Simulating Detection of Dioxine-like Pollutants with 2D Surface Enhanced Raman Spectroscopy using h-BNC substrates

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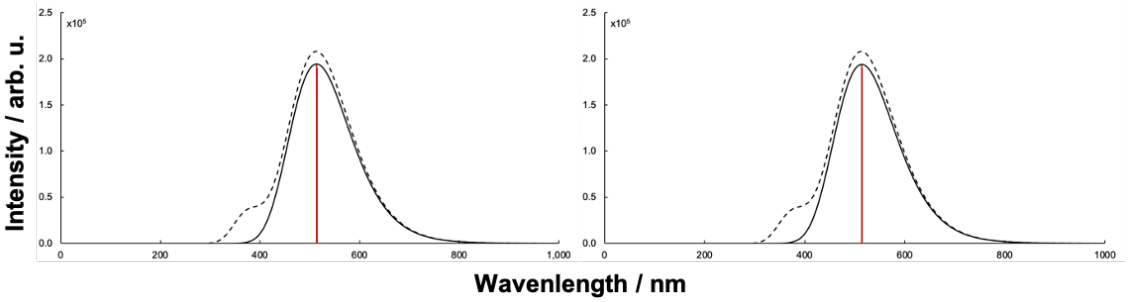


Figure S1. Main electronic adsorption band obtained for BCN96-TCDD and BCN96-TCDF complexes (solid lines) compared to that obtained for BCN96 (dashed lines). The excitation wavelengths employed as reference for the calculation of pre-resonance Raman spectra are indicated by vertical lines in red.

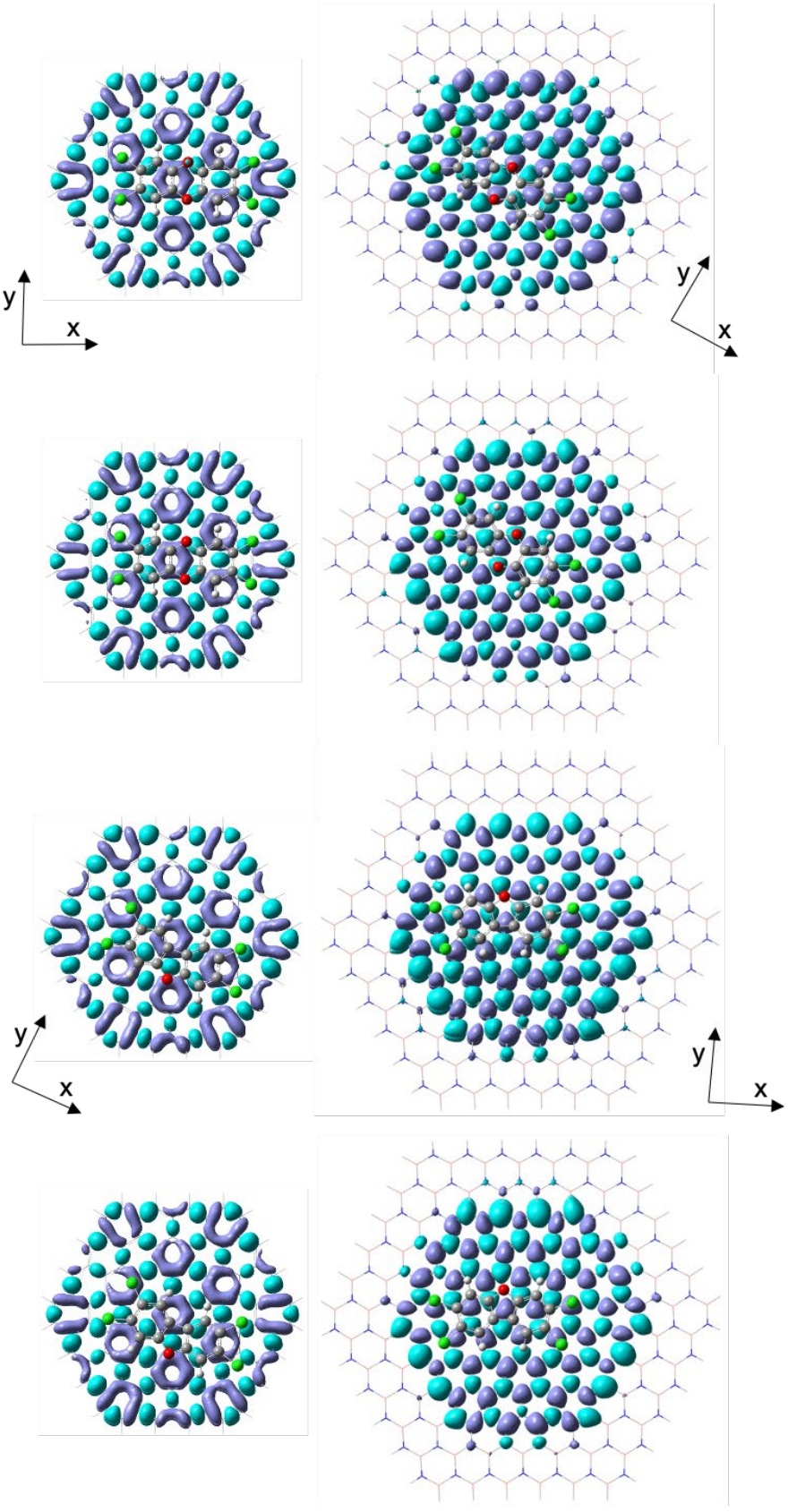


Figure S2. Ground to excited state density differences (DDs) in BNC96-TCDD and BNC96-TCDF (right) and C96-TCDD and C96-TCDF (left) complexes. Isosurface value is $4 \cdot 10^{-4}$.

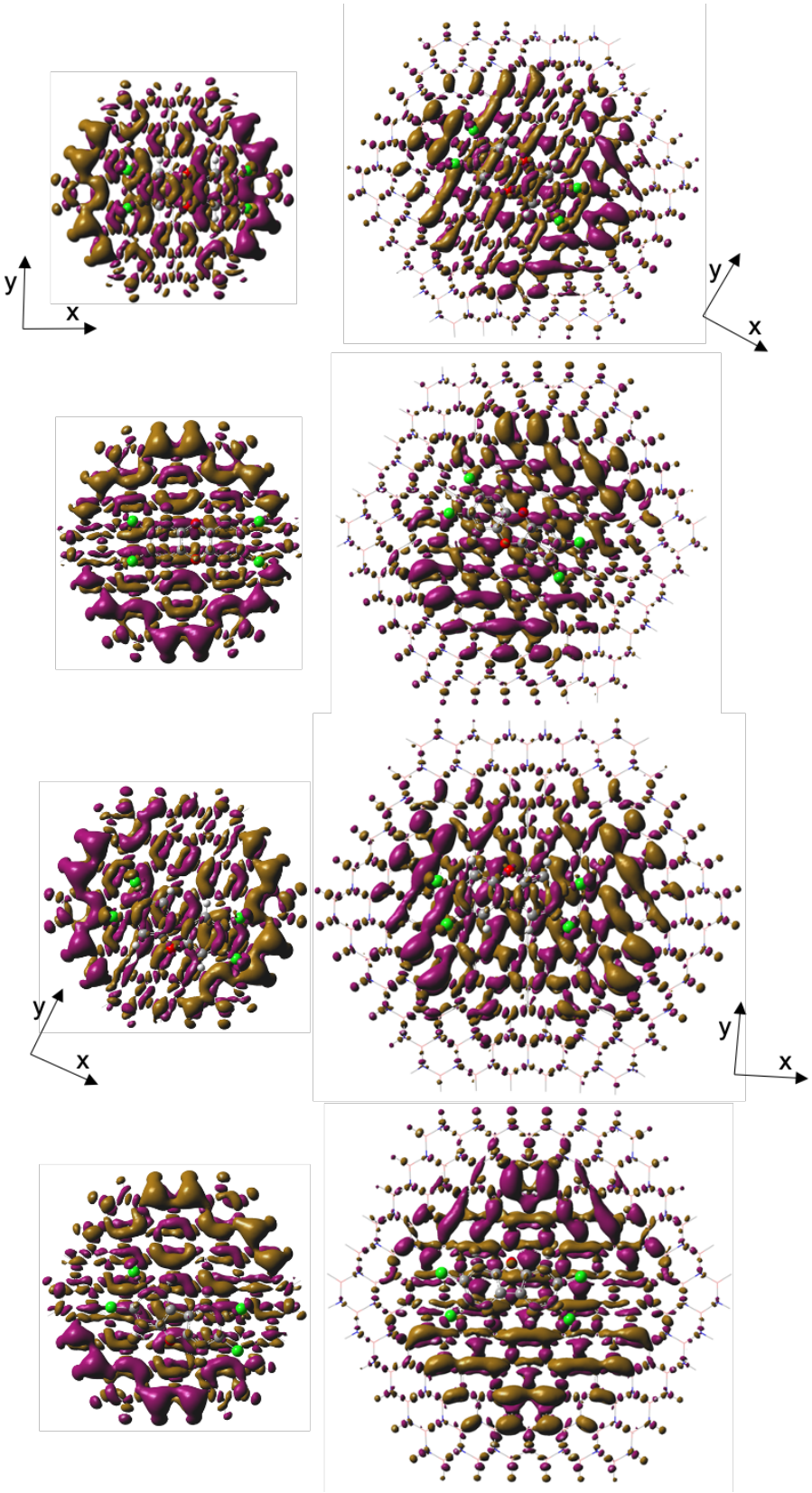


Figure S3. Transition densities (TDs) in BNC96-TCDD and BNC96-TCDF (right) and C96-TCDD and C96-TCDF (left) complexes. Isosurface value is $1 \cdot 10^{-4}$.

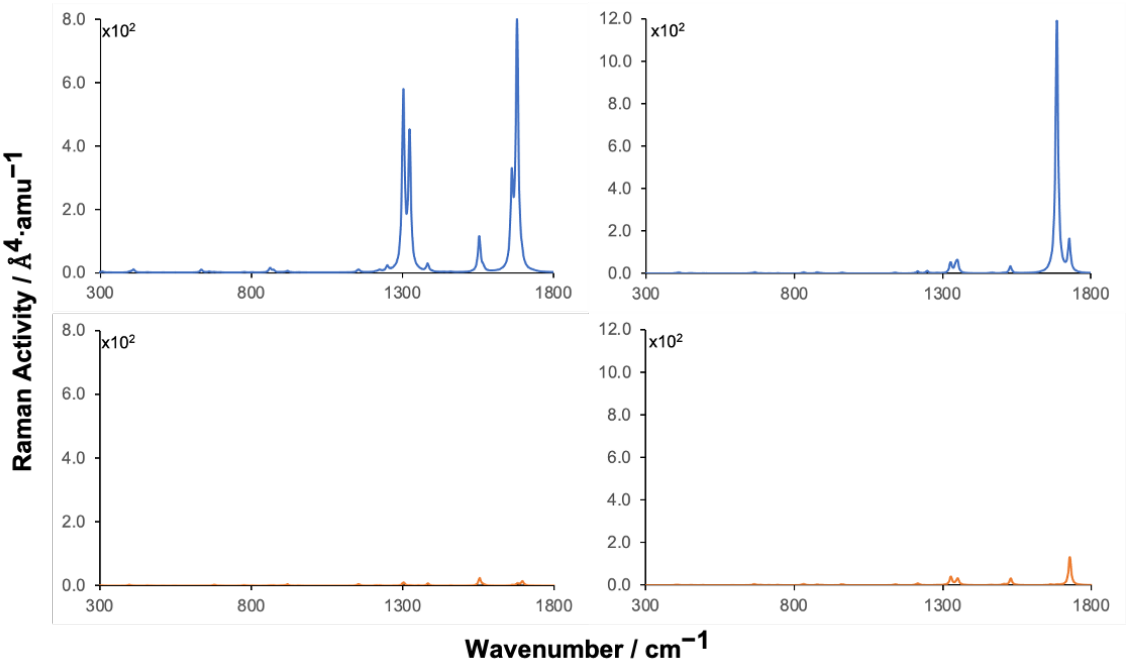


Figure S4. Simulated static Raman spectra of TCDD (left) and TCDF (right) adsorbed on BNC96 (first row) and hypothetical spectra obtained from the contributions to the Raman activity of the molecule (second row).

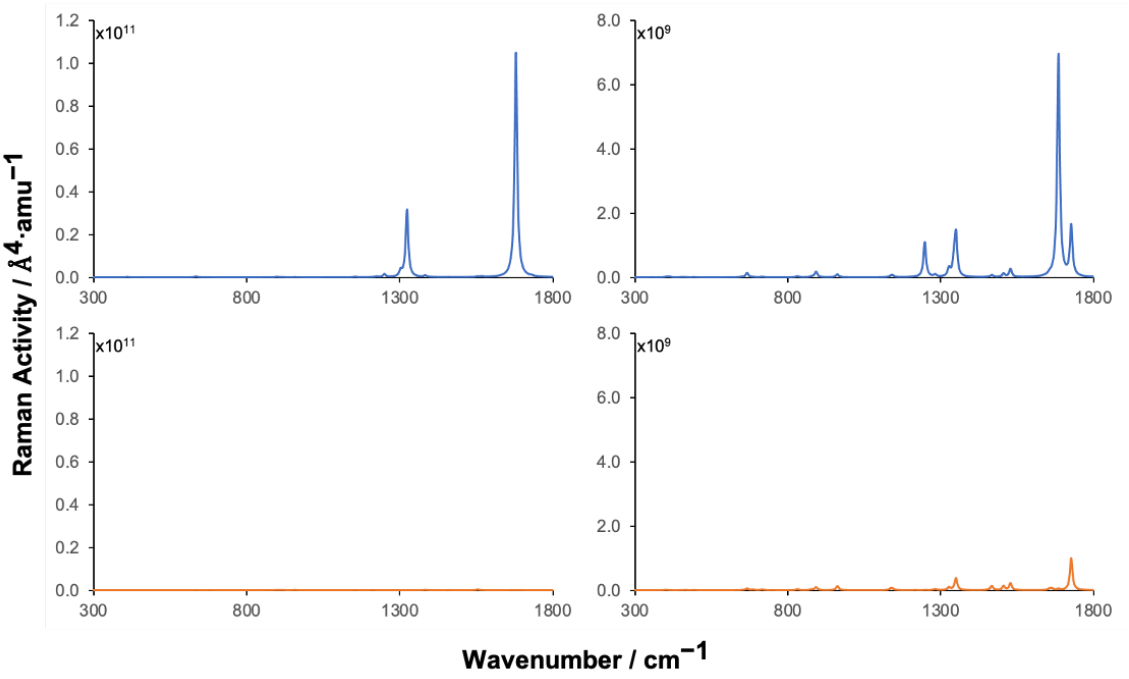


Figure S5. Simulated pre-resonance Raman spectra of TCDD (left) and TCDF (right) adsorbed on BNC96 obtained, respectively, with excitation wavelengths of 512.0 and 512.2 nm (first row) and hypothetical spectra obtained from the contributions to the Raman activity of the molecule (second row).

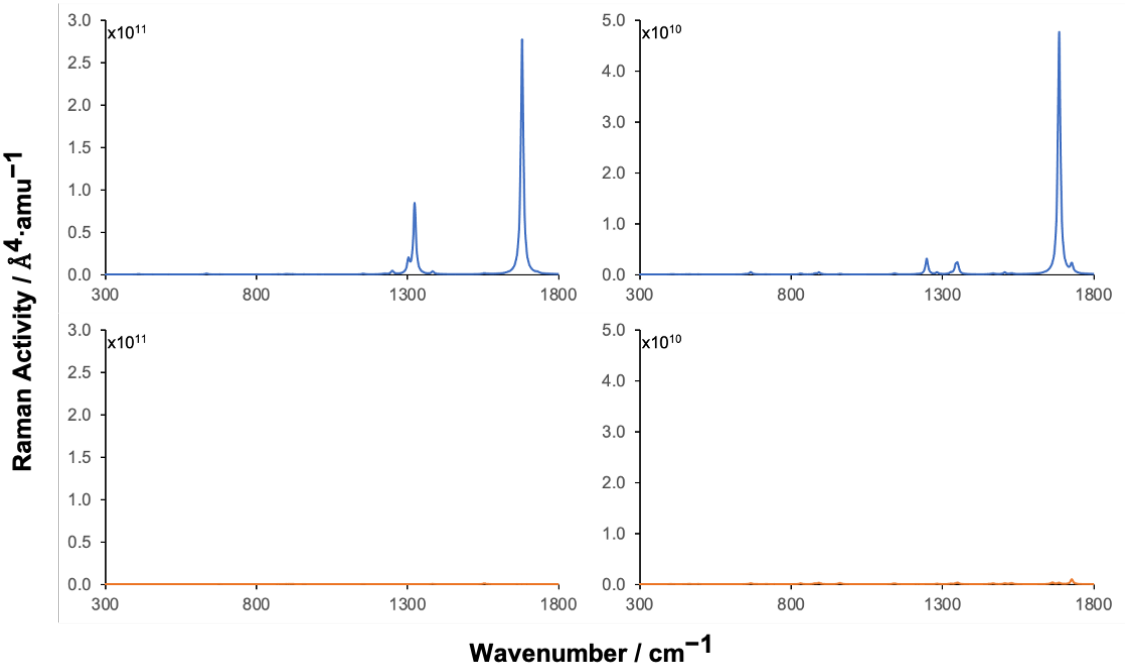


Figure S6. Simulated pre-resonance Raman spectra of TCDD (left) and TCDF (right) adsorbed on BNC96 obtained, respectively, with excitation wavelengths of 516.0 and 516.2 nm (first row) and hypothetical spectra obtained from the contributions to the Raman activity of the molecule (second row).

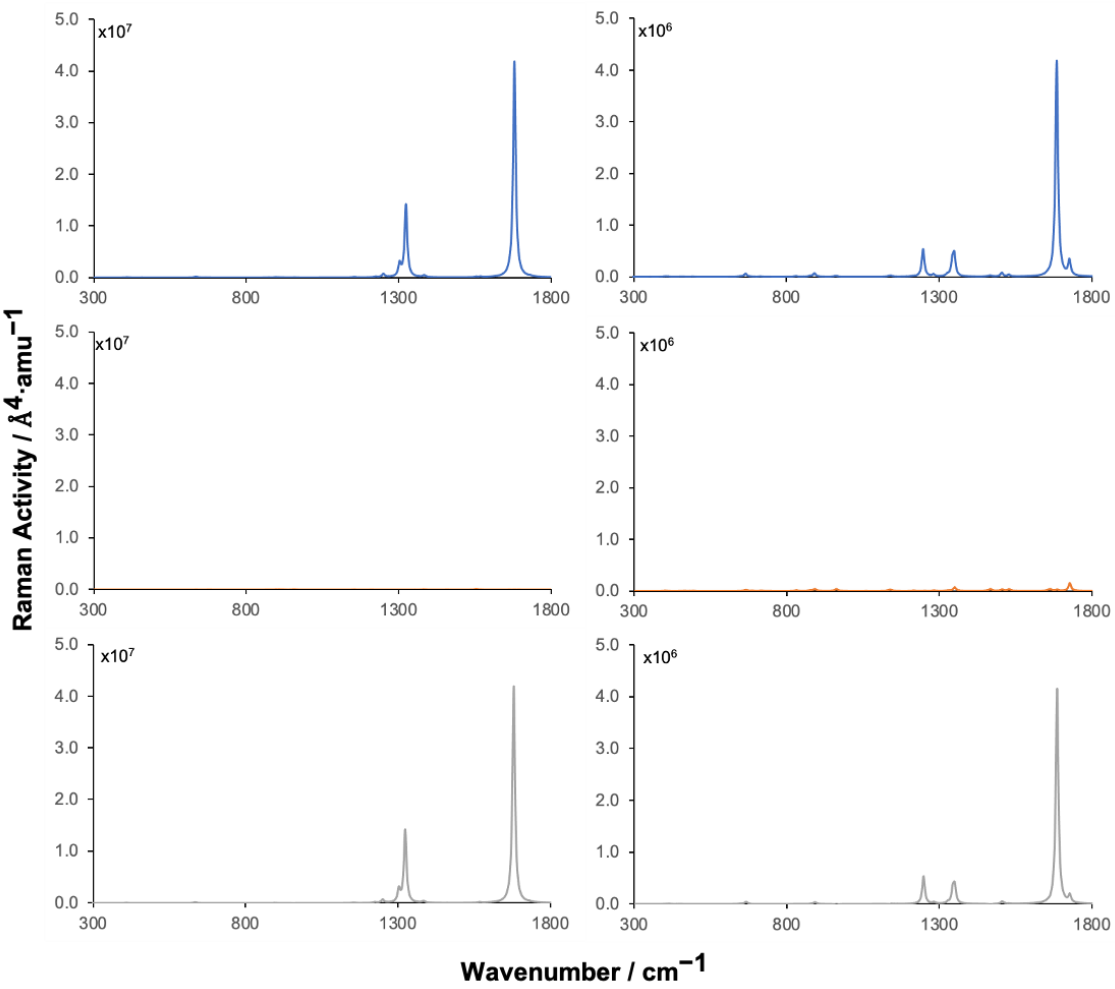
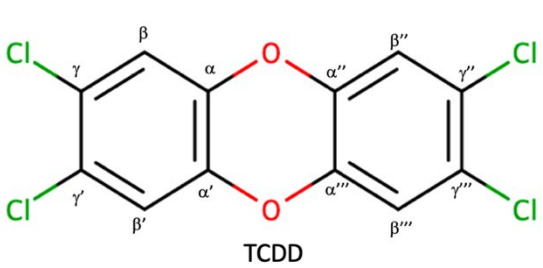


Figure S7. Simulated Raman spectra of TCDD (left) and TCDF (right) adsorbed on BNC96 obtained with an excitation wavelength of 488 nm (first row) and hypothetical spectra obtained from the contributions to the Raman activity of the molecule (second row) and the surface (third row).

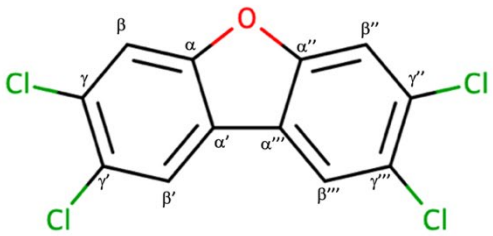
Table S1. Vibrational frequencies (in cm^{-1}) and Raman activities ($Å^4 \cdot amu^{-1}$) for the vibrational modes whose Raman activities are greater than 10 $Å^4 \cdot amu^{-1}$ in the isolated molecules or in the molecules adsorbed on the BNC96 surface. The values corresponding to the adsorbed molecules are given in parenthesis with respect to those of the isolated molecules.

TCDD		TCDF	
Wavenumber	Raman Activity	Wavenumber	Raman Activity
1249.89 (-0.52)	0.53 (16.45)	1218.82 (-3.28)	55.35 (10.39)
1299.06 (3.69)	185.23 (556.02)	1253.44 (-5.65)	0.79 (11.58)
1340.88 (-17.47)	11.37 (421.08)	1325.56 (1.36)	215.13 (51.31)
1389.92 (-6.72)	0.00 (23.66)	1337.11 (6.48)	3.07 (28.97)
1566.27 (-12.22)	20.75 (112.31)	1348.90 (1.08)	315.81 (52.34)
1658.12 (3.86)	0.00 (269.71)	1531.03 (-2.55)	233.9 (33.09)
1675.38 (3.95)	86.96 (781.51)	1684.79 (0.20)	20.21 (505.97)
1691.51 (3.65)	118.66 (18.17)	1684.79 (0.82)	20.21 (603.33)
		1726.98 (0.24)	899.49 (149.31)

Table S2. Geometrical parameters of TCDD and TCDF adsorbed on BNC96 and (isolated). Distances in Å, bond angles and dihedral angles in degrees.



TCDD



TCDF

TCDD								
	Distances (Å)			Angles θ (°)			Dihedral ϕ (°)	
C-C	C_{α}-C_{β}	1.381 (1.384)	C-C-C	C_{α}-C_{β}-C_{γ}	120.08 (120.15)	C-C-C-C	$C_{\beta'}$-$C_{\alpha'}$-C_{α}-C_{β}	-0.01 (0.00)
	C_{β}-C_{γ}	1.392 (1.394)		C_{β}-C_{γ}-$C_{\gamma'}$	119.89 (119.82)		$C_{\alpha'}$-C_{α}-C_{β}-C_{γ}	-0.10 (0.00)
	C_{α}-$C_{\alpha'}$	1.397 (1.396)		C_{γ}-$C_{\gamma'}$-$C_{\beta'}$	119.89 (119.82)		C_{α}-C_{β}-C_{γ}-$C_{\gamma'}$	0.11 (0.01)
	C_{γ}-$C_{\gamma'}$	1.391 (1.395)		$C_{\gamma'}$-$C_{\beta'}$-$C_{\alpha'}$	120.08 (120.15)		C_{β}-C_{γ}-$C_{\gamma'}$-$C_{\beta'}$	0.00 (-0.01)
	$C_{\alpha'}$-$C_{\beta'}$	1.381 (1.384)		$C_{\beta'}$-$C_{\alpha'}$-C_{α}	120.03 (120.03)		C_{γ}-$C_{\gamma'}$-$C_{\beta'}$-$C_{\alpha'}$	-0.10 (0.01)
	$C_{\beta'}$-$C_{\gamma'}$	1.392 (1.394)		$C_{\alpha'}$-C_{α}-C_{β}	120.03 (120.03)		$C_{\gamma'}$-$C_{\beta'}$-$C_{\alpha'}$-C_{α}	0.11 (0.00)
	$C_{\alpha''}$-$C_{\beta''}$	1.383 (1.384)		$C_{\alpha''}$-$C_{\beta''}$-$C_{\gamma''}$	120.17 (120.15)		$C_{\beta'''}$-$C_{\alpha'''}$-$C_{\alpha''}$-$C_{\beta''}$	0.01 (0.00)
	$C_{\beta''}$-Cγ''	1.389 (1.394)		$C_{\beta''}$-$C_{\gamma''}$-$C_{\gamma'''}$	119.81 (119.82)		$C_{\alpha'''}$-$C_{\alpha''}$-$C_{\beta''}$-$C_{\gamma''}$	-0.15 (0.00)
	$C_{\alpha''}$-$C_{\alpha'''}$	1.392 (1.396)		$C_{\gamma''}$-$C_{\gamma'''}$-$C_{\beta'''}$	119.81 (119.82)		$C_{\alpha''}$-$C_{\beta''}$-$C_{\gamma''}$-$C_{\gamma'''}$	0.15 (0.01)
	$C_{\gamma''}$-$C_{\gamma'''}$	1.394 (1.395)		$C_{\gamma'''}$-$C_{\beta'''}$-$C_{\alpha'''}$	120.17 (120.15)		$C_{\beta''}$-$C_{\gamma''}$-$C_{\gamma'''}$-$C_{\beta'''}$	0.00 (-0.01)

	$C_{\alpha'''}$-$C_{\beta'''}$	1.383 (1.384)		$C_{\beta'''}$-$C_{\alpha'''}$-$C_{\alpha''}$	120.02 (120.03)		$C_{\gamma''}$-$C_{\gamma'''}$-$C_{\beta'''}$-$C_{\alpha'''}$	-0.14 (0.01)
	$C_{\beta'''}$-$C_{\gamma'''}$	1.389 (1.394)		$C_{\alpha'''}$-$C_{\alpha''}$-$C_{\beta''}$	120.02 (120.03)		$C_{\gamma'''}$-$C_{\beta'''}$-$C_{\alpha'''}$-$C_{\alpha''}$	0.14 (0.00)
	C_{α}-O	1.371 (1.372)		C_{α}-O-$C_{\alpha''}$	115.79 (115.87)		$C_{\alpha'}$-C_{α}-O-$C_{\alpha''}$	-2.92 (0.00)
	$C_{\alpha'}$-O	1.371 (1.372)	C-O-C	$C_{\alpha'}$-O-$C_{\alpha'''}$	115.79 (115.87)		C_{α}-$C_{\alpha'}$-O-$C_{\alpha'''}$	2.92 (0.00)
C-O	$C_{\alpha''}$-O	1.371 (1.372)		$C_{\alpha'}$-C_{α}-O	122.02 (120.06)	C-C-O-C	$C_{\alpha'''}$-$C_{\alpha''}$-O-C_{α}	2.92 (0.00)
	$C_{\alpha'''}$-O	1.371 (1.372)		$C_{\alpha'''}$-$C_{\alpha''}$-O	122.12 (120.06)		$C_{\alpha''}$-$C_{\alpha'''}$-O-$C_{\alpha'}$	-2.93 (0.00)
	C_{β}-H	1.083 (1.087)	C-C-O	C_{α}-$C_{\alpha'}$-O	122.02 (120.06)		O-C_{α}-$C_{\alpha'}$-O	0.01 (0.00)
	$C_{\beta'}$-H	1.083 (1.087)		$C_{\alpha''}$-$C_{\alpha'''}$-O	122.12 (120.06)	O-C-C-O	O-$C_{\alpha''}$-$C_{\alpha'''}$-O	0.01 (0.00)
C-H	$C_{\beta''}$-H	1.083 (1.087)		C_{α}-C_{β}-H	119.18 (119.19)		H-C_{β}-C_{α}-O	0.28 (0.00)
	$C_{\beta'''}$-H	1.083 (1.087)		C_{γ}-C_{β}-H	120.74 (120.66)		H-$C_{\beta'}$-$C_{\alpha'}$-O	-0.29 (0.00)
	C_{γ}-Cl	1.734 (1.730)		$C_{\alpha'}$-$C_{\beta'}$-H	119.18 (119.19)	H-C-C-O	H-$C_{\beta''}$-$C_{\alpha''}$-O	0.00 (0.00)
	$C_{\gamma'}$-Cl	1.734 (1.730)		$C_{\gamma'}$-$C_{\beta'}$-H	120.73 (120.66)		H-$C_{\beta'''}$-$C_{\alpha'''}$-O	0.00 (0.00)
C-Cl	$C_{\gamma''}$-Cl	1.732 (1.730)	C-C-H	$C_{\alpha''}$-$C_{\beta''}$-H	119.08 (119.19)		H-C_{β}-C_{γ}-Cl	-1.62 (0.00)
	$C_{\gamma'''}$-Cl	1.732 (1.730)		$C_{\gamma''}$-$C_{\beta''}$-H	120.75 (120.66)		H-$C_{\beta'}$-$C_{\gamma'}$-Cl	1.62 (0.00)
				$C_{\alpha'''}$-$C_{\beta'''}$-H	119.08 (119.19)	H-C-C-Cl	H-$C_{\beta''}$-$C_{\gamma''}$-Cl	0.97 (0.00)
				$C_{\gamma'''}$-$C_{\beta'''}$-H	120.74 (120.66)		H-$C_{\beta'''}$-$C_{\gamma'''}$-Cl	-0.97 (0.00)
				C_{β}-C_{γ}-Cl	118.70 (118.69)		Cl-C_{γ}-$C_{\gamma'}$-Cl	0.00 (0.00)
			C-C-Cl	C_{γ}-C_{γ}-Cl	121.40 (121.49)	Cl-C-C-Cl	Cl-$C_{\gamma''}$-$C_{\gamma'''}$-Cl	-0.01 (0.00)
				$C_{\beta'}$-$C_{\gamma'}$-Cl	118.70 (118.69)			

				C_{γ}-$C_{\gamma'}$-Cl	121.40 (121.49)			
				$C_{\beta''}$-$C_{\gamma''}$-Cl	118.70 (118.69)			
				$C_{\gamma'''}$-$C_{\gamma''}$-Cl	121.48 (121.49)			
				$C_{\beta'''}$-$C_{\gamma'''}$-Cl	118.70 (118.69)			
				$C_{\gamma''}$-$C_{\gamma'''}$-Cl	121.48 (121.49)			

TCDF

Distances (Å)			Angles θ (°)			Dihedral ϕ (°)		
C-C	C_{α}-C_{β}	1.381 (1.383)	C-C-C	C_{α}-C_{β}-C_{γ}	116.76 (116.82)	C-C-C-C	$C_{\beta'}$-$C_{\alpha'}$-C_{α}-C_{β}	-0.19 (0.02)
	C_{β}-C_{γ}	1.389 (1.391)		C_{β}-C_{γ}-$C_{\gamma'}$	121.30 (121.17)		$C_{\alpha'}$-C_{α}-C_{β}-C_{γ}	0.58 (-0.03)
	C_{α}-$C_{\alpha'}$	1.400 (1.408)		C_{γ}-$C_{\gamma'}$-$C_{\beta'}$	120.71 (120.83)		C_{α}-C_{β}-C_{γ}-$C_{\gamma'}$	-0.39 (0.02)
	C_{γ}-$C_{\gamma'}$	1.405 (1.408)		$C_{\gamma'}$-$C_{\beta'}$-$C_{\alpha'}$	118.79 (118.65)		C_{β}-C_{γ}-$C_{\gamma'}$-$C_{\beta'}$	-0.18 (0.00)
	$C_{\alpha'}$-$C_{\beta'}$	1.392 (1.392)		$C_{\beta'}$-$C_{\alpha'}$-C_{α}	119.10 (119.34)		C_{γ}-$C_{\gamma'}$-$C_{\beta'}$-$C_{\alpha'}$	0.58 (-0.01)
	$C_{\beta'}$-$C_{\gamma'}$	1.389 (1.390)		$C_{\alpha'}$-C_{α}-C_{β}	123.34 (123.19)		$C_{\gamma'}$-$C_{\beta'}$-$C_{\alpha'}$-C_{α}	-0.40 (0.00)
	$C_{\alpha''}$-$C_{\beta''}$	1.381 (1.383)		$C_{\alpha''}$-$C_{\beta''}$-$C_{\gamma''}$	116.75 (116.82)		$C_{\beta'''}$-$C_{\alpha'''}$-$C_{\alpha''}$-$C_{\beta''}$	-0.87 (-0.01)
	$C_{\beta''}$-$C\gamma''$	1.389 (1.391)		$C_{\beta''}$-$C_{\gamma''}$-$C_{\gamma''}$	121.23 (121.17)		$C_{\alpha'''}$-$C_{\alpha''}$-$C_{\beta''}$-$C_{\gamma''}$	0.22 (0.01)
	$C_{\alpha''}$-$C_{\alpha'''}$	1.400 (1.401)		$C_{\gamma''}$-$C_{\gamma'''}$-$C_{\beta'''}$	120.81 (120.83)		$C_{\alpha''}$-$C_{\beta''}$-$C_{\gamma''}$-$C_{\gamma'''}$	0.59 (-0.01)
	$C_{\gamma''}$-$C_{\gamma'''}$	1.406 (1.401)		$C_{\gamma'''}$-$C_{\beta'''}$-$C_{\alpha'''}$	118.71 (118.64)		$C_{\beta''}$-$C_{\gamma''}$-$C_{\gamma'''}$-$C_{\beta'''}$	-0.75 (0.01)
	$C_{\alpha'''}$-$C_{\beta'''}$	1.392 (1.392)		$C_{\beta'''}$-$C_{\alpha'''}$-$C_{\alpha''}$	119.13 (119.34)		$C_{\gamma''}$-$C_{\gamma'''}$-$C_{\beta'''}$-$C_{\alpha'''}$	0.08 (-0.01)
	$C_{\beta'''}$-$C_{\gamma'''}$	1.389 (1.340)		$C_{\alpha'''}$-$C_{\alpha''}$-$C_{\beta''}$	123.36 (123.19)		$C_{\gamma'''}$-$C_{\beta'''}$-$C_{\alpha'''}$-$C_{\alpha''}$	0.69 (0.01)
	$C_{\alpha'}$-$C_{\alpha'''}$	1.454 (1.451)		C_{α}-$C_{\alpha'}$-$C_{\alpha''}$	105.00 (105.12)		C_{α}-$C_{\alpha'}$-$C_{\alpha'''}$-$C_{\alpha''}$	0.26 (0.04)
C-O	C_{α}-O	1.365 (1.366)		$C_{\alpha''}$-$C_{\alpha'''}$-$C_{\alpha'}$	105.08 (105.12)	C-C-O-C	$C_{\alpha'}$-C_{α}-O-$C_{\alpha''}$	-1.21 (0.02)
	$C_{\alpha'}$-O	1.365 (1.366)	C-O-C	C_{α}-O-$C_{\alpha''}$	106.01 (105.96)		$C_{\alpha'''}$-$C_{\alpha''}$-O-C_{α}	1.38 (0.00)
C-H	C_{β}-H	1.082 (1.086)	C-C-O	$C_{\alpha'}$-C_{α}-O	111.98 (111.90)	C-C-C-O	$C_{\alpha'''}$-$C_{\alpha'}$-C_{α}-O	0.59 (-0.04)

	$C_{\beta'}$-H	1.083 (1.088)		$C_{\alpha'''}$-$C_{\alpha''}$-O	111.91 (111.91)		$C_{\alpha'}$-$C_{\alpha'''}$-$C_{\alpha''}$-O	-1.03 (-0.02)
	$C_{\beta''}$-H	1.082 (1.086)		C_{α}-C_{β}-H	121.91 (122.03)	H-C-C-O	H-C_{β}-C_{α}-O	0.70 (0.03)
	$C_{\beta'''}$-H	1.083 (1.088)		C_{γ}-C_{β}-H	121.33 (121.15)		H-$C_{\beta''}$-$C_{\alpha''}$-O	-0.26 (-0.01)
	C_{γ}-Cl	1.734 (1.730)		$C_{\alpha'}$-$C_{\beta'}$-H	121.79 (121.76)	H-C-C-C	H-$C_{\beta'}$-$C_{\alpha'}$-$C_{\alpha'''}$	-1.64 (0.02)
C-Cl	$C_{\gamma'}$-Cl	1.736 (1.733)	C-C-H	$C_{\gamma'}$-$C_{\beta'}$-H	119.42 (119.59)		H-$C_{\beta'''}$-$C_{\alpha'''}$-$C_{\alpha'}$	1.34 (0.03)
	$C_{\gamma''}$-Cl	1.734 (1.730)		$C_{\alpha''}$-$C_{\beta''}$-H	121.93 (122.03)		H-C_{β}-C_{γ}-Cl	-1.06 (-0.03)
	$C_{\gamma'''}$-Cl	1.737 (1.733)		$C_{\gamma''}$-$C_{\beta''}$-H	121.32 (121.15)	H-C-C-Cl	H-$C_{\beta'}$-$C_{\gamma'}$-Cl	1.59 (-0.02)
				$C_{\alpha'''}$-$C_{\beta'''}$-H	121.74 (121.76)		H-$C_{\beta''}$-$C_{\gamma''}$-Cl	1.47 (0.03)
				$C_{\gamma'''}$-$C_{\beta'''}$-H	119.55 (119.60)		H-$C_{\beta'''}$-$C_{\gamma'''}$-Cl	-0.93 (0.00)
				C_{β}-C_{γ}-Cl	117.97 (118.16)	Cl-C-C-Cl	Cl-C_{γ}-$C_{\gamma'}$-Cl	-0.48 (0.05)
				$C_{\gamma'}$-C_{γ}-Cl	120.73 (120.67)		Cl-$C_{\gamma''}$-$C_{\gamma'''}$-Cl	-0.55 (-0.01)
				$C_{\beta'}$-$C_{\gamma'}$-Cl	118.56 (118.55)			
				C_{γ}-$C_{\gamma'}$-Cl	120.72 (120.61)			
			C-C-Cl	$C_{\beta''}$-$C_{\gamma''}$-Cl	117.92 (118.16)			
				$C_{\gamma'''}$-$C_{\gamma''}$-Cl	120.85 (120.67)			
				$C_{\beta'''}$-$C_{\gamma'''}$-Cl	118.58 (118.56)			
				$C_{\gamma''}$-$C_{\gamma'''}$-Cl	120.61 (120.61)			

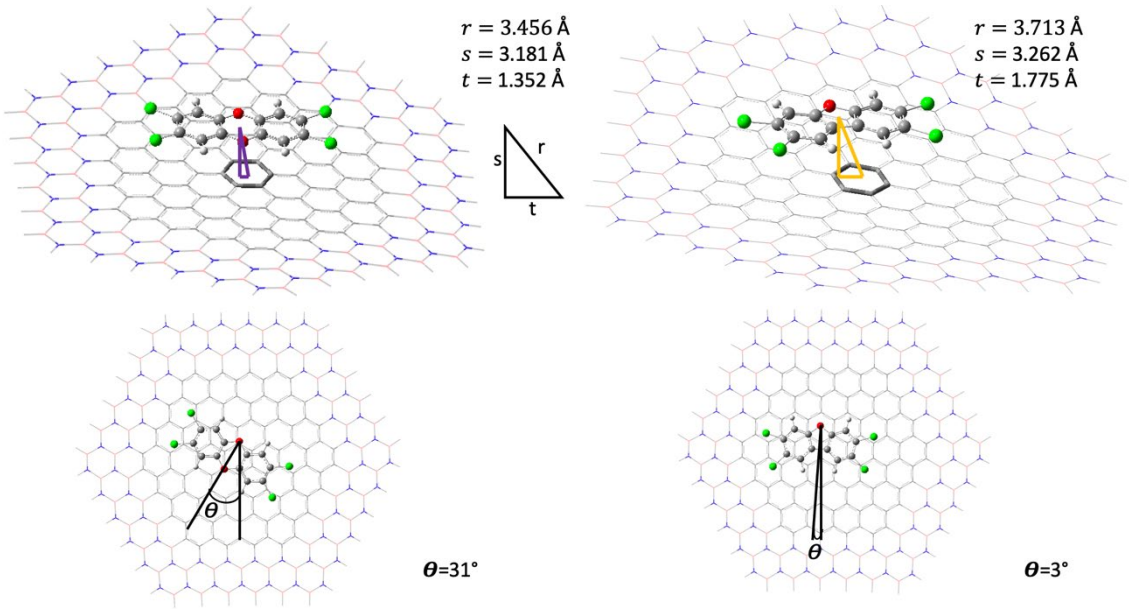


Figure S8. Some selected parameters reflecting the relative disposition of TCDD and TCDF on BNC96. Distances in Å and torsional angles in degrees. The distances above represent: the distance between the geometrical centers of the molecule and surface (r), the projection of r on the surface plane (t) and the projection of r on a perpendicular axis to the molecule and the surface (s). The torsional angle below (θ) represent the angle formed by the C_2 symmetry axis of the molecule and the surface.