Electronic Supplementary Information

Suppressing triplet decay in quinoidal singlet fission materials: the role of molecular planarity and rigidity

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Table S1. Excitation energies of the T_1 state calculated by DFT, TDDFT, and TDA with the B3LYP functional based on the S_0- and T_1-geometries and the T_1/S_0-MECP (in unit of eV).

	S_0-geometry			T_1-geometry			T_1/S_0-MECP		
	DFT	**TDA**	**TDDFT**	**DFT**	**TDA**	**TDDFT**	**DFT**	**TDA**	**TDDFT**
ThBF-c	1.211	1.211	0.957	0.738	0.807	-0.067	0.755	0.836	0.114
ThBF-p	1.206	1.207	0.953	0.774	0.841	-0.110	0.843	0.932	0.169
LThBF	1.246	1.247	1.018	0.956	0.996	0.524	1.645	1.726	0.981
TThBF-c	0.965	0.985	0.685	0.587	0.664	-0.225	0.646	0.738	-0.015
TThBF-p	0.970	0.989	0.690	0.569	0.647	-0.197	0.585	0.673	-0.059
LTThBF	0.973	0.990	0.715	0.698	0.754	-0.168	1.005	1.088	0.362

Table S2. Excitation energies of the T_2 state calculated by TDDFT and TDA with the B3LYP functional based on the S_0- and T_2-geometries (in unit of eV).

	S_0-geometry		T_2-geometry	
	TDA	**TDDFT**	**TDA**	**TDDFT**
ThBF-c	2.310	2.240	1.896	1.823
ThBF-p	2.314	2.243	1.900	1.827
LThBF	2.530	2.440	2.134	2.048
TThBF-c	2.231	2.171	1.814	1.750
TThBF-p	2.233	2.173	1.814	1.750
LTThBF	2.424	2.346	2.043	1.968

Table S3. Calculated vertical excitation energies of the S_1, T_1, and T_2 states for the studied compounds (in unit of eV).

	B3LYP					M06-2X				
	S_1	T_1	T_2	ΔE^a	ΔE^b	S_1	T_1	T_2	ΔE^a	ΔE^b
ThBF-c	2.365	1.211	2.310	-0.057	-0.112	2.682	1.541	2.996	-0.401	-0.087
ThBF-p	2.365	1.206	2.314	-0.047	-0.098	2.686	1.543	3.001	-0.399	-0.084
LThBF	2.380	1.246	2.530	-0.113	0.038	2.683	1.569	3.131	-0.455	-0.006
TThBF-c	2.191	0.965	2.231	0.260	0.301	2.492	1.280	2.774	-0.067	0.215
TThBF-p	2.190	0.970	2.233	0.249	0.293	2.493	1.285	2.785	-0.077	0.215
LTThBF	2.148	0.973	2.424	0.202	0.478	2.434	1.271	2.768	-0.109	0.226

[a]$\Delta E = E(S_1) - E(T_1) \times 2$, [b]$\Delta E = E(T_2) - E(T_1) \times 2$

Table S4. Reorganization Energies for the $T_1 \rightarrow S_0$ (λ_{S0}) and $S_0 \rightarrow T_1$ (λ_{T1}) processes calculated from potential energy surfaces (PES) and normal mode analyses (NM) (in unit of eV).

	PES		NM	
	λ_{S0}	λ_{T1}	λ_{S0}	λ_{T1}
ThBF-c	0.533	0.473	0.511	0.488
ThBF-p	0.442	0.431	0.467	0.437
LThBF	0.262	0.290	0.282	0.282
TThBF-c	0.371	0.378	0.398	0.377
TThBF-p	0.410	0.401	0.406	0.409
LTThBF	0.243	0.275	0.259	0.268

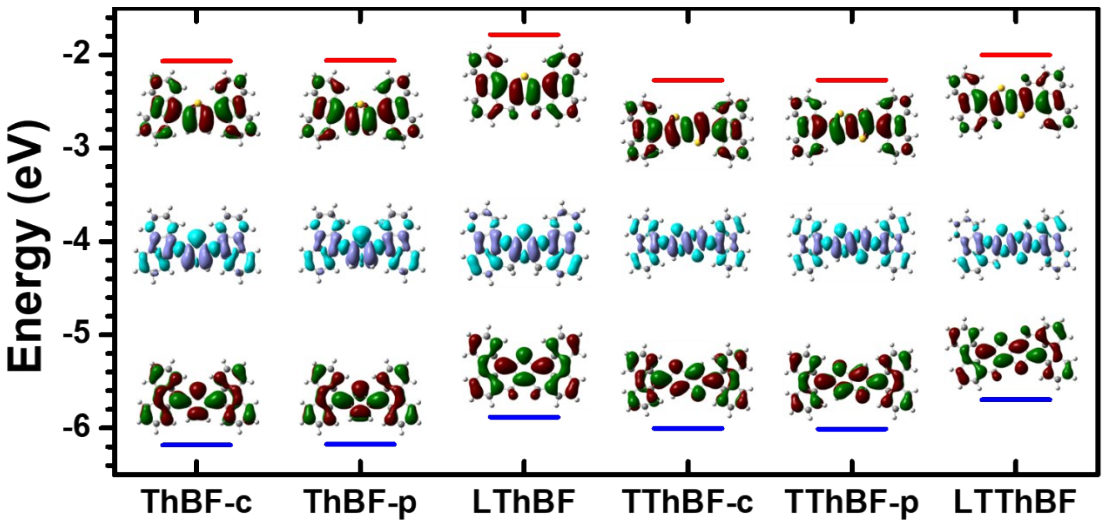

Figure S1. Energy levels and pictorial representation of the HOMO and LUMO, and charge density difference (CDD) for the vertical T_1 excitation calculated at the (TD)DFT-M06-2X/6-31G** level (purple/blue color in CDD means an increase/decrease in charge density).

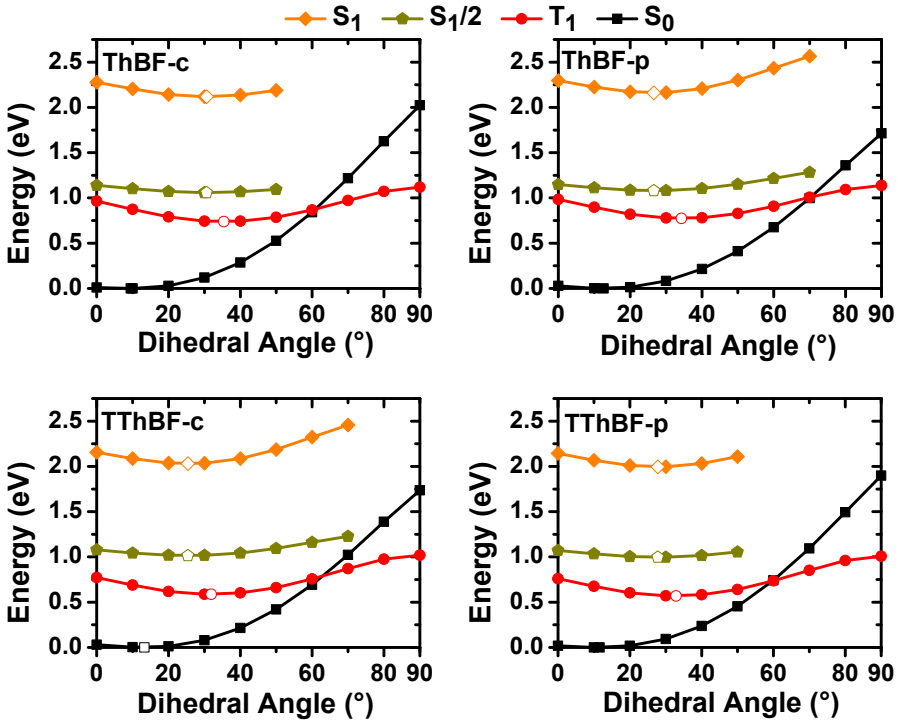

Figure S2. Potential energies of S_0, S_1, $S_1/2$, and T_1 as a function of the dihedral angles between the central thiophene/bithiophene and the two end fluorene groups for the unlocked compounds obtained using the B3LYP functional. The empty dots denote the energy minima of S_0, S_1, and T_1. The two dihedral angles change at the same time in the relaxed scan and the absolute values of the dihedral angles are used here.