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Electronic Supplementary Information

Importance of molecular rigidity on reducing the energy losses in organic solar cells: Implication from geometric relaxations of A-D-A electron acceptors

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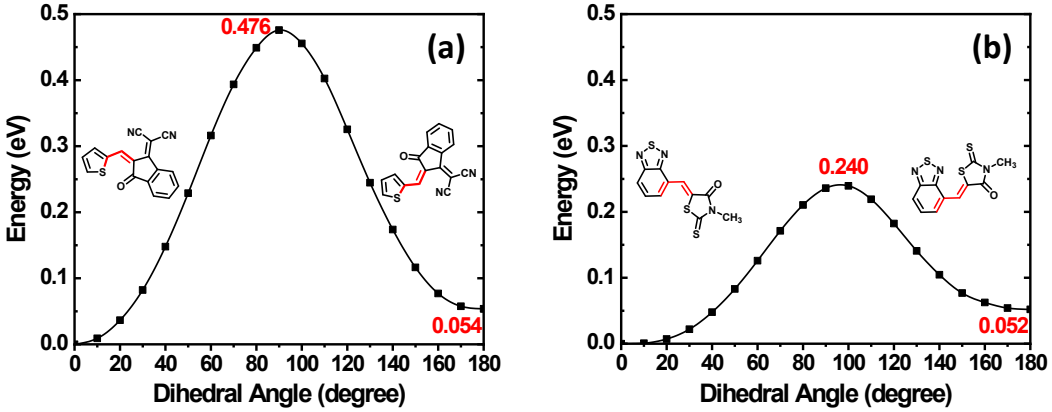

Figure S1. Potential energy curves of the relaxed scan for thiophene-IC (a) and benzothiadiazole-Rhodanine (b).

In order to determine the relative orientations of the terminal acceptor units and the central donor units, we performed relaxed scan of thiophene-IC and benzothiadiazole-Rhodanine at the DFT-B3LYP/6-311++G** level. As seen in **Figure S1**, the energy of the O···S conformer is 0.054 eV lower than that of the O···H conformer for thiophene-IC. Although the energy difference is not very large, the transition barrier from the O···S to O···H conformer is as high as 0.476 eV. Similarly, in the case of benzothiadiazole-rhodanine, the energy of the S···H conformer is slightly lower than that of the S···N conformer by 0.052 eV, but the transition barrier is quite high (0.240 eV). Therefore, only the O···S conformer of thiophene-IC and the S···H conformer of benzothiadiazole-Rhodanine are considered in the calculations of the A-D-A molecules.

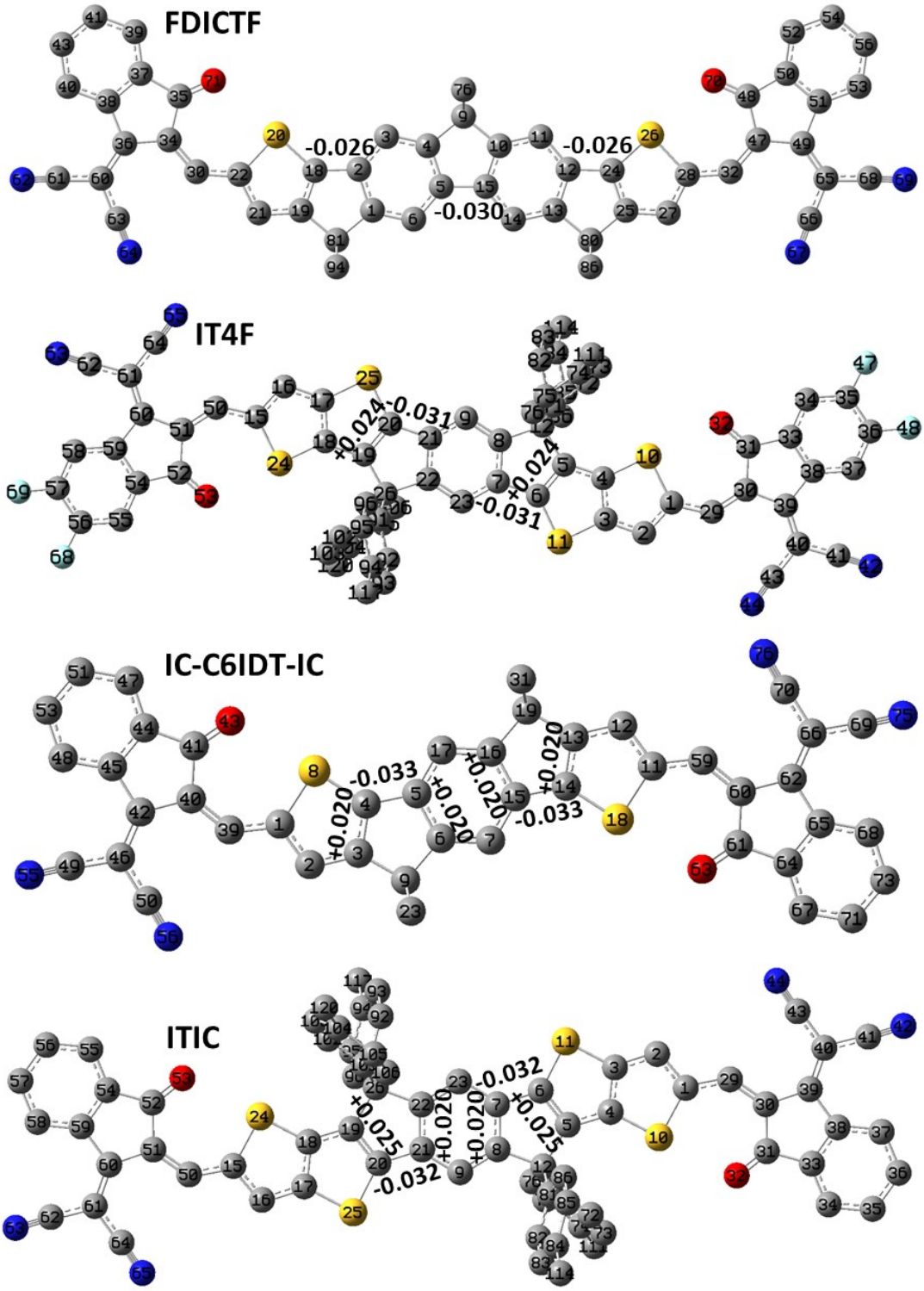

Figure S2. Significant bond length changes between the S_0 and S_1 states ($\Delta B = B(S_1) - B(S_0)$) for the fused molecules with $|\Delta B| \geq 0.02$ Å.

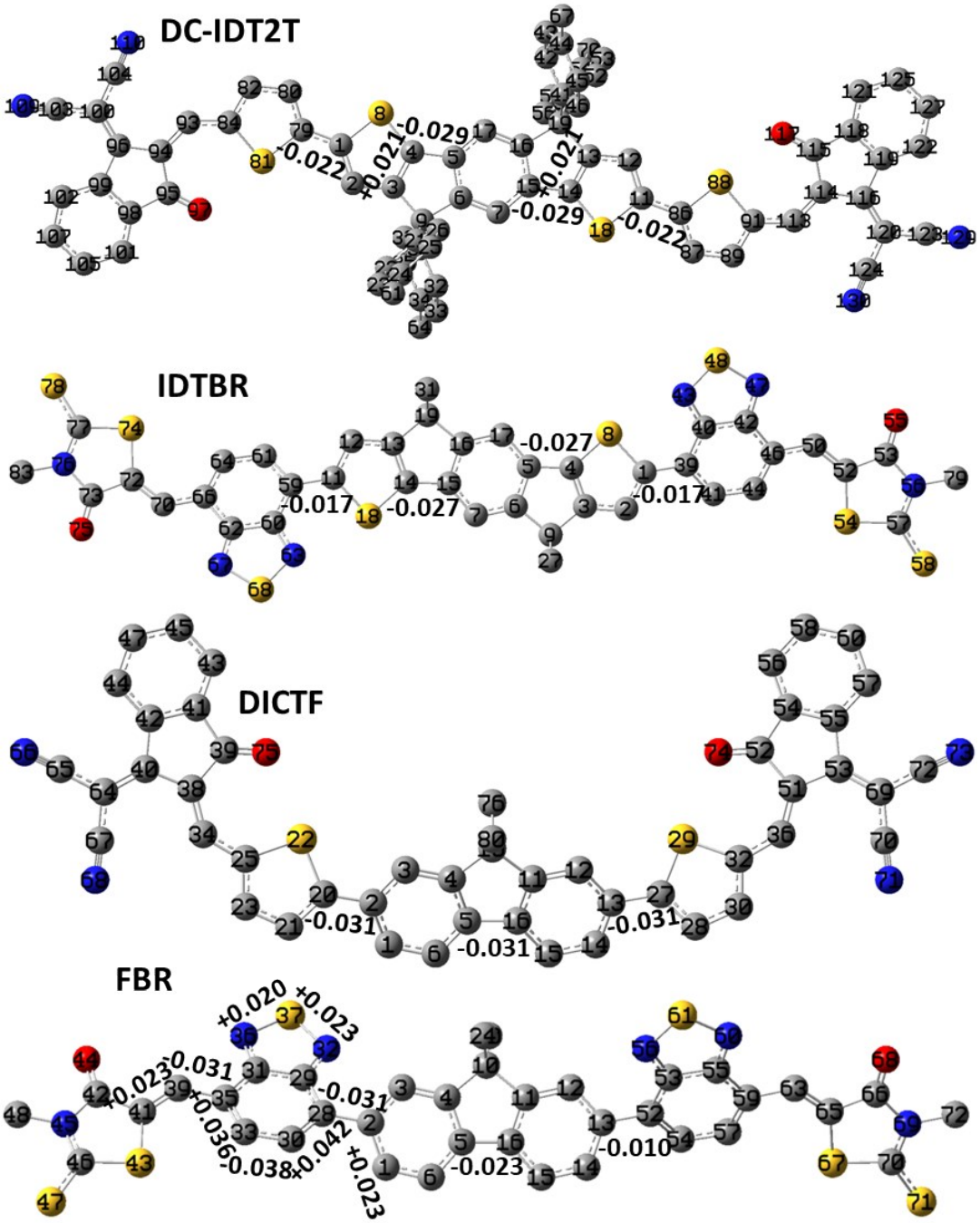

Figure S3. Significant bond length changes between the S_0 and S_1 states ($\Delta B = B(S_1) - B(S_0)$) for the non-fused molecules with $|\Delta B| \geq 0.02$ Å.

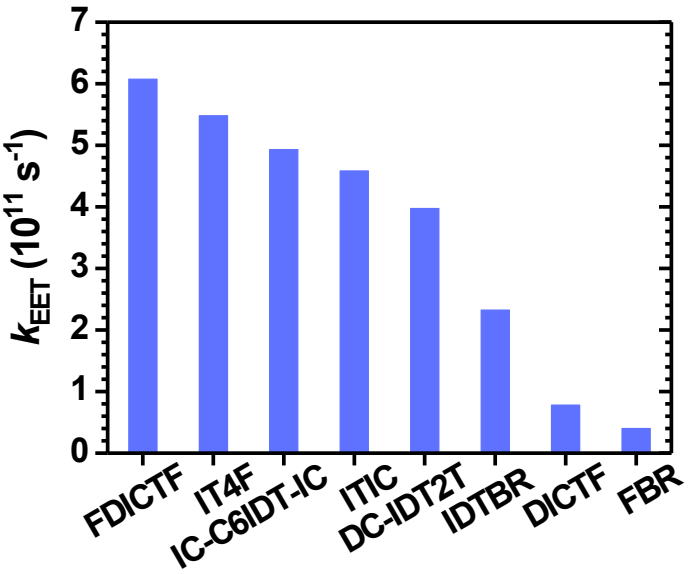

Figure S4. Exciton energy transfer rates calculated by the Marcus theory at room temperature (T = 300K) and the excitonic coupling V = 0.01 eV.

Table S1. Optimal ω values, oscillator strengths *f*, vertical excitation and emission energies for the S_1 state, and the contributions of the H→L and H-1→L+1 configurations to the $S_0 \rightarrow S_1$ excitation.

	ω	Excitation		Emission		Configuration	
	(bohr^{-1})	*f*	E_{vert} (eV)	*f*	E_{vert} (eV)	H → L	H-1 → L+1
FDICTF	0.105	3.10	2.359	3.25	2.168	79.1%	16.1%
IT4F	0.090	2.94	2.171	3.08	1.972	85.8%	9.9%
IC-C6IDT-IC	0.105	2.62	2.324	2.73	2.116	88.0%	8.7%
ITIC	0.095	2.95	2.215	3.09	2.001	84.8%	10.6%
DC-IDT2T	0.095	3.27	2.130	3.47	1.905	77.8%	14.4%
IDTBR	0.105	2.59	2.103	2.82	1.831	80.4%	15.4%
DICTF	0.125	2.25	2.661	2.48	2.293	68.2%	23.4%
FBR	0.130	2.18	2.745	1.96	2.314	69.5%	24.6%

Table S2. Experimental vertical excitation energies (eV) obtained from the peak wavelengths of absorption spectra in the solution (E_{sol}) and film (E_{film}) phases.

	E_{sol}	E_{film}	Reference
FDICTF	1.865	1.800	1
IT4F	-	1.729	2
IC-C6IDT-IC	1.867	1.732	3
ITIC	1.867	1.771	4
DC-IDT2T	1.771	-	5
IDTBR	1.950	1.884	6
DICTF	2.112	1.987	1
FBR	2.541	2.436	7

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Table S3. Reorganization energies of the electronic processes related to the acceptors in organic solar cells (all in unit of eV).

	$S_0 \rightarrow S_1$	$S_1 \rightarrow S_0$	EET[a]	$S_1 \rightarrow A^-$	$S_0 \rightarrow A^-$	$A^- \rightarrow S_0$	ET[b]
FDICTF	0.097	0.093	0.191	0.057	0.116	0.134	0.250
IT4F	0.100	0.099	0.199	0.068	0.124	0.142	0.266
IC-C6IDT-IC	0.104	0.104	0.208	0.067	0.160	0.177	0.337
ITIC	0.108	0.106	0.214	0.064	0.126	0.146	0.272
DC-IDT2T	0.110	0.116	0.226	0.058	0.118	0.139	0.257
IDTBR	0.120	0.151	0.272	0.051	0.171	0.161	0.333
DICTF	0.175	0.194	0.369	0.060	0.148	0.169	0.318
FBR	0.221	0.209	0.430	0.073	0.189	0.208	0.397

[a] Exciton energy transfer.

[b] Electron transfer.