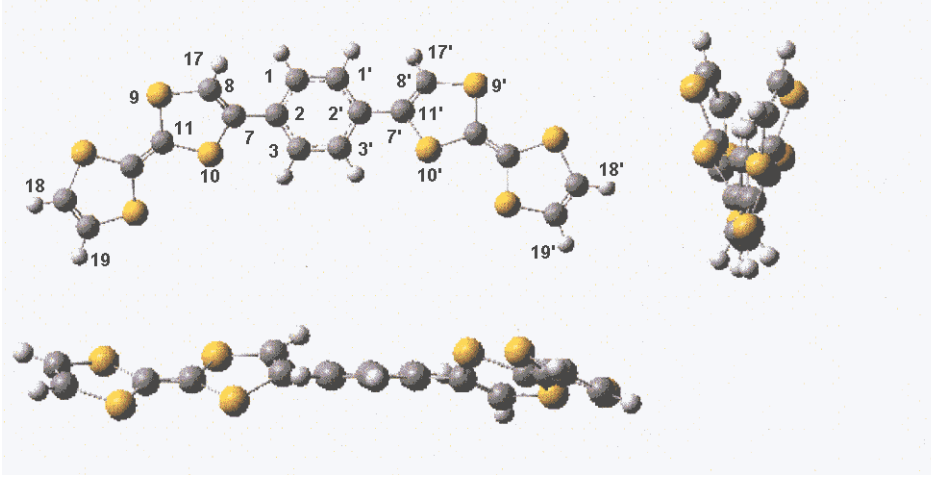
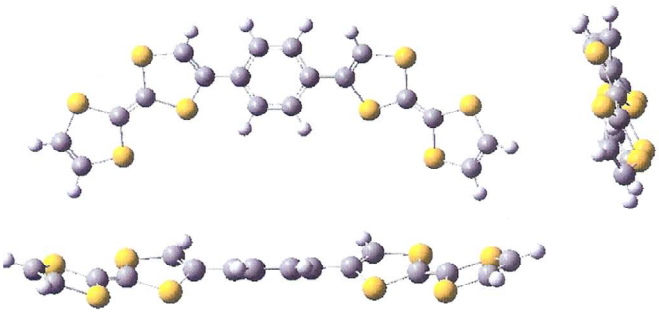
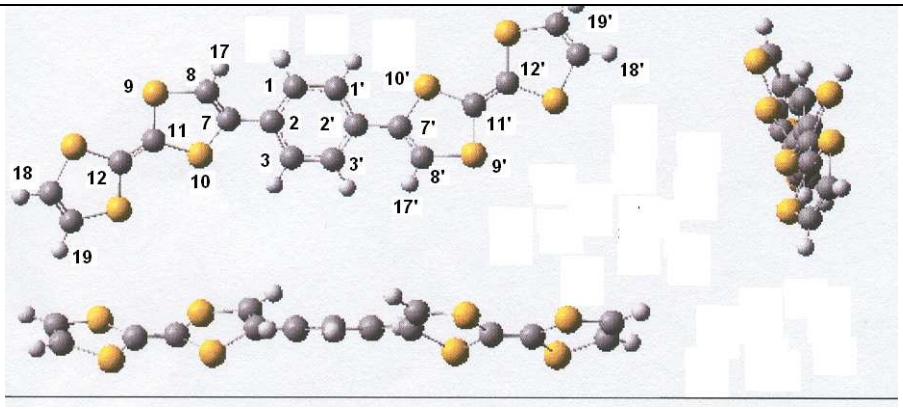
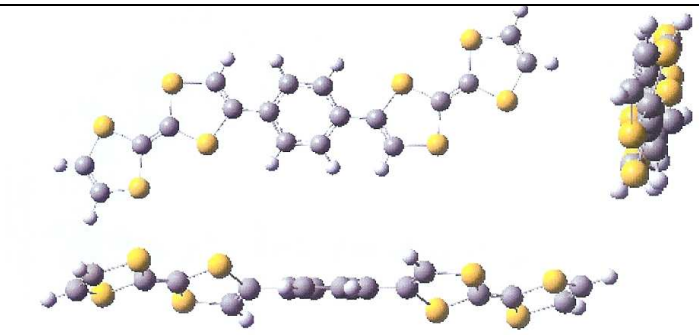
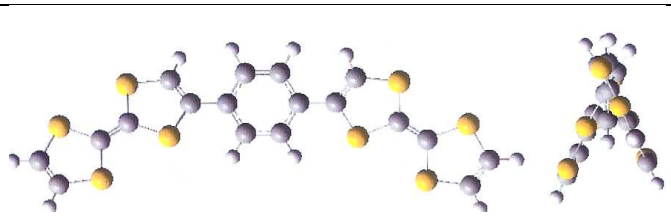
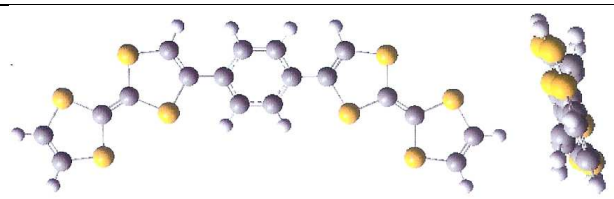
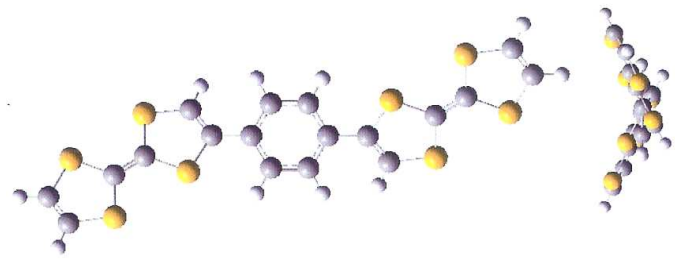
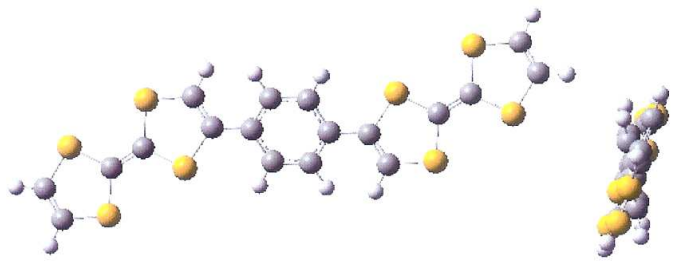
Rotamer AA (C2) E = -3877.34089 h ξ_1= -28.8° θ_1 = -163.5° ξ_2= -28.8° θ_2 = 163.5°	
Rotamer AA (Cs) E= -3877.34096 h ξ_1= 29.6° θ_1 = 163.7° ξ_2= -29.6° θ_2 = -163.7°	
Rotamer AB (C2) E = -3877.34085 h ξ_1= -29.8° θ_1 = -163.6° ξ_2= 150.4° θ_2 = -163.5°	
Rotamer AB (Ci) E = -3877.34103h ξ_1= 29.7° θ_1 = 163.8° ξ_2= 149.8° θ_2 = -163.8°	

Table S9. Conformations for $(TTF\text{-}Bz\text{-}TTF)^{+\bullet}_{para}$

E = -3877.34085 h Min1 C2 ξ_1= -28.4° θ_1 = -175.6° ξ_2= -28.2° θ_2 = -175.6	
E = -3877.34085 h Min1 Cs ξ_1= 28.8° θ_1 = -175.5° ξ_2= -28.5° θ_2 = -175.5°	
E = -3877.13528 h Min2 C2 ξ_1= -28.4° θ_1 = -175.7° ξ_2= 151.3° θ_2 = -175.7°	
E = -3877.13543 h Min2 Ci ξ_1= -27.9° θ_1 = -175.6° ξ_2= -151.8° θ_2 = 175.6°	

Same atom numbering as in Table sup.7.

ξ_1= C1C2C7C8, θ_1 = C7C10C9C11, ξ_2= C1'C2'C7'C8', θ_2 = C7C10C9C11

Table S10. calculated J values for $(TTF\text{-}Bz\text{-}TTF)^{2+}_{para}$

	Isomer AA				Isomer AB			
	C2		Cs		C2		Cs	
	J_N	J_Y	J_N	J_Y	J_N	J_Y	J_N	J_Y
	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)
TZV	-9.11 (-34.50)	-9.08 (-33.33)	-11.67 (-42.29)	-11.63 (-40.60)	-10.31 (-41.27)	-10.2 (-39.89)	-11.45 (-41.62)	-11.42 (-39.99)
Aug-cc-pVDZ	-8.60 (-31.95)	-8.57 (-30.91)	-11.67 (-44.54)	-11.63 (-42.97)	-10.30 (-36.89)	-10.27 (-35.55)	-11.00 (-39.05)	-10.96 (-37.57)
IGLO-III	-8.02 (-33.23)	-8.00 (-32.33)	-11.59 (-39.81)	-11.55 (-38.28)	-10.57 (-40.10)	-10.54 (-38.83)	-10.24 (-36.60)	-10.21 (-35.29)

Electrochemical studies. Cyclic voltammetry measurements were performed using a three-electrode cell equipped with a platinum millielectrode of 0.126 cm^2 area, an Ag/Ag^+ pseudo-reference and a platinum wire counter-electrode. The potential values were then re-adjusted with respect to the saturated calomel electrode (SCE). The electrolytic media involved a 0.1 $mol.L^{-1}$ solution of (n-Bu_4N)PF_6 in benzonitrile. All experiments have been performed at room temperature at 0.1 $V.s^{-1}$. Experiments have been carried out with an EGG PAR 273A potentiostat with positive feedback compensation.

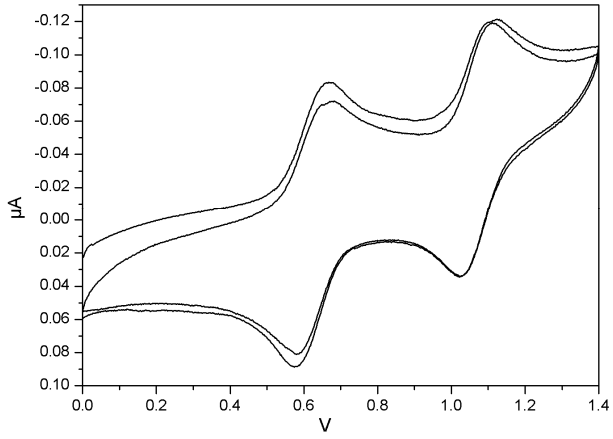


Fig. S7 Cyclic voltammetry of **TTF-Bz-TTF$_{meta}$**.

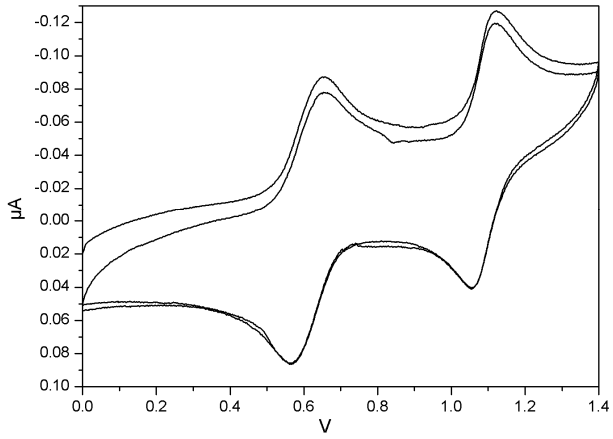


Fig. S8 Cyclic voltammetry of **TTF-Pyr-TTF$_{meta}$**.