

Supporting information

The structures of transition state were optimized without solvent effect. The results showed that the transition state structures in gas phase were almost the same as that of in acetonitrile solvent. As shown in Table S1, the corresponding transition state structure had the same vibration mode with almost the same value, and there was one and only one imaginary component in transition state structure. In addition, the reaction potential barrier energy (E^*) on each site was calculated and showed in Table S1. The reaction potential barrier energy of gas phase is lower than that of liquid phase. Moreover, we checked the relative energies of intermediates. We found that the relative energy of CTC2' was the lowest, so the structure of CTC2' was the most stable state (see Table S2).

It should be mentioned that TS4 has not been obtained by calculation. We tracked the optimization trajectory of TS4 and found that the optimized structure was similar to TS2'. This result indirectly suggested that C4 position was hard to react with NO₃ radical and C2' position was right site for being attacked by NO₃ radical.

Table S1. Imaginary frequency f ($i\text{ cm}^{-1}$) calculation of transient state in gas phase.

		TS4'	TS3'	TS2'	TS2	TS3
f	Gas	3179.18	3206.53	2082.28	2066.96	765.31
	liquid	3207.76	3207.76	2082.27	2066.96	765.31
E^*	Gas	24.556	22.551	25.514	24.060	23.784
	liquid	24.204	24.103	30.953	24.650	24.650

Table S2. Relative energy (E) of six CTCs calculated in gas phase.

		CTC4'	CTC3'	CTC2'	CTC2	CTC3	CTC4
E	Gas	2.73	1.77	0.00	0.51	2.13	3.34
	liquid	1.11	0.31	0.00	0.0075	0.81	1.41

In Table S3, the charge population of 4-CB was calculated in gas phase. The calculation result was unchanged whether with or without acetonitrile solvent, except

for C3 position. Because C3 could withdraw electrons by inductive effect (-I effect) from lone pairs electrons on -Cl group, so it presented slightly negative charge. However, considering the influence of inductive effect and resonance effects, C2' was the optimal reaction site in 4-CB. The difference was that the charge was populated evenly on Ring1 and Ring2 in gas phase.

Table S3. Population charge of 4-CB without solvent effect.

	Chelp	ChelpG	MK	NPA
C1	-0.239093	0.088680	0.165462	-0.052400
C2	0.111454	-0.134462	-0.236521	-0.174290
C3	-0.203991	-0.082933	-0.030936	-0.220760
C4	0.212074	0.110802	-0.027722	-0.038160
C1'	0.134527	0.017485	0.033323	-0.053750
C2'	-0.074429	-0.086390	-0.131816	-0.190780
C3'	0.011074	-0.089065	-0.148491	-0.196700
C4'	-0.224183	-0.089845	-0.117296	-0.204080
Cl	-0.142682	-0.161095	-0.109398	-0.000780
Ring 1	-0.090819	0.004373	0.016148	-0.006680
Ring 2	0.090819	-0.004375	-0.016150	0.006660

Note: C1 represents the sequence number of carbon is 1.

Based on the results of relative energy and charge population, CTC2' was the optimal intermediate. We calculated the excited state spectrum of CTC2' and observed the absorption blueshift in gas phase. The energy gaps E(LUMO)-E(HOM) were calculated with and without acetonitrile solvent. The results showed that the energy

gaps $E(\text{LUMO}) - E(\text{HOMO})$ in the presence of acetonitrile solvent were smaller than that in the gas phase, so we observed the absorption blueshift with the absence of acetonitrile solvent. The acetonitrile solvent affects the absorption spectrum, but the structure of transient state has not been changed.

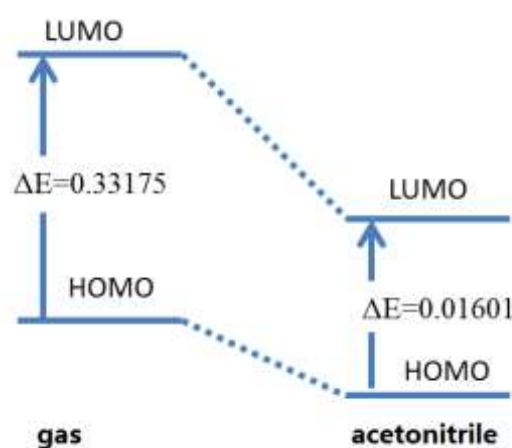


Figure S1. a: the $\Delta E(\text{LUMO-HOMO})$ in gas phase and in acetonitrile solvent.
b: the possible energy gap for electron transition

The population charge of CTC2' was calculated in gas phase and showed in Table 4S. C2 atom of CTC2' contains a little negative charge, so N atom tends to localize on C2 position. The re-arrangement of CTC2' was the main channel in subsequent reaction, and 4-chloro,2-nitrobiphenyl as the main final product was formed in this channel. From Table S4, the CTC2' had a charge transfer character with about 0.5 charge transferred to NO_3 radical. The difference was that almost a full charge transferred to NO_3 radical acceptor in acetonitrile solvent. However, the structure of CTC2' and the other subsequence reactions were checked by calculating without solvent effect. The results show that the parameters of CTC2' calculated without solvent effect was rarely different from the parameters of CTC2' calculated with acetonitrile solvent effect. Moreover, the formation of chlorinated dibenzofuran had the same pathway with and without solvent effect, except for the redshift of absorption spectrum.

Table S4. Population charge of CTC2'. Charge transfer value (q) calculated in gas phase with CHelp, CHelpG, MK, and NPA models.

	Chelp	ChelpG	MK	NPA
C1	-0.194205	0.139965	0.104249	-0.070290
C2	-0.005196	-0.166134	-0.203235	-0.159900
C3	-0.417107	-0.036399	-0.038510	-0.210700
C4	0.682465	0.079626	0.010842	-0.027290
C1'	0.286638	-0.005031	0.091548	-0.046940
C2'	0.157015	0.148444	0.073397	0.007400
C3'	-0.306416	-0.122999	-0.100790	-0.203360
C4'	-0.025162	-0.095294	-0.209014	-0.202400
O	-0.574147	-0.530493	-0.492856	-0.426980
N	1.184157	1.144741	1.048057	0.723820
O	-0.586302	-0.587441	-0.563146	-0.463230
O	-0.527272	-0.510001	-0.475615	-0.358510
Ring 1	0.509980	0.359814	0.388935	0.451950
Ring 2	-0.006412	0.123379	0.094626	0.072970
ΔQ	-0.503564	-0.483194	-0.483560	-0.524900

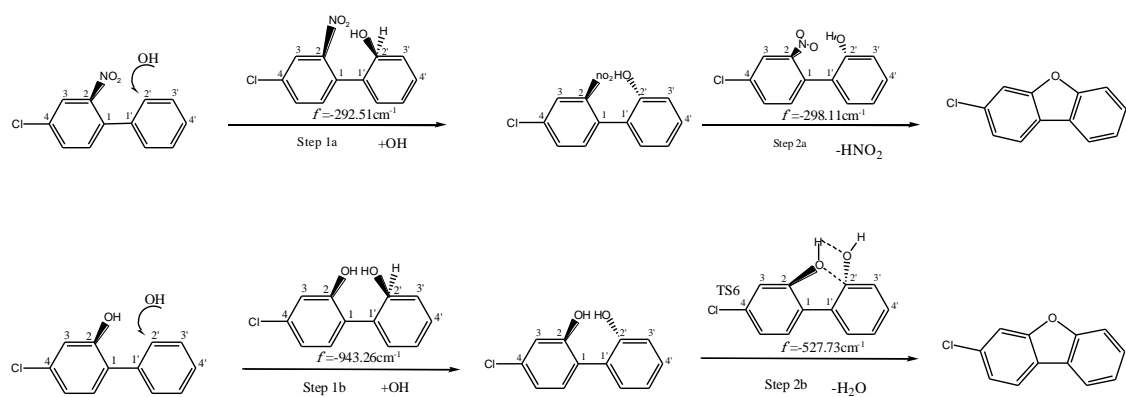


Figure S2. Probable formation pathway of chlorinated dibenzofuran in gas phase.

From these results, acetonitrile solvent has well promoted the process of charge transfer in CTC2' and affected the absorption spectrum, while the reaction mechanism between 4-CB and NO₃ radical has not been changed.