Supporting Information

for

Design of Donor-Acceptor Copolymers for Organic Photovoltaic Materials: A Computational Study

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Content

1. Benchmark Studies

Table S1. Benchmark studies for the experimentally investigated copolymers

ωB97XD/6-311G*							
	E_g	E_{opt}	LUMO Neutral Model 1	LUMO αHOMO Model 4	HOMO Neutral Model 1	HOMO*	V_{oc}
C/CPDP-T-BT-T[51]	5.72	2.35	-1.22	-5.71	-6.94	-8.06	3.66
C/CPT-BT[52]	5.12	2.75	-1.41	-5.50	-6.52	-8.25	3.85
BDT2-T-BT-T[53]	4.35	2.52	-2.04	-5.35	-6.39	-7.87	3.47
BDT2-T-ffBT-T[54]	5.46	2.68	-1.56	-5.89	-7.03	-8.57	4.17
Si/CPDP-T-BT-T[55]	5.76	2.78	-1.26	-5.76	-7.03	-8.54	4.14
BDT2-T-HTAz-T[56]	5.75	2.84	-1.08	-5.49	-6.84	-8.33	3.93
Si/CPT-TPD	5.30	2.62	-1.62	-5.28	-6.91	-7.90	3.50
PBE0/6-311G*							
	E_g	E_{opt}	LUMO Neutral Model 1	LUMO αHOMO Model 4	HOMO Neutral Model 1	HOMO*	V_{oc}
C/CPDP-T-BT-T[51]	2.35	2.01	-2.90	-3.87	-5.25	-5.88	1.48
C/CPT-BT[52]	1.88	1.54	-3.01	-3.76	-4.89	-5.30	0.90
BDT2-T-BT-T[53]	2.22	1.83	-3.10	-3.99	-5.32	-5.82	1.42
BDT2-T-ffBT-T[54]	2.16	1.86	-3.27	-3.97	-5.42	-5.83	1.43
Si/CPDP-T-BT-T[55]	2.33	2.04	-2.99	-3.94	-5.33	-5.98	1.58
BDT2-T-HTAz-T[56]	2.48	2.06	-2.74	-3.66	-5.23	-5.72	1.32
Si/CPT-TPD	2.43	2.00	-3.06	-3.91	-5.48	-5.91	1.81
B3LYP/6-311G*							
C/CPDP-T-BT-T[51]	2.09	1.86	-2.96	-3.70	-5.04	-5.56	1.16
C/CPT-BT[52]	1.64	1.39	-3.06	-3.60	-4.70	-4.99	0.59
BDT2-T-BT-T[53]	1.97	1.68	-3.15	-3.81	-5.12	-5.49	1.09
BDT2-T-ffBT-T[54]	1.99	1.68	-3.32	-3.83	-5.22	-5.51	1.11
Si/CPDP-T-BT-T[55]	2.06	1.88	-3.05	-3.77	-5.12	-5.65	1.25
BDT2-T-HTAz-T[56]	2.22	1.90	-2.80	-3.52	-5.02	-5.43	1.03
Si/CPT-TPD	2.16	1.84	-3.12	-3.74	-5.28	-5.58	1.18
Experimental							
	E_g		LUMO		HOMO	V_{oc}	
C/CPDP-T-BT-T[51]	1.90				-5.70	1.04	
C/CPT-BT[52]	1.40				-5.30	0.62	
BDT2-T-BT-T[53]	1.65		-3.13		-5.42	0.87	
BDT2-T-ffBT-T[54]	1.70		-3.33		-5.50	0.91	
Si/CPDP-T-BT-T[55]	1.82				-5.40	0.90	
BDT2-T-HTAz-T[56]	1.98		-2.87		-5.29	0.70	
Si/CPT-TPD	1.70		-3.17		-5.44	0.91	

Two hybrid and a long range corrected (LC) functionals have been applied to seven tetramers in a benchmark study; the results are compared to the experimental values. The hybrid functionals B3LYP and PBE0 contain HF exchange ratios of 20% and 25%, respectively, while ωB97XD has a HF exchange ratio of 22%. Furthermore, ωB97XD contains empirical atom-atom dispersion corrections.

Surprisingly, ωB97XD, which is known for its accuracy in excited state calculations, has shown results that are not comparable to the experimental values. On the other hand, B3LYP and PBE0 results are comparable. In optical band gap calculations, the mean absolute errors (MAE) of B3LYP and PBE0 are 0.04 eV and 0.18 eV, respectively. B3LYP has a MAE of 0.15 eV and 0.04 eV for the HOMO and LUMO energy calculations; while PBE0 has a MAE of 0.34 eV and 0.08 eV for the same orbitals.

Overall, B3LYP is the best choice for the functional to be used in this study, in terms of accuracy and computational time.

2. Effect of the Side Chains

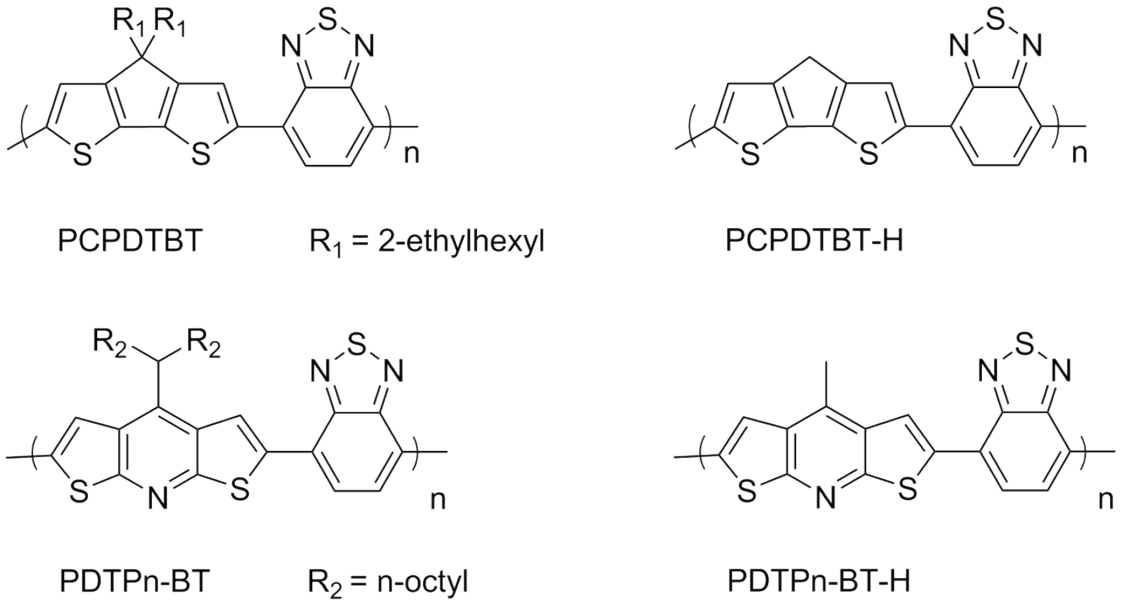

Figure S1. Chemical structures of investigated oligomers.

Table S2. Calculated and experimental HOMO energies, band gaps (E_g) and calculated LUMO energies (eV) of the oligomers with or without side chains (B3LYP/6-311G*).

Oligomers	HOMO	E_{opt}	Exp. HOMO	Exp. E_{opt}
PCPDTBT[a, 1]	-4.68	1.36	-5.3	1.4
PCPDTBT-H	-4.70	1.39		
PCPDTBT-CH_3	-4.67	1.36		
PDTPnBT[a, 1]	-5.59	2.05	-5.6	2.1
PDTPn-BT-H	-5.64	2.07		
PDTPn-BT- CH_3	-5.50	2.06		

[a].The oligomers have side chains

As can be seen from Table 1, the effect of side chains to the band gap energies was negligible. Energy differences are 0.02 eV and 0.07 eV for PCPDTBT and PDTPnBT, respectively.

3. Distortion Energies and Bong Length Alternation

Table S3. Distortion energies (kcal/mol) and dihedral angles (°) (B3LYP/6-311G*).

Oligomers	φ_1	φ_2	φ_3	φ_4	ΔE_{dis}
C/CPTz-BT	0	0			0
N/CPTz-BT	0	0			0
Si/CPTz-BT	0	0			0
C/DTPn-BT	0	0			0
Si/DTPn-BT	0	0			0
BDT1-BT	1	1			0
BDT2-BT	0	0			0
C/CPDP-BT	38	38			21.3
N/CPDP-BT	37	37			21.2
Si/CPDP-BT	37	37			20.9
C/CPTz-T-BT-T	0	0	1	1	0.0
N/CPTz-T-BT-T	0	0	0	0	0.0
Si/CPTz-T-BT-T	0	0	0	0	0.0
C/DTPn-T-BT-T	14	25	8	7	1.3
Si/DTPn-T-BT-T	14	25	3	5	1.1
BDT1-T-BT-T	15	17	6	6	0.6
BDT2-T-BT-T	15	15	6	5	0.4
C/CPDP-T-BT-T	28	27	7	6	3.6
N/CPDP-T-BT-T	29	28	7	9	4.6
Si/CPDP-T-BT-T	28	27	5	5	3.5
C/CPTz-BX	0	0			0
N/CPTz-BX	0	0			0
Si/CPTz-BX	0	0			0
C/DTPn-BX	0	0			0
Si/DTPn-BX	1	1			0
BDT1-BX	0	0			0
BDT2-BX	0	0			0
C/CPDP-BX	31	31			9.9
N/CPDP-BX	31	30			10.0
Si/CPDP-BX	31	31			9.7
C/CPTz-T-BX-T	0	0	0	0	0.0

N/CPTz-T-BX-T	0	0	0	0	0.0
Si/CPTz-T-BX-T	0	0	0	0	0.0
C/DTPn-T-BX-T	15	26	2	2	1.2
Si/DTPn-T-BX-T	14	23	1	2	0.9
BDT1-T-BX-T	15	14	2	2	0.4
BDT2-T-BX-T	6	8	1	1	0.1
C/CPDP-T-BX-T	28	27	3	3	3.5
N/CPDP-T-BX-T	30	28	3	1	4.3
Si/CPDP-T-BX-T	28	27	2	2	3.4
C/CPTz-BSe	0	0			0
N/CPTz-BSe	0	0			0
Si/CPTz-BSe	0	0			0
C/DTPn-BSe	0	0			0
Si/DTPn-BSe	2	2			0
BDT1-BSe	4	4			0.1
BDT2-BSe	0	0			0
C/CPDP-BSe	38	38			26.6
N/CPDP-BSe	38	38			26.9
Si/CPDP-BSe	39	38			26.2
C/CPTz-T-BSe-T	0	0	2	0	0.0
N/CPTz-T-BSe-T	0	0	4	1	0.0
Si/CPTz-T-BSe-T	0	0	6	5	0.1
C/DTPn-T-BSe-T	15	25	10	8	1.5
Si/DTPn-T-BSe-T	4	7	5	4	1.3
BDT1-T-BSe-T	16	15	9	8	0.8
BDT2-T-BSe-T	13	13	10	7	0.5
C/CPDP-T-BSe-T	28	27	11	7	3.7
N/CPDP-T-BSe-T	29	28	12	7	4.7
Si/CPDP-T-BSe-T	28	27	11	9	3.7
C/CPTz-HTAZ	0	0			0
N/CPTz-HTAZ	0	0			0
Si/CPTz-HTAZ	0	0			0
C/DTPn-HTAZ	0	0			0
Si/DTPn-HTAZ	1	0			0
BDT1-HTAZ	1	1			0
BDT2-HTAZ	0	0			0
C/CPDP-HTAZ	33	32			11.8
N/CPDP-HTAZ	33	32			12.1
Si/CPDP-HTAZ	33	33			11.4
C/CPTz-T-HTAZ-T	0	0	1	0	0.0
N/CPTz-T-HTAZ-T	0	0	0	0	0.0
Si/CPTz-T-HTAZ-T	0	0	0	0	0.0
C/DTPn-T-HTAZ-T	14	26	3	3	1.3
Si/DTPn-T-HTAZ-T	14	24	1	2	1.0
BDT1-T-HTAZ-T	17	15	2	3	0.5

BDT2-T-HTAZ-T	13	13	2	1	0.2
C/CPDP-T-HTAZ-T	28	27	3	4	3.6
N/CPDP-T-HTAZ-T	30	28	3	3	4.5
Si/CPDP-T-HTAZ-T	27	27	4	2	3.4

Table S4. Bond length alternations (BLA, Å) values (B3LYP/6-311G*).

Donor-Acceptor				
	BT	BX	BSe	HTAZ
C/CPDP	0.042	0.042	0.045	0.039
N/CPDP	0.034	0.034	0.036	0.031
Si/CPDP	0.045	0.045	0.048	0.042
BDT1	0.040	0.040	0.042	0.039
BDT2	0.039	0.040	0.041	0.034
Donor-Thiophene-Acceptor-Thiophene				
	BT	BX	BSe	HTAZ
C/CPDP	0.042	0.042	0.043	0.041
N/CPDP	0.037	0.037	0.039	0.036
Si/CPDP	0.043	0.043	0.045	0.043
BDT1	0.043	0.043	0.044	0.042
BDT2	0.042	0.041	0.043	0.041

4. Reorganization Energies

Table S5. Electron Reorganization Energy ($\lambda_{electron}$), Adiabatic Ionization Potential (AIP), Adiabatic Electron Affinity (AEA), Vertical Ionization Potential (VIP), Vertical Electron Afinity (VEA) values (B3LYP/6-311G*).

Compounds	**$\lambda_{electron}$ (meV)**	**AIP (eV)**	**AEA (eV)**	**VIP (eV)**	**VEA (eV)**
C/CPTz-BT	122.50	5.66	-2.81	5.75	-2.75
N/CPTz-BT	124.04	5.60	-2.78	5.68	-2.72
Si/CPTz-BT	112.16	5.91	-2.87	6.00	-2.81
C/DTPn-BT	64.65	6.29	-2.58	6.34	-2.55
Si/DTPn-BT	55.39	5.95	-2.48	5.98	-2.45
BDT1-BT	75.38	5.87	-2.53	5.93	-2.49
BDT2-BT	79.64	5.85	-2.59	5.91	-2.55
C/CPDP-BT	106.46	6.01	-2.08	6.08	-2.03
N/CPDP-BT	112.84	5.97	-2.05	6.04	-2.00
Si/CPDP-BT	105.09	6.15	-2.18	6.22	-2.13
C/CPTz-T-BT-T	64.68	5.46	-2.79	5.51	-2.76

N/CPTz-T-BT-T	64.53	5.42	-2.77	5.47	-2.74
Si/CPTz-T-BT-T	63.30	5.61	-2.83	5.66	-2.80
C/DTPn-T-BT-T	62.18	5.79	-2.67	5.84	-2.64
Si/DTPn-T-BT-T	53.61	5.65	-2.62	5.69	-2.59
BDT1-T-BT-T	67.16	5.55	-2.64	5.60	-2.60
BDT2-T-BT-T	72.03	5.55	-2.68	5.60	-2.64
C/CPDP-T-BT-T	63.73	5.53	-2.45	5.58	-2.41
N/CPDP-T-BT-T	62.91	5.52	-2.42	5.56	-2.39
Si/CPDP-T-BT-T	64.38	5.61	-2.51	5.66	-2.48
C/CPTz-BX	146.87	5.89	-3.04	5.98	-2.97
N/CPTz-BX	147.60	5.83	-3.02	5.92	-2.95
Si/CPTz-BX	133.37	6.13	-3.08	6.22	-3.01
C/DTPn-BX	75.45	6.51	-2.75	6.55	-2.71
Si/DTPn-BX	63.47	6.14	-2.64	6.17	-2.61
BDT1-BX	90.25	6.11	-2.75	6.16	-2.70
BDT2-BX	95.87	6.06	-2.79	6.11	-2.74
C/CPDP-BX	137.79	6.17	-2.29	6.24	-2.22
N/CPDP-BX	139.51	6.13	-2.26	6.19	-2.19
Si/CPDP-BX	148.10	6.31	-2.41	6.37	-2.33
C/CPTz-T-BX-T	73.16	5.61	-2.95	5.66	-2.91
N/CPTz-T-BX-T	73.64	5.57	-2.93	5.62	-2.89
Si/CPTz-T-BX-T	70.66	5.76	-2.99	5.81	-2.95
C/DTPn-T-BX-T	61.60	5.94	-2.81	5.99	-2.78
Si/DTPn-T-BX-T	54.10	5.79	-2.75	5.83	-2.72
BDT1-T-BX-T	69.94	5.69	-2.78	5.74	-2.75
BDT2-T-BX-T	73.74	5.69	-2.83	5.74	-2.79
C/CPDP-T-BX-T	66.97	5.68	-2.58	5.73	-2.54
N/CPDP-T-BX-T	73.16	5.66	-2.55	5.72	-2.51
Si/CPDP-T-BX-T	73.64	5.77	-2.64	5.81	-2.60
C/CPTz-BSe	62.10	5.56	-2.85	5.66	-2.80
N/CPTz-BSe	119.54	5.50	-2.82	5.59	-2.77
Si/CPTz-BSe	106.06	5.82	-2.91	5.91	-2.86
C/DTPn-BSe	61.11	6.21	-2.64	6.26	-2.61
Si/DTPn-BSe	53.55	5.89	-2.54	5.92	-2.51
BDT1-BSe	70.72	5.80	-2.58	5.86	-2.55
BDT2-BSe	73.40	5.79	-2.64	5.84	-2.61
C/CPDP-BSe	87.84	5.96	-2.15	6.03	-2.1
N/CPDP-BSe	95.39	5.92	-2.12	5.98	-2.08
Si/CPDP-BSe	97.30	6.09	-2.24	6.16	-2.19
C/CPTz-T-BSe-T	60.60	5.41	-2.82	5.46	-2.79
N/CPTz-T-BSe-T	61.46	5.38	-2.81	5.42	-2.78
Si/CPTz-T-BSe-T	63.84	5.56	-2.87	5.62	-2.83
C/DTPn-T-BSe-T	63.42	5.74	-2.73	5.79	-2.69
Si/DTPn-T-BSe-T	54.36	5.61	-2.67	5.65	-2.64
BDT1-T-BSe-T	67.48	5.50	-2.69	5.55	-2.65

BDT2-T-BSe-T	70.05	5.50	-2.73	5.55	-2.69
C/CPDP-T-BSe-T	61.69	5.49	-2.51	5.54	-2.48
N/CPDP-T-BSe-T	60.60	5.47	-2.49	5.52	-2.45
Si/CPDP-T-BSe-T	61.46	5.56	-2.57	5.61	-2.53
C/CPTz-HTAZ	146.68	5.55	-2.43	5.64	-2.36
N/CPTz-HTAZ	147.78	5.49	-2.38	5.57	-2.31
Si/CPTz-HTAZ	135.53	5.81	-2.51	5.89	-2.44
C/DTPn-HTAZ	78.93	6.15	-2.09	6.20	-2.09
Si/DTPn-HTAZ	65.84	5.83	-2.08	5.86	-2.04
BDT1-HTAZ	95.51	5.72	-2.06	5.78	-2.01
BDT2-HTAZ	102.02	5.72	-2.16	5.77	-2.11
C/CPDP-HTAZ	173.94	5.82	-1.58	5.89	-1.49
N/CPDP-HTAZ	185.49	5.78	-1.53	5.85	-1.44
Si/CPDP-HTAZ	183.20	5.96	-1.73	6.03	-1.64
C/CPTz-T-HTAZ-T	79.63	5.36	-2.49	5.41	-2.45
N/CPTz-T-HTAZ-T	80.43	5.33	-2.46	5.37	-2.42
Si/CPTz-T-HTAZ-T	76.19	5.51	-2.55	5.56	-2.51
C/DTPn-T-HTAZ-T	75.83	5.68	-2.31	5.73	-2.27
Si/DTPn-T-HTAZ-T	62.84	5.56	-2.27	5.60	-2.24
BDT1-T-HTAZ-T	88.34	5.45	-2.29	5.50	-2.24
BDT2-T-HTAZ-T	82.16	5.45	-2.34	5.49	-2.29
C/CPDP-T-HTAZ-T	83.42	5.43	-2.04	5.47	-2.00
N/CPDP-T-HTAZ-T	79.63	5.41	-2.00	5.46	-1.95
Si/CPDP-T-HTAZ-T	80.43	5.61	-2.51	5.66	-2.48

Table S6. Calculated V_{D-A} values of the molecules. (B3LYP/6-311G*)

V_{D-A}(eV) for Hole Transfer				
Donor - Acceptor				
	BT	BX	BSe	HTAZ
C/CPTz	0.12	0.12	0.14	0.12
N/CPTz	0.13	0.14	0.14	0.13
Si/CPTz	0.11	0.10	0.11	0.11
C/DTPn	0.01	0.04	0.01	0.04
Si/DTPn	0.03	0.04	0.02	0.02
BDT1	0.08	0.10	0.10	0.08
BDT2	0.06	0.09	0.09	0.06
C/CPDP	0.09	0.10	0.09	0.09
N/CPDP	0.10	0.10	0.10	0.10
Si/CPDP	0.09	0.09	0.09	0.19
Donor - Thiophene - Acceptor - Thiophene				
	BT	BX	BSe	HTAZ

C/CPTz	0.05	0.04	0.04	0.05
N/CPTz	0.04	0.04	0.04	0.05
Si/CPTz	0.05	0.05	0.04	0.05
C/DTPn	0.02	0.02	0.01	0.02
Si/DTPn	0.02	0.04	0.03	0.01
BDT1	0.04	0.04	0.04	0.04
BDT2	0.04	0.04	0.03	0.04
C/CPDP	0.04	0.04	0.03	0.03
N/CPDP	0.04	0.04	0.03	0.03
Si/CPDP	0.03	0.03	0.03	0.03

V_{D-A} (eV) for Electron Transfer				
Donor - Acceptor				
	BT	BX	BSe	HTAZ
C/CPTz	0.10	0.12	0.10	0.13
N/CPTz	0.11	0.14	0.11	0.14
Si/CPTz	0.09	0.10	0.09	0.13
C/DTPn	0.05	0.05	0.04	0.06
Si/DTPn	0.03	0.04	0.02	0.05
BDT1	0.07	0.10	0.07	0.09
BDT2	0.08	0.11	0.08	0.11
C/CPDP	0.06	0.07	0.04	0.09
N/CPDP	0.05	0.07	0.04	0.08
Si/CPDP	0.05	0.08	0.05	0.21
Donor - Thiophene - Acceptor - Thiophene				
	BT	BX	BSe	HTAZ
C/CPTz	0.05	0.05	0.03	0.06
N/CPTz	0.05	0.05	0.03	0.06
Si/CPTz	0.04	0.06	0.03	0.06
C/DTPn	0.02	0.03	0.01	0.03
Si/DTPn	0.02	0.02	0.02	0.03
BDT1	0.03	0.04	0.03	0.05
BDT2	0.04	0.05	0.02	0.05
C/CPDP	0.03	0.04	0.02	0.03
N/CPDP	0.03	0.04	0.02	0.03
Si/CPDP	0.03	0.03	0.02	0.04

5. HOMO-LUMO Energies

Table S7. HOMO, LUMO energies (eV) (B3LYP/6-311G*).

HOMO				
Donor - Acceptor				
	BT	BX	BSe	HTAZ
C/CPTz	-5.41	-5.69	-5.32	-5.34
N/CPTz	-5.34	-5.63	-5.25	-5.27
Si/CPTz	-5.65	-5.92	-5.57	-5.59
C/DTPn	-5.43	-6.50	-6.09	-6.14
Si/DTPn	-5.81	-6.12	-5.73	-5.88
BDT1	-5.61	-5.90	-5.54	-5.52
BDT2	-5.62	-5.88	-5.44	-5.55
C/CPDP	-5.89	-6.16	-5.90	-5.76
N/CPDP	-5.52	-6.05	-5.83	-5.75
Si/CPDP	-6.07	-6.33	-6.07	-5.92
Donor - Thiophene - Acceptor - Thiophene				
	BT	BX	BSe	HTAZ
C/CPTz	-5.29	-5.46	-5.25	-5.20
N/CPTz	-5.23	-5.41	-5.20	-5.12
Si/CPTz	-5.50	-5.68	-5.43	-5.39
C/DTPn	-5.84	-6.07	-5.75	-5.80
Si/DTPn	-5.63	-5.89	-5.62	-5.48
BDT1	-5.49	-5.70	-5.44	-5.44
BDT2	-5.49	-5.68	-5.18	-5.43
C/CPDP	-5.56	-5.74	-5.52	-5.51
N/CPDP	-5.51	-5.77	-5.46	-5.51
Si/CPDP	-5.65	-5.89	-5.58	-5.59
LUMO				
Donor - Thiophene - Acceptor - Thiophene				
	BT	BX	BSe	HTAz
C/CPTz	-3.42	-3.65	-3.45	-2.97
N/CPTz	-3.38	-3.62	-3.42	-2.96
Si/CPTz	-3.50	-3.69	-3.42	-3.12
C/DTPn	-3.35	-3.57	-3.27	-2.77
Si/DTPn	-3.18	-3.36	-3.16	-2.69
BDT1	-3.24	-3.40	-3.22	-2.70
BDT2	-3.30	-3.41	-3.26	-2.81
C/CPDP	-2.90	-3.22	-2.93	-2.45
N/CPDP	-2.91	-3.21	-2.93	-2.43
Si/CPDP	-3.03	-3.30	-3.00	-2.56
Donor - Thiophene - Acceptor - Thiophene				
	BT	BX	BSe	HTAZ
C/CPTz	-3.27	-3.42	-3.30	-2.84

N/CPTz	-3.24	-3.40	-3.29	-2.78
Si/CPTz	-3.30	-3.48	-3.35	-3.03
C/DTPn	-3.17	-3.32	-3.21	-2.71
Si/DTPn	-3.14	-3.24	-3.14	-2.74
BDT1	-3.11	-3.27	-3.17	-2.75
BDT2	-3.15	-3.31	-3.19	-2.80
C/CPDP	-2.96	-3.09	-2.99	-2.48
N/CPDP	-3.00	-3.07	-2.96	-2.46
Si/CPDP	-3.05	-3.12	-3.04	-2.57

6. References

(1) Zhou, H.; Yang, L.; You, W. Rational Design of High Performance Conjugated Polymers for Organic Solar Cells. *Macromolecules* **2012**, 45, 607-632.