Supplemental Material

Significant Role of DNA Backbone in Mediating the Transition Origin of Electronic Excitations of B-DNA – Implication from Long Range Corrected TDDFT and Quantified NTO Analysis

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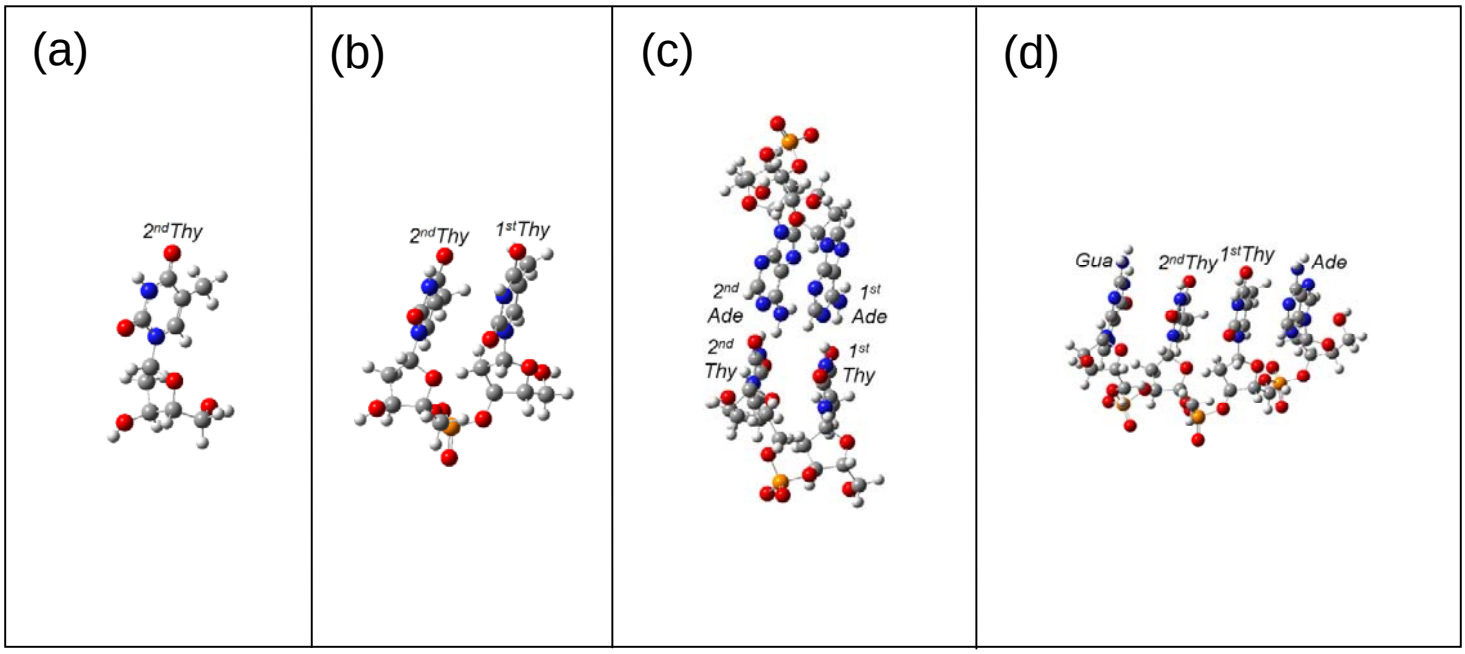

Figure S1. Various molecular segments extracted from X-ray diffraction determined B-DNA (PDB code 3BSE). The strucutres of (a) dT, (b)dTpdT, (c) dTpdT--dApdA, and (d) dApdTpdTpdG under study are shown.

TABLE S1: The major internal coordinates of DNA backbone – nucleic-acid torsion angles – of non-relaxed and partially relaxed ideal and 3BSE dTpdT shown in Figure 1 and S1, adopted from the conventions defined in Chap. 5 of Ref. S1. All the torsion-angles of the two dTpdTs, whether relaxation has been performed or not, are fairly within the common ranges of B-DNA structures (p.132 of Ref. S1).

		Non-relaxed ideal dTpdT	Ideal dTpdT	Non-relaxed 3BSE dTpdT	3BSE dTpdT
Angle	Sequence	Value(°)	Value(°)	Value(°)	Value(°)
β_{T1}	H*-O5'-C5'-C4'	-146.02040	-169.40853	-171.79766	179.98084
γ_{T1}	O5'-C5'-C4'-C3'	36.36158	50.94523	40.98660	57.25397
δ_{T1}	C5'-C4'-C3'-O3'	156.40092	133.80945	132.93283	107.69943
ε_{T1}	C4'-C3'-O3'-P	154.98268	175.21786	-172.21242	-176.35060
ζ_{T1}	C3'-O3'-P-O5'	-95.17465	-97.41396	-109.65894	-85.03841
α_{T2}	O3'-P-O5'-C5'	-46.83902	-61.78024	-43.83471	-60.41274
β_{T2}	P-O5'-C5'-C4'	-146.00015	-171.22393	172.24216	178.70789
γ_{T2}	O5'-C5'-C4'-C3'	36.37464	50.67285	36.97245	49.02761
δ_{T2}	C5'-C4'-C3'-O3'	156.39855	133.33265	146.88308	138.98368
ε_{T2}	C4'-C3'-O3'-H*	154.94931	173.65856	-115.74378	-140.36987
χ_{T1}	O4'-C1'-N1-C2	-97.99829	-108.82575	-110.05868	-127.10523
χ_{T2}	O4'-C1'-N1-C2	-98.01020	-111.93144	-97.36020	-105.49150

H* denotes the P atom that is replaced with H atom upon molecule extraction.

TABLE S2: The first 10 SO-hosted excitations predicted by TD-ωB97X[S2] calculation of (a) non-relaxed ideal dTpdT without optimizing hydrogen and backbone atoms first (see main text), (b) ideal dTpdT with large basis set 6-311+G(df,p)[S3, S4], and (c) ideal dTpdT put in water solvent of Polarisable Continuum Model (PCM)[S5] around the optimized dTp(dApdTpdTpdG)pdC--AdTp(dApdA)pdCG (see main text). The basis set used in (a) and (c) is 6-31G(d). $\sigma_{G/E/B}$ stand for the variations of transition origin[S6] caused by the change of conformation, surrounding environment, and used basis set, respectively. The results of (a) and (c) are referenced to those of the ideal dTpdT shown in Table 1(b), also adopted here in the lower-right corner for a guide to the eye.

N; P	λ (nm)	f	NTO1(2)	$\sigma_{G/E}$	%	Type	N; P	λ (nm)	f	NTO1(2)	σ_{B}	%	Type
(a) Non-relaxed ideal dTpdT							(b) Ideal dTpdT [6-311+G(df,p)]						
1	239.30	0.0370	P1t2 - S1t2	0.034	67	B2	1	243.96	0.0375	P1t2 - S1t2	0.029	65	B2
-			P1t1 - S1t1		30		-			P1t1 - S1t1		31	
2	236.23	0.4157	P1t1 - S1t1	0.022	67	B1	2	241.43	0.4295	P1t1(2) - S1t1(2)	0.067	67	B1
+			P1t2 - S1t2		30		+			P1t(1)2 - S1t(1)2		28	
3	235.97	0.0044	N1t2 - S1t2 (S2t2)	0.042	98	(A2)	3	238.39	0.0045	N1t1 - S1t1	0.054	95	A1
4	235.06	0.0001	N1t1 - S1t1 (S2t1)	0.025	98	(A1)	4	238.09	0.0000	N1t2 - S1t2	0.022	96	A2
6	192.01	0.0001	N1t1 N2t1 - (S1t1) S2t1	0.021	96	C1	5	194.30	0.0175	P1t1 (N2t1) - S1t2 S2t1	0.165	80	(E1B12)
7	189.63	0.0292	P1t1 - S1t2 S2t1	0.024	94	E1B12	6	193.40	0.0043	(P1t1) (N1t1) N2t1 - (S1t2) S2t1	0.163	80	(C1)
8	188.34	0.0037	N1t2 N2t2 - (S1t2) S2t2	0.036	95	C2	7	189.75	0.0193	(N1t2) N2t2 - (S1t2) S2t2	0.069	88	(C2)
9	186.74	0.0478	P1t2 B - S1t1 (S2t2)	0.157	88	(E2B21)	8	189.57	0.1248	P1t2 - S1t1 S2t2	0.070	81	E2B21
10	185.94	0.0382	P1t2 B - S1t1	-	87	(B21)	12	182.59	0.0963	P2t1 - S1t1	0.082	54	D1
12	179.79	0.0912	P1t2 - S1t1 S2t2	-	92	E2B21	+			P1t1 - (S1t2) S2t1 O		31	
							13	181.18	0.0015	P2t2 B - S1t2 (O)	-	56	(D2)
							-			(P2t2) B - O		21	
(c) Ideal dTpdT with PCM solvent							Ideal dTpdT						
1	241.74	0.0002	(P2t1) B - S1t2	-	98	-	1	237.59	0.0002	N1t2 - S1t2 (S2t2)	-	86	(A2)
11	173.28	0.0031	(P1t12) (N1t1) B - S1t2	-	98	-	2	237.48	0.0006	N1t1 - S1t1 (S2t1)	-	87	(A1)
12	170.91	0.0040	(P1t2) (N1t1) (B) - S1t2	-	92	-	3	234.83	0.0455	P1t2 - S1t2	-	71	B2
13	170.67	0.0130	(P1t12) (P2t1) B - S1t1(2)	-	87	-	4	232.27	0.4242	P1t1 - S1t1	-	72	B1
14	168.71	0.0116	(P1t12) B - S1t(1)2	-	83	-	5	192.51	0.0015	N1t1 N2t1 - S2t1	-	96	(C1)
15	167.20	0.0318	P2t1 B - S1t12	-	69	-	6	188.85	0.0203	P1t1 (B) - S1t2 (S2t1)	-	92	(E1B12)
+			N2t2 B - S1t(1)2		23		7	188.26	0.0009	N1t2 N2t2 - (S1t2) S2t2	-	93	C2
16	166.14	0.1027	N2t2 (B) - S1t(1)2	-	67	-	9	183.96	0.1209	P1t2 - S1t1 S2t2	-	89	(E2B21)
-			P2t1 B - S1t1(2)		25		10	177.62	0.0686	P2t1 B - S1t1	-	72	(D1)
18	164.31	0.0094	P1t1 B - S1t2	-	92	-	12	176.87	0.0592	P1t1(2) - (S1t2) S2t1	-	54	(E1B12
22	160.29	0.0309	P2t1 B - S1t(1)2 (S2t1)	-	80	-	-			P1t(1)2 (P2t1) - S1t1		40	
26	153.48	0.0317	N1t1 B - (S1t1) S2t(1)2	-	70	-							

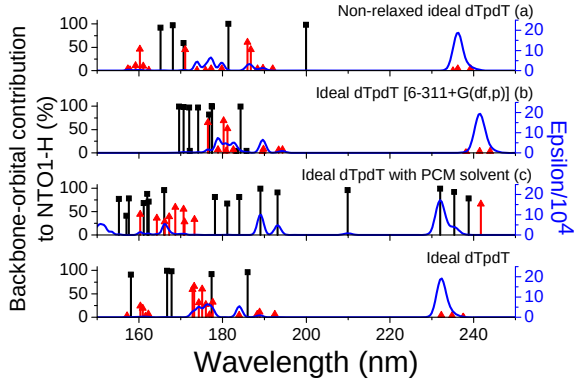

Figure S2 Percentage of backbone density contribution to the NTO1-H (red and black columns) and calculated absorption cross sections (curves) of the first 25 electronic excitations of dTpdT systems discussed in Table S2. Red and black columns correspond to the SO-hosted and non-SO-hosted excitations, respectively. The absorption cross sections are plotted by broadening the oscillator strength of each excitation with 0.03eV of Half-Width at Half-Height.

Relaxation and Basis Set Effect

From panels a and b of Table S2, it can be seen that up to some excitation reordering, the first several SO-hosted excitations remain in existence referencing the results of ideal dTpdT, namely, local Type-As, Type-Bs, Type-Cs, and Type-E1B12, Type-E2B21, except the highest two of ideal dTpdT that are replaced by Type-B21, Type-E2B21 in Table S2(a) and Type-D1, Type-D2 in Table S2(b). For the absorption energies of counterpart excitations, the two local Type-Bs, Type-E1B12, and Type-E2B21 have appreciable red-shifts both in (a) and (b) while the local Type-As and Type-Cs are all rather intact. For the oscillator strength, more noticeable changes can be found in (a) for Type-E1B12 and Type-E2B21, the former becoming stronger which should have something to do with the lifted backbone-orbitals in its NTO1-H, whereas the latter becoming weaker due to the involvement of backbone-orbitals in its NTO1-H. Finally, for the transition origin variations, most of the excitations in (a) and (b) have small values except the Type-E2B21 in (a) and the Type-E1B12 and Type-C1 in (b) that have pronounced transition origin variations.

From another aspect of view, Figure S2 shows that the absorption spectra for (a) and (b) are highly analogous to that of the ideal dTpdT, up to small energy-shifts. Taking a look at backbone-orbital contributions to NTO1-H, however, we see that the geometry relaxation lifts up the absorption energy of the lowest strong-backbone-involved excitation. It also makes several SO-hosted excitations around 170nm~180nm become strongly backbone-involved in their NTO1-Hs. Therefore, geometry relaxation effect is made clear only by analyzing the transition origins of excitations, giving another example that similar absorption spectrum can be borne by excitations of distinct transition origins. As the larger basis set 6-311G+(df,p) is used in calculation for the case (b), on the other hand, it happens that more backbone-dominant excitations are found around 170nm~190nm, which, accompanied with the results in Table S2(b), suggests that for higher-lying excitations formed by local Type-D/E and CT Type-B transitions a larger basis set than the economic 6-31G(d) become more important for obtaining consistent results. For lowering-lying excitations, however, the economic basis set 6-31G(d) has been good enough to produce reliable results.

PCM Solvent Effect

Table S2(c) shows the results of ideal dTpdT affected by PCM solvent built around the optimized dTp(dApdTpdTpdG)pdC--AdTp(dApdA)pdCG. Surprisingly, not like the case of Table S2(a) and (b), the first several SO-hosted electronic excitations are qualitatively changed. Firstly, these SO-hosted excitations are generally located at higher positions with larger absorption energies. Secondly, the compositions of their transition origin are qualitatively different from those of the ideal dTpdT such that correspondences cannot be built. In addition, backbone orbital component is pervasively involved in their transition origins. Figure S2 provides a clearer demonstration of this situation, despite that the absorption spectrum does not bear so much change.

However, since the solvent is only taken into account classically exhibiting polarization field, more quantum mechanical tests are still needed. In a detail, the used PCM model creates solute cavity via a set of overlapping spheres around atoms and employs a continuous surface charge whose field is determined self-consistently with the solute electrostatic potential. Therefore, a solvent, when included, is only classically taken into account providing polarization field. With actual solvent molecules surrounding solutes should be indispensible for correct description of excitation properties as, for instance, the CT contribution has been shown to play a role in the excitations of dTpdT--dApdA and dApdTpdTpdG discussed in the main text.

TABLE S3: The detailed standard-orbitals projection coefficients or coefficients square of NTO1(2)-H(E) of several SO-hosted excitations of (a) ideal Thy, dT, di-Thy, dTpdT, dTpdT--dApdA, and dApdTpdTpdG and (b) 3BSE dT, dTpdT, dTpdT--dApdA, and dApdTpdTpdG calculated by TD-ωB97X/6-31G(d). For orbital-fraction from backbone, the coefficients square which corresponds to electronic density contribution is shown instead. (c) The data for the coefficients square of orbitals from adenine and/or guanine in the ideal dTpdT--dApdA and dApdTpdTpdG cases.

(a)	λ (nm)	h-orbital									e-orbital			
		$P1_{T1}$	$P1_{T2}$	$N1_{T1}$	$N1_{T2}$	$P2_{T1}$	$P2_{T2}$	$N2_{T1}$	$N2_{T2}$	$(B)^2$	$S1_{T1}$	$S1_{T2}$	$S2_{T1}$	$S2_{T2}$
Ideal Thy	242.48	0.00	-0.01	0.00	0.96	0.00	-0.28	0.00	0.00		0.00	0.92	0.00	0.31
	224.84	0.00	1.00	0.00	0.00	0.00	0.00	0.00	-0.04		0.00	1.00	0.00	-0.04
	190.96	0.00	0.01	0.00	0.58	0.00	0.81	0.00	0.00		0.00	-0.32	0.00	0.91
	177.69	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.99		0.00	1.00	0.00	0.05
	173.93	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.04		0.00	0.05	0.00	1.00
	163.47	0.00	-0.01	0.00	0.27	0.00	0.94	0.00	0.00		0.00	0.96	0.00	0.28
	158.23	0.00	0.00	0.00	0.82	0.00	-0.55	0.00	0.01		0.00	-0.35	0.00	0.90
Ideal dT	241.11	0.00	-0.01	0.00	0.96	0.00	-0.28	0.00	0.00	0.00	0.00	0.92	0.00	0.32
	228.88	0.00	0.98	0.00	0.01	0.00	0.00	0.00	-0.02	0.03	0.00	0.99	0.00	-0.02
	189.38	0.00	0.01	0.00	0.58	0.00	0.78	0.00	0.00	0.04	0.00	-0.29	0.00	0.92
	178.50	0.00	0.97	0.00	0.02	0.00	-0.02	0.00	0.08	0.04	0.00	0.05	0.00	0.98
	176.13	0.00	-0.01	0.00	-0.01	0.00	-0.04	0.00	0.98	0.01	0.00	0.99	0.00	0.08
	167.70	0.00	0.06	0.00	0.18	0.00	0.67	0.00	0.10	0.42	0.00	0.96	0.00	0.19
	158.12	0.00	0.00	0.00	0.72	0.00	-0.62	0.00	0.05	0.03	0.00	-0.56	0.00	0.80
Ideal di-Thy	245.43	-0.02	0.00	0.95	0.00	-0.29	0.00	0.00	0.01		0.93	0.01	0.30	0.04
	242.48	-0.01	-0.01	0.00	0.96	0.01	-0.28	0.00	-0.01		0.03	0.92	0.06	0.31
	228.88	-0.11	0.99	-0.01	0.00	-0.02	0.00	0.00	-0.04		0.02	0.99	0.08	-0.02
	225.66	0.98	-0.15	0.02	-0.01	0.00	0.01	0.01	-0.02		0.99	-0.07	-0.07	0.06
	191.30	0.00	0.02	0.00	0.58	-0.01	0.81	0.01	0.01		0.05	-0.35	-0.01	0.91
	190.76	0.00	-0.02	0.61	0.00	0.78	0.00	0.01	0.01		-0.29	0.14	0.91	0.01
	183.11	0.99	0.02	-0.01	0.00	0.00	0.01	-0.06	0.11		0.02	0.79	0.62	0.07
	180.26	0.15	0.69	0.00	0.03	-0.01	0.01	-0.59	0.38		0.87	0.36	0.10	0.32
		0.15	-0.29	0.01	0.00	0.03	0.03	0.27	0.90		-0.35	0.93	0.06	-0.12
	179.02	-0.28	0.03	0.02	-0.01	0.03	-0.01	-0.03	0.95		-0.09	0.99	0.11	0.03
	177.93	0.10	0.56	-0.01	0.03	-0.03	-0.02	0.81	0.05		-0.96	-0.02	0.00	-0.27
Ideal dTpdT	237.59	-0.02	0.04	0.03	0.95	0.00	-0.28	0.01	-0.02	0.00	0.04	0.91	0.06	0.33
	237.48	-0.09	0.01	0.95	-0.03	-0.27	0.01	0.01	0.02	0.00	0.92	0.02	0.32	0.05
	234.83	-0.22	0.94	-0.04	-0.03	-0.01	0.00	0.01	0.00	0.03	0.21	0.96	0.09	0.04
	232.27	0.93	-0.27	0.06	-0.01	0.00	0.01	-0.01	-0.01	0.04	0.95	-0.25	-0.04	0.06
	192.51	-0.07	-0.02	0.56	0.00	0.78	0.01	0.00	0.00	0.06	-0.31	0.17	0.90	0.01
	188.85	0.92	0.05	0.03	0.02	0.04	0.01	-0.07	0.03	0.11	-0.01	0.84	0.53	0.07
	188.26	-0.02	0.01	0.00	0.57	-0.01	0.77	0.01	0.00	0.06	0.04	-0.35	-0.01	0.90
	183.96	0.06	0.96	-0.01	0.02	-0.03	0.00	-0.08	0.10	0.04	0.64	0.06	0.04	0.75
	177.62	0.02	-0.03	-0.04	0.00	-0.21	-0.01	0.76	-0.04	0.32	0.97	0.07	0.16	0.07
	176.87	0.89	-0.35	0.00	-0.01	-0.01	-0.01	0.07	-0.02	0.05	0.21	0.49	-0.80	-0.19
		0.36	0.78	0.01	0.01	0.01	-0.01	-0.46	0.11	0.04	0.88	-0.28	0.12	-0.31
Ideal dTpdT--dApdA	237.62	-0.21	0.94	0.00	0.00	-0.02	0.00	0.02	-0.09	0.03	0.21	0.96	0.09	0.09
	235.23	0.93	-0.25	-0.02	-0.02	0.00	0.00	-0.08	0.00	0.04	0.96	-0.22	0.02	0.05
	226.00	0.04	-0.01	0.94	0.00	-0.23	0.00	-0.01	0.00	0.01	0.92	0.02	0.31	0.05
	224.87	-0.01	0.00	-0.01	0.93	0.00	-0.23	0.01	-0.01	0.01	0.03	0.91	0.06	0.33
	193.13	-0.02	-0.02	0.53	-0.01	0.80	0.00	0.00	0.02	0.05	-0.30	0.16	0.91	0.02
	189.37	-0.01	0.02	0.00	0.53	-0.01	0.81	-0.01	0.01	0.05	0.05	-0.32	-0.01	0.92
	186.43	0.00	0.86	-0.01	0.00	-0.01	0.01	-0.32	0.09	0.02	0.88	-0.01	0.14	0.42
		0.86	0.07	0.02	0.01	0.01	0.01	-0.13	-0.25	0.05	-0.13	0.84	0.49	0.11
	185.87	0.69	0.09	-0.01	0.01	0.01	-0.01	-0.18	0.36	0.03	0.09	0.91	0.35	0.13
	185.10	0.47	0.61	-0.02	0.00	-0.07	0.01	-0.31	-0.13	0.02	0.61	0.67	0.18	0.33
		-0.38	0.65	0.01	-0.01	-0.02	-0.01	-0.17	0.21	0.04	0.67	-0.66	-0.13	0.21
	182.27	0.08	0.27	-0.04	0.01	-0.14	0.00	0.55	-0.01	0.05	0.78	0.15	0.09	0.14
		0.06	0.31	-0.01	0.00	-0.14	-0.02	0.52	0.00	0.05	0.57	-0.14	0.03	0.11
Ideal dApdTp dTpdG	239.17	0.94	-0.17	-0.03	-0.02	0.00	0.01	-0.03	-0.01	0.04	0.97	0.09	0.02	0.07
	235.85	-0.14	0.95	0.00	-0.02	-0.01	0.00	-0.01	-0.01	0.04	-0.13	0.97	0.10	-0.03
	233.13	0.02	0.01	0.96	0.00	-0.26	0.01	0.00	0.00	0.00	0.91	0.00	0.32	0.05
	232.75	-0.01	0.00	0.00	0.96	-0.01	-0.27	0.02	0.00	0.00	0.03	0.91	0.08	0.34
	193.01	-0.05	-0.08	0.54	0.00	0.76	-0.01	0.02	0.00	0.09	-0.40	0.13	0.87	0.00
	191.28	0.08	0.96	0.02	0.00	0.00	-0.01	-0.07	0.10	0.04	0.80	-0.01	0.05	0.52
	187.48	0.00	0.02	-0.01	0.56	0.00	0.76	-0.01	0.00	0.08	0.05	-0.37	-0.02	0.89
	187.00	0.93	-0.06	0.00	0.00	-0.02	0.01	0.00	0.02	0.07	0.01	0.50	0.75	0.06
	184.40	-0.08	0.94	0.00	-0.01	-0.03	-0.02	-0.01	-0.03	0.07	0.39	0.01	0.01	-0.44
	179.35	-0.09	0.94	-0.01	-0.02	-0.02	-0.02	-0.03	0.01	0.06	-0.30	0.01	0.04	0.68

(b)	λ (nm)	h-orbital									e-orbital			
		$P1_{T1}$	$P1_{T2}$	$N1_{T1}$	$N1_{T2}$	$P2_{T1}$	$P2_{T2}$	$N2_{T1}$	$N2_{T2}$	$(B)^2$	$S1_{T1}$	$S1_{T2}$	$S2_{T1}$	$S2_{T2}$
3BSE dT	238.70		0.02		0.95		-0.31		-0.03	0.00		0.92		0.33
	224.38		0.98		-0.02		0.01		-0.02	0.03		0.99		-0.02
	189.93		0.06		0.60		0.76		0.06	0.03		-0.29		0.91
	176.14		0.97		-0.03		-0.03		0.12	0.03		0.08		0.98
	174.97		-0.02		0.00		-0.06		0.99	0.00		0.99		0.07
	166.91		0.02		0.21		0.68		0.04	0.42		0.96		0.19
	158.09		0.02		0.57		-0.69		0.00	0.12		-0.71		0.68
3BSE dTpdT	238.62	-0.10	0.01	0.94	0.01	-0.28	-0.01	0.02	0.01	0.00	0.92	0.01	0.32	0.01
	235.78	-0.02	0.05	0.00	0.94	0.00	-0.30	0.00	-0.04	0.00	0.01	0.91	0.01	0.34
	231.46	0.93	-0.22	0.12	0.00	-0.04	0.01	0.00	-0.03	0.05	0.97	0.21	-0.04	0.01
		0.22	0.94	0.04	-0.10	-0.03	0.01	0.01	0.02	0.04	-0.21	0.97	0.02	0.01
	226.76	-0.19	0.95	-0.01	-0.03	0.00	0.00	0.02	-0.02	0.04	-0.18	0.97	0.01	-0.03
		0.94	0.21	0.05	-0.02	-0.01	0.01	-0.03	-0.02	0.05	0.97	0.18	-0.02	0.00
	191.98	-0.11	0.01	0.58	0.01	0.77	0.01	-0.02	-0.01	0.04	-0.29	0.02	0.92	0.00
	189.60	0.00	0.07	-0.01	0.59	0.00	0.76	0.00	0.05	0.05	0.01	-0.33	0.01	0.91
	185.01	0.91	0.07	-0.01	0.01	-0.01	0.00	-0.01	-0.03	0.14	0.01	0.97	0.17	0.05
	179.79	0.93	-0.17	0.08	0.00	0.06	0.01	0.07	-0.02	0.05	0.04	-0.21	0.94	0.16
	178.10	0.01	0.55	-0.02	0.02	-0.09	0.00	0.53	0.08	0.37	0.94	0.00	0.04	0.30
	176.54	0.00	0.49	0.00	-0.01	0.01	0.00	0.67	0.09	0.30	0.96	-0.04	0.05	-0.23
3BSE dTpdT--dApdA	233.55	0.88	-0.14	-0.14	-0.01	0.02	0.01	-0.08	-0.02	0.06	0.97	0.12	0.04	0.01
	228.95	-0.07	0.90	0.00	0.10	0.01	-0.02	0.00	-0.10	0.05	-0.05	0.97	0.03	0.06
		-0.16	-0.01	0.19	0.02	-0.05	0.00	0.02	0.00	0.01	0.27	0.03	0.05	0.01
	227.76	0.16	-0.01	0.92	-0.01	-0.24	0.01	-0.02	-0.01	0.02	0.92	0.02	0.31	0.02
	226.04	-0.01	-0.06	0.00	0.93	0.01	-0.27	0.00	-0.01	0.01	0.01	0.92	0.00	0.33
	192.02	-0.09	0.01	0.55	-0.01	0.79	0.00	-0.02	0.01	0.04	-0.27	0.01	0.91	0.00
	190.13	0.00	0.06	0.01	0.56	0.01	0.78	0.00	0.06	0.04	0.01	-0.31	-0.01	0.90
	184.59	0.05	0.02	-0.04	0.00	-0.06	0.01	0.67	0.01	0.03	0.94	0.12	0.15	0.05
	182.45	-0.08	0.05	0.03	0.03	0.01	-0.02	0.05	0.71	0.01	0.05	0.94	0.03	0.16
		0.00	-0.03	-0.02	-0.02	0.00	0.03	-0.06	-0.25	0.01	0.06	-0.19	-0.01	-0.05
	180.33	0.86	0.07	-0.01	0.02	-0.02	0.02	-0.09	0.16	0.10	-0.03	0.94	0.27	0.08
	180.05	0.08	0.89	0.01	0.04	0.02	0.00	-0.07	0.07	0.05	0.96	0.02	0.05	0.18
3BSE dApdTp dTpdG	236.44	0.89	-0.12	-0.29	-0.01	0.08	0.00	-0.02	-0.02	0.06	0.98	0.09	0.02	0.01
	233.70	0.22	-0.02	0.93	0.00	-0.26	0.01	0.00	0.00	0.01	0.92	0.03	0.30	0.01
	230.11	-0.10	0.96	0.00	0.03	0.00	-0.01	0.02	-0.01	0.05	-0.07	0.99	0.03	-0.01
	227.65	-0.01	-0.04	0.00	0.94	0.00	-0.29	0.01	-0.02	0.00	0.01	0.91	0.01	0.34
	192.96	0.03	-0.01	0.58	0.00	0.76	-0.01	-0.02	-0.01	0.06	-0.35	-0.01	0.89	0.01
	188.75	-0.02	0.07	0.00	0.57	0.01	0.74	0.00	0.05	0.09	0.01	-0.38	-0.01	0.89
	183.57	0.14	0.88	-0.01	0.01	-0.07	0.00	0.12	0.11	0.15	0.96	0.05	0.02	0.16
		0.60	-0.22	0.01	0.00	-0.01	0.02	0.08	-0.02	0.07	-0.13	0.17	0.37	-0.04
	182.41	-0.16	0.88	-0.01	0.00	-0.05	0.00	0.22	0.02	0.12	0.46	-0.03	-0.08	-0.79
		0.20	-0.31	-0.02	-0.01	-0.16	0.00	0.44	0.01	0.53	0.78	0.20	0.30	0.39
	181.67	0.09	0.57	0.01	0.00	0.14	-0.02	-0.17	0.04	0.58	0.93	0.02	0.03	-0.26
	181.06	0.84	0.08	-0.01	0.01	-0.02	-0.04	-0.01	-0.01	0.25	-0.01	0.97	0.16	0.09

(c)	dTpdT--dApdA					dApdTpdTpdG				
	λ (nm)	h-orbital		e-orbital		λ (nm)	h-orbital		e-orbital	
		(A1)	(A2)	(A1)	(A2)		$(G)^2$	$(A)^2$	$(G)^2$	$(A)^2$
Ideal	237.62	0.00	0.00	0.00	0.00	239.17	0.00	0.00	0.01	0.01
	235.23	0.00	0.00	0.00	0.00	235.85	0.00	0.00	0.00	0.00
	226.00	0.05	0.00	0.00	0.00	233.13	0.00	0.00	0.00	0.01
	224.87	0.00	0.05	0.00	0.00	232.75	0.00	0.00	0.00	0.00
	193.13	0.00	0.00	0.00	0.00	193.01	0.00	0.00	0.00	0.01
	189.37	0.00	0.00	0.00	0.00	191.28	0.01	0.07	0.00	0.01
	186.43	0.07	0.04	0.00	0.01	187.48	0.00	0.01	0.00	0.00
		0.00	0.12	0.00	0.00	187.00	0.00	0.00	0.03	0.17
	185.87	0.01	0.29	0.00	0.00	184.40	0.01	0.61	0.00	0.01
	185.10	0.02	0.24	0.01	0.01	179.35	0.01	0.41	0.00	0.00
		0.01	0.29	0.02	0.01					
	182.27	0.06	0.46	0.30	0.02					
		0.08	0.44	0.58	0.04					
3BSE	233.55	0.00	0.00	0.00	0.00	236.44	0.00	0.00	0.01	0.01
	228.95	0.02	0.00	0.00	0.00	233.70	0.01	0.00	0.00	0.00
		0.79	0.13	0.84	0.07	230.11	0.00	0.00	0.00	0.00
	227.76	0.02	0.00	0.00	0.00	227.65	0.00	0.00	0.01	0.00
	226.04	0.00	0.04	0.00	0.00	192.96	0.00	0.00	0.00	0.02
	192.02	0.01	0.00	0.00	0.00	188.75	0.00	0.01	0.00	0.00
	190.13	0.00	0.01	0.01	0.00	183.57	0.00	0.00	0.01	0.02
	184.59	0.11	0.38	0.02	0.02		0.00	0.00	0.50	0.80
	182.45	0.10	0.35	0.03	0.02	182.41	0.00	0.12	0.01	0.01
		0.76	0.14	0.33	0.58		0.00	0.02	0.08	0.06
	180.33	0.00	0.00	0.00	0.00	181.67	0.00	0.02	0.01	0.01
	180.05	0.04	0.00	0.00	0.00	181.06	0.00	0.00	0.01	0.00

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