Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary Information

Ultrasensitive and multiplex SERS determination of anthropogenic phenols in oil fuel and environmental samples

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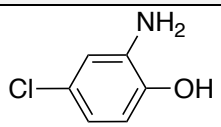
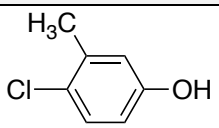
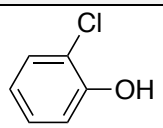
1. Phenolic compounds in environmental samples

Table S1. Phenolic compounds included in the European Community Directive 76/464/EEC and the US-EPA list of priority pollutants.

Commission of the European Communities Directive 76/464/EC		
		
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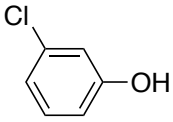
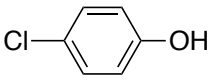
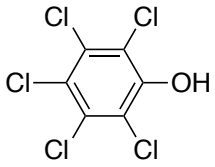
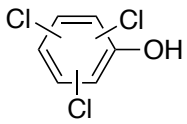
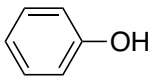
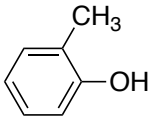
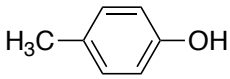
		
3-Chlorophenol	4-Chlorophenol	Pentachlorophenol
		
	Trichlorophenols	
US-EPA list of priority pollutants (EPA 8041)		
		
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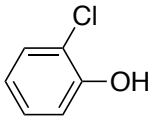	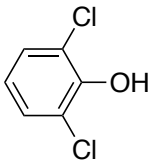	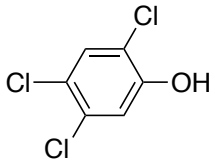
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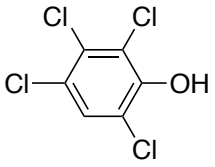
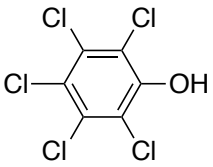
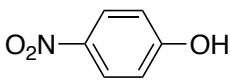
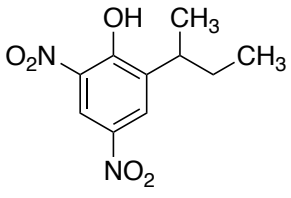
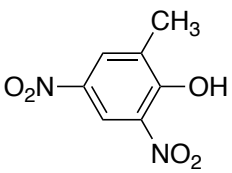
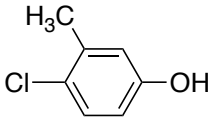
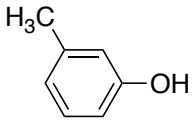
		
2,3,4,5-Tetrachlorophenol	Pentachlorophenol	4-Nitrophenol
		
Dinoseb (DNMP)	4,6-Dinitro-2-methylphenol	4-Chloro-3-methylphenol



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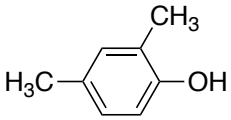

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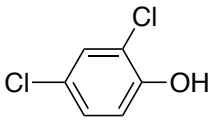

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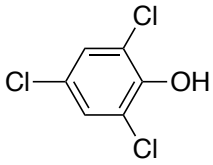

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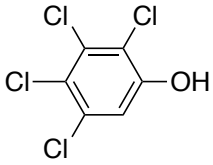

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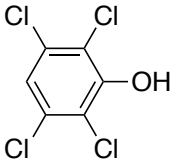

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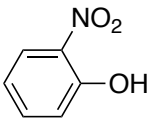
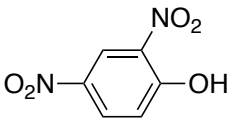


2-Nitrophenol



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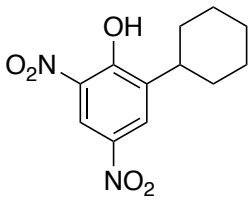

2-Cyclohexyl-4,6-dinitrophenol

2. DFT calculations for charge-transfer complexes of phenolic compounds

Table S2. Calculated properties of the CTCs with phenols (at PBE0/6-31+G(d,p)-SMD level). Solvent effects are included.

Charge-transfer complex	E_{HOMO}, Eh	E_{HOMO}, eV	E_{LUMO}, Eh	E_{LUMO}, eV	$\Delta_{LU\text{-}HO}$,[a] eV	E_{bind}, kcal/mol	DCT[b]	R_{D-A},[c] Å
Charge-transfer complexes of phenol								
Phenol – DDQ	–0.253	–6.88	–0.170	–4.67	2.21	4.7	0.114	3.455
Phenol – TCNQ	–0.244	–6.64	–0.165	–4.49	2.15	3.9	0.007	4.197
Phenol – TNF	–0.245	–6.67	–0.151	–4.11	2.56	41.1	0.003	4.207
Charge-transfer complexes of chlorophenols								
o-Chlorophenol – DDQ	–0.257	–6.99	–0.173	–4.71	2.28	3.0	0.073	3.623
o-Chlorophenol – TCNQ	–0.249	–6.78	–0.165	–4.49	2.29	2.2	0.007	4.216
o-Chlorophenol – TNF	–0.250	–6.80	–0.151	–4.11	2.69	41.6	0.003	4.250
p-Chlorophenol – DDQ	–0.250	–6.80	–0.172	–4.68	2.12	2.6	0.097	3.498
p-Chlorophenol – TCNQ	–0.244	–6.64	–0.166	–4.52	1.12	2.0	0.006	4.210
p-Chlorophenol – TNF	–0.246	–6.69	–0.150	–4.08	2.61	39.7	0.012	3.397
Charge-transfer complexes of cresols								
m-cresol – DDQ (1)	–0.251	–6.83	–0.168	–4.57	2.26	3.5	0.135	3.250
m-cresol – DDQ (2)	–0.251	–6.83	–0.167	–4.54	2.29	4.0	0.125	3.377
m-cresol – TCNQ	–0.241	–6.56	–0.165	–4.49	2.07	2.1	0.008	4.176
m-cresol – TNF	–0.242	–6.59	–0.150	–4.08	2.51	41.7	0.001	4.369
o-cresol – DDQ (1)	–0.250	–6.80	–0.167	–4.54	2.26	5.9	0.157	3.249
o-cresol – DDQ (2)	–0.250	–6.80	–0.168	–4.57	2.23	3.4	0.145	3.408
o-cresol – TCNQ	–0.239	–6.50	–0.165	–4.49	2.01	2.0	0.007	4.161
o-cresol – TNF	–0.240	–6.53	–0.150	–4.08	2.45	41.2	0.003	4.056
Charge-transfer complexes of xylenols								
2,5-xylenol – DDQ (1)	–0.247	–6.72	–0.166	–4.52	2.20	3.8	0.179	3.233
2,5-xylenol – DDQ (2)	–0.248	–6.75	–0.164	–4.46	2.29	4.9	0.208	3.276
2,5-xylenol – TCNQ	–0.235	–6.40	–0.165	–4.49	1.91	2.1	0.006	4.203
2,5-xylenol – TNF	–0.234	–6.37	–0.151	–4.11	2.26	41.7	0.001	4.200
2,6-xylenol – DDQ	–0.247	–6.72	–0.166	–4.52	2.20	4.5	0.180	3.287
2,6-xylenol – TCNQ	–0.235	–6.40	–0.165	–4.49	1.91	2.3	0.006	4.508
2,6-xylenol – TNF	–0.236	–6.42	–0.150	–4.08	2.44	41.8	0.002	4.150
Individual phenolic compounds								
PhOH	–0.239	–6.50	–0.010	–0.27	6.23	N/A	N/A	N/A
ClPhOH	–0.239	–6.50	–0.020	–0.54	5.96	N/A	N/A	N/A
m-cresol	–0.236	–6.42	–0.009	–0.24	6.18	N/A	N/A	N/A
o-cresol	–0.234	–6.37	–0.005	–0.14	6.23	N/A	N/A	N/A

Charge-transfer complex	E_{HOMO}, Eh	E_{HOMO}, eV	E_{LUMO}, Eh	E_{LUMO}, eV	$\Delta_{LU\text{-}HO}$,[a] eV	E_{bind}, kcal/mol	DCT[b]	$R_{D–A}$,[c] Å
2,5-xylenol	–0.229	–6.23	–0.005	–0.14	6.09	N/A	N/A	N/A
2,6-xylenol	–0.230	–6.26	0.000	0.00	6.26	N/A	N/A	N/A
DDQ	–0.310	–8.44	–0.179	–4.87	3.57	N/A	N/A	N/A
TCNQ	–0.271	–7.37	–0.167	–4.54	2.83	N/A	N/A	N/A
TNF	–0.310	–8.44	–0.154	–4.19	4.25	N/A	N/A	N/A

[a] $\Delta_{LU\text{-}HO}$, energy difference between LUMO and HOMO;

[b] DCT, degree of charge transfer;

[c] $R_{D–A}$, intermolecular distance between the donor (D) and the acceptor (A);

E_{bind}, binding energy between D and A [$–E_{bind} = E_{D\text{-}A} – E_D – E_A$].

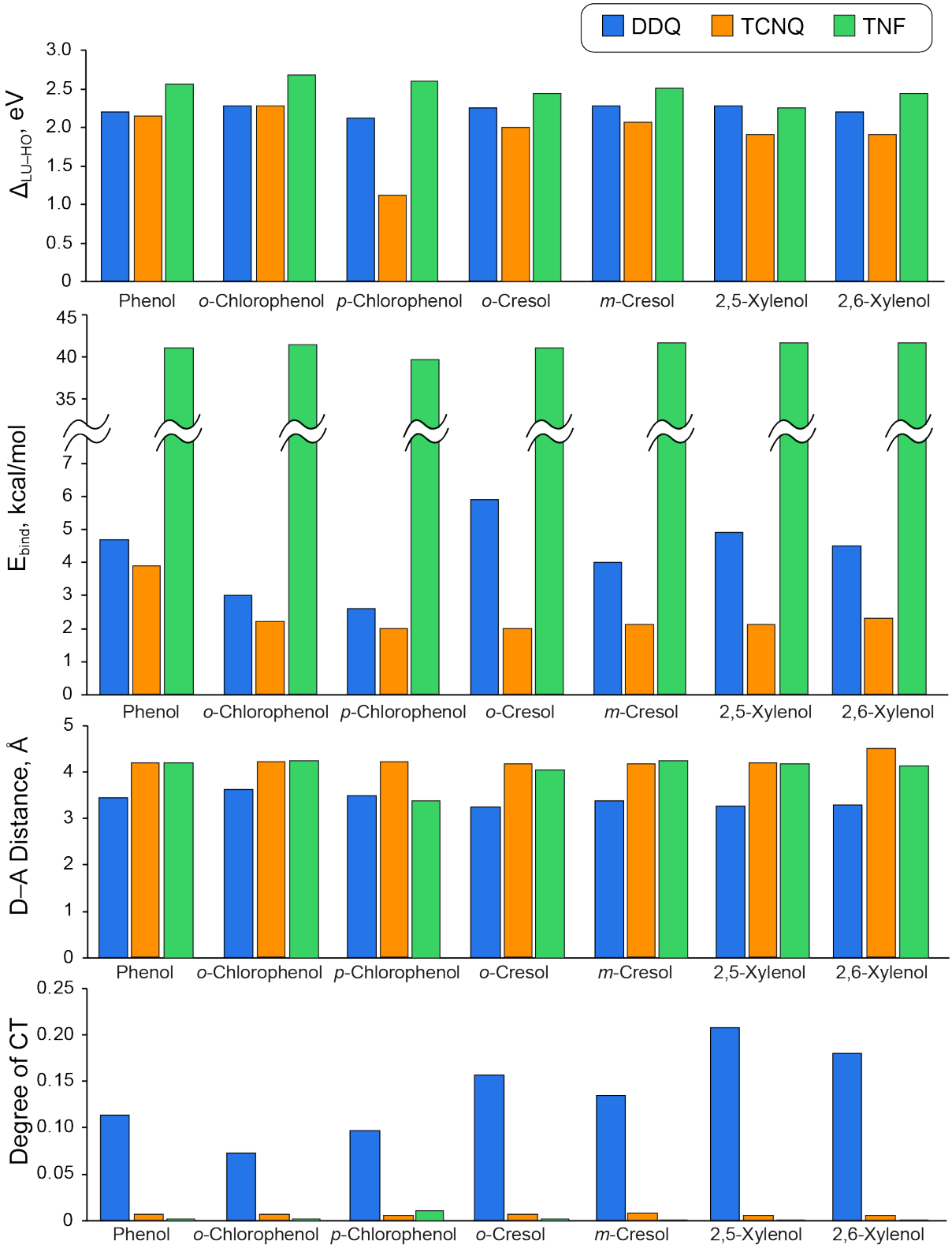

Figure S1. Calculated properties of the CTCs with phenols (at PBE0/6-31+G(d,p) level, solvent effects are included): energy difference between LUMO and HOMO (Δ_{LU-HO}), binding energy between the donor (D) and acceptor (A) (E_{bind}), distance between the donor and acceptor, and degree of charge transfer (CT). Values refer to the lowest-energy geometry of each complex: (1) or (2), from Table S2.

2.1. Optimized geometry and MO of CTCs with phenol

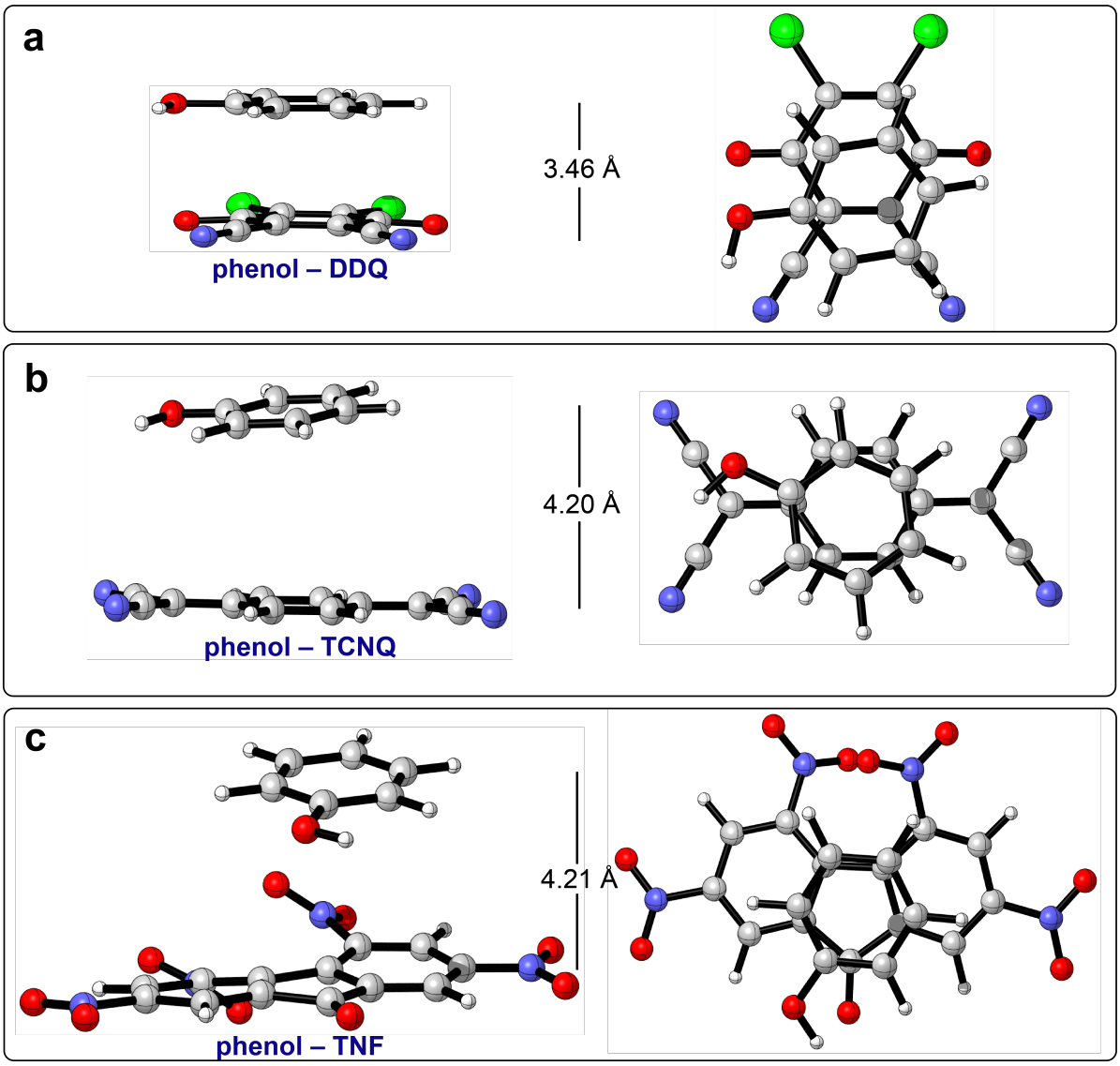

Figure S2. Conformations of phenol–DDQ (a), phenol–TCNQ (b), and phenol–TNF (c) charge-transfer complexes solvated in chloroform at PBE0/6-31+G(d,p) level.

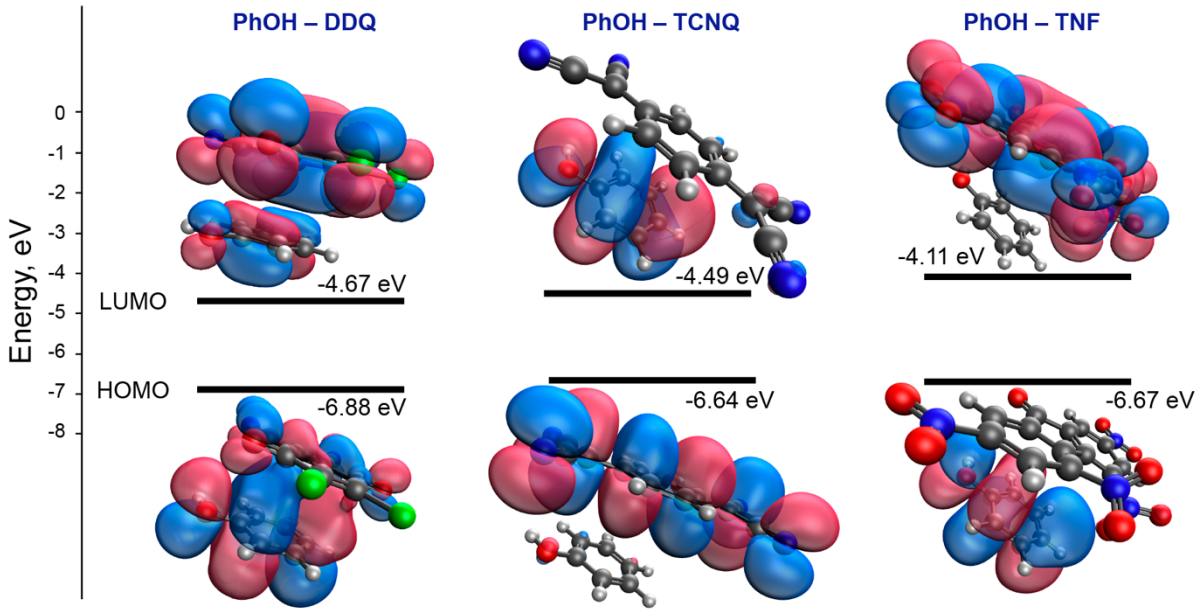

Figure S3. MO energy-level diagrams of CT complexes of phenol solvated in chloroform at PBE0/6-31+G(d,p) level.

2.2. Optimized geometry and MO of CTCs with chlorophenols

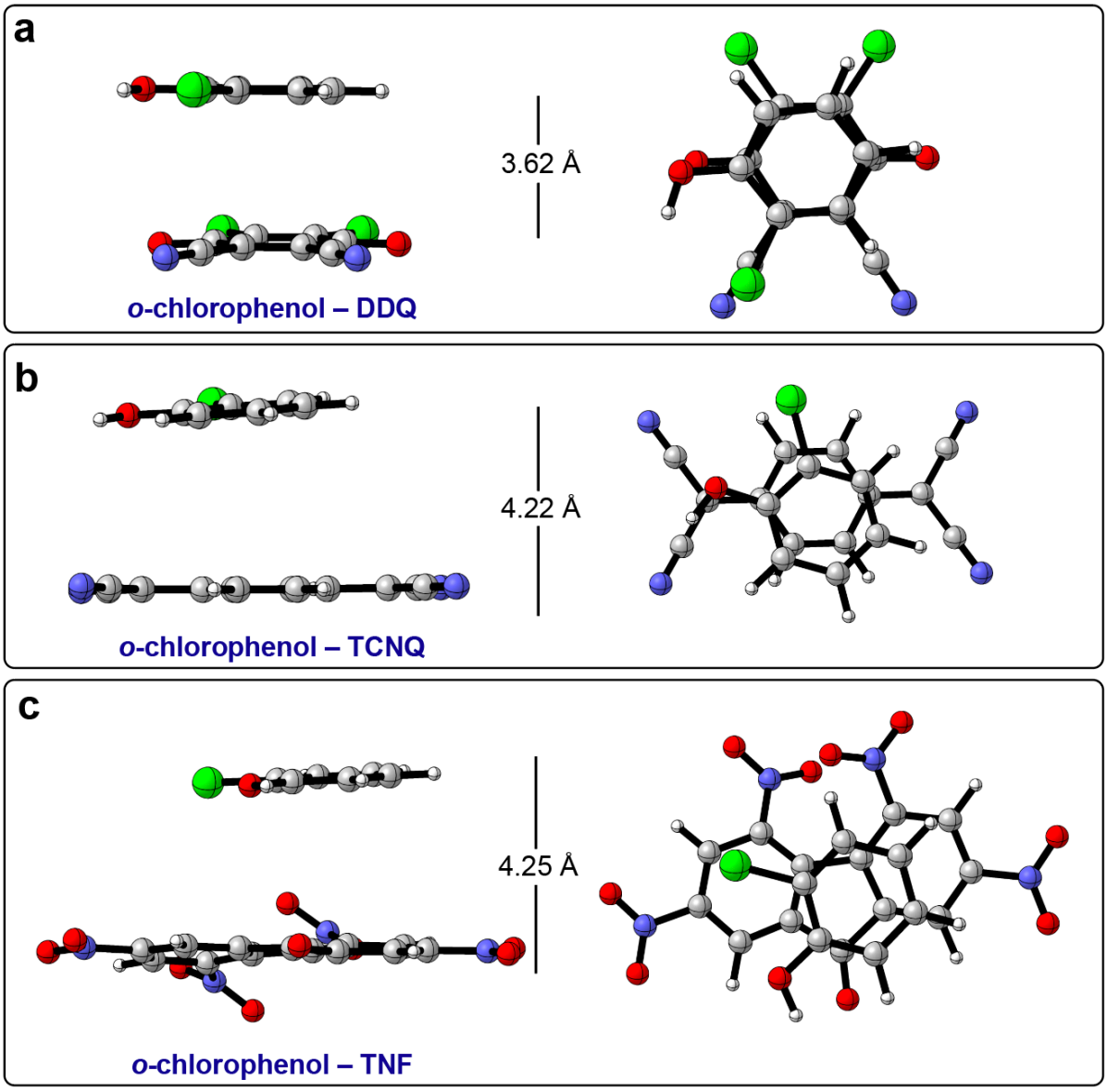

Figure S4. Conformations of *o*-chlorophenol–DDQ (a), *o*-chlorophenol–TCNQ (b), and *o*-chlorophenol–TNF (c) charge-transfer complexes solvated in chloroform at PBE0/6-31+G(d,p) level.

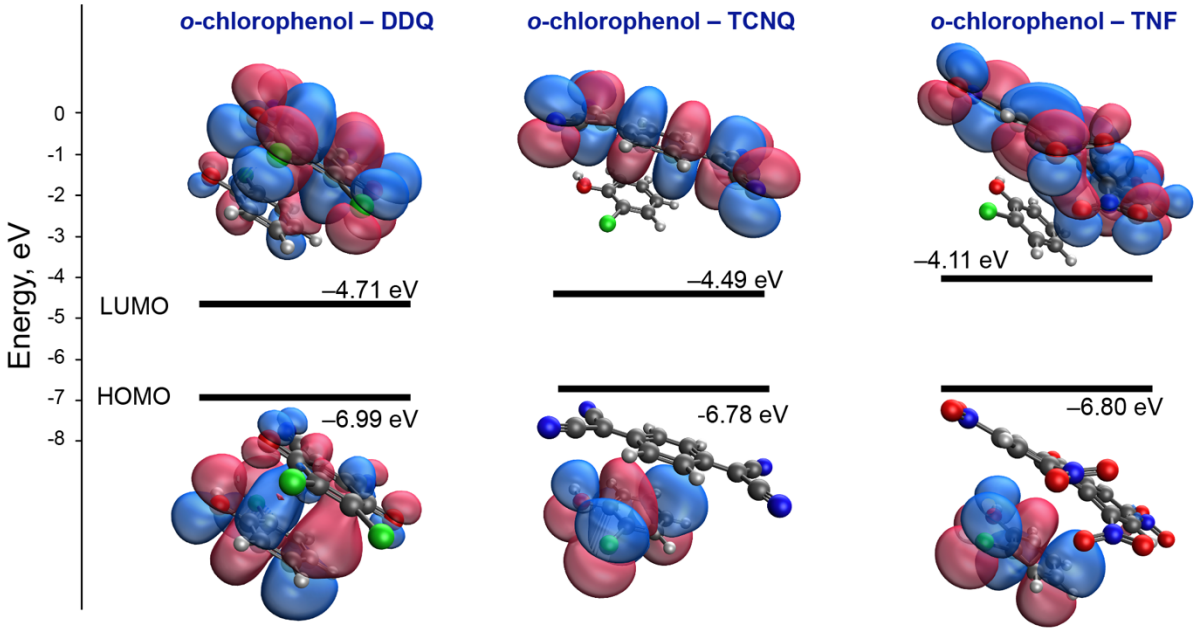

Figure S5. MO energy-level diagrams of CT complexes of *o*-chlorophenol solvated in chloroform at PBE0/6-31+G(d,p) level.

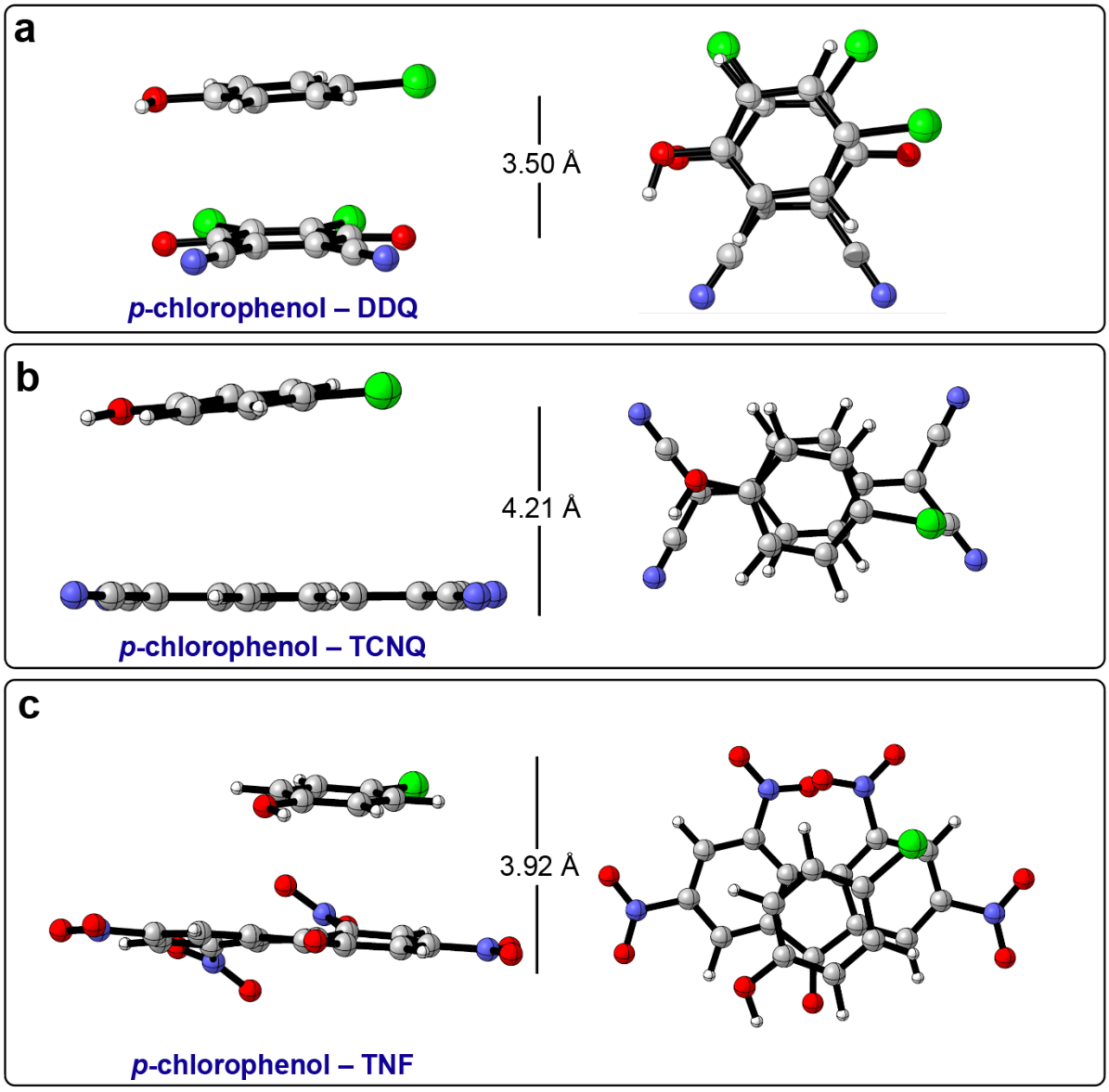

Figure S6. Conformations of *p*-chlorophenol–DDQ (a), *p*-chlorophenol–TCNQ (b), and *p*-chlorophenol–TNF (c) charge-transfer complexes solvated in chloroform at PBE0/6-31+G(d,p) level.

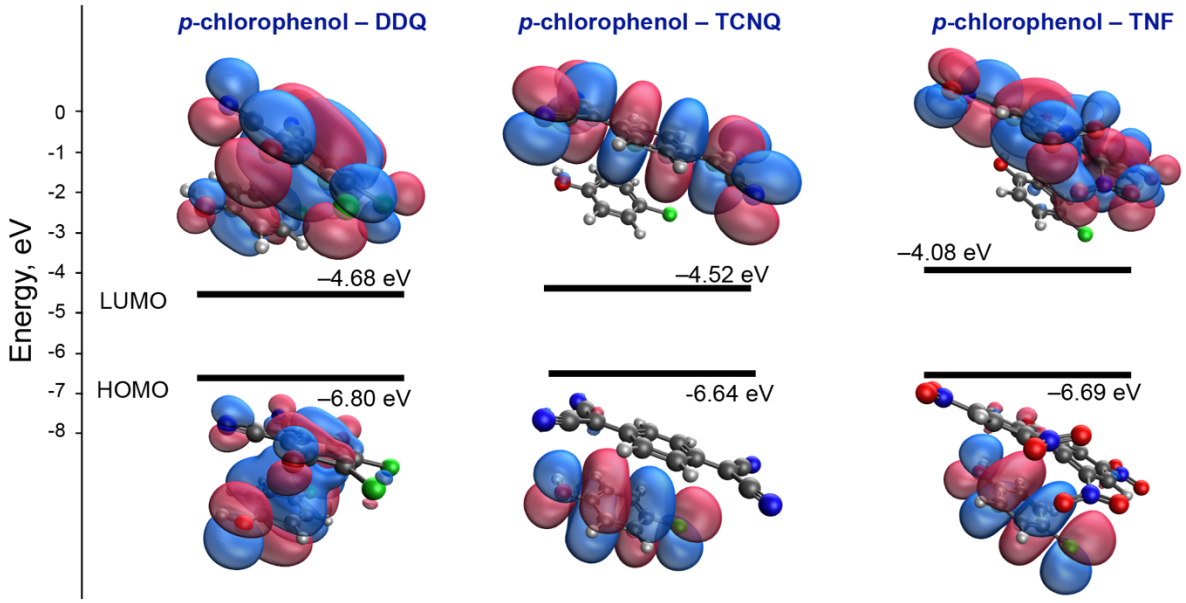

Figure S7. MO energy-level diagrams of CT complexes of *p*-chlorophenol solvated in chloroform at PBE0/6-31+G(d,p) level.

2.3. Optimized geometry and MO of CTCs with cresols

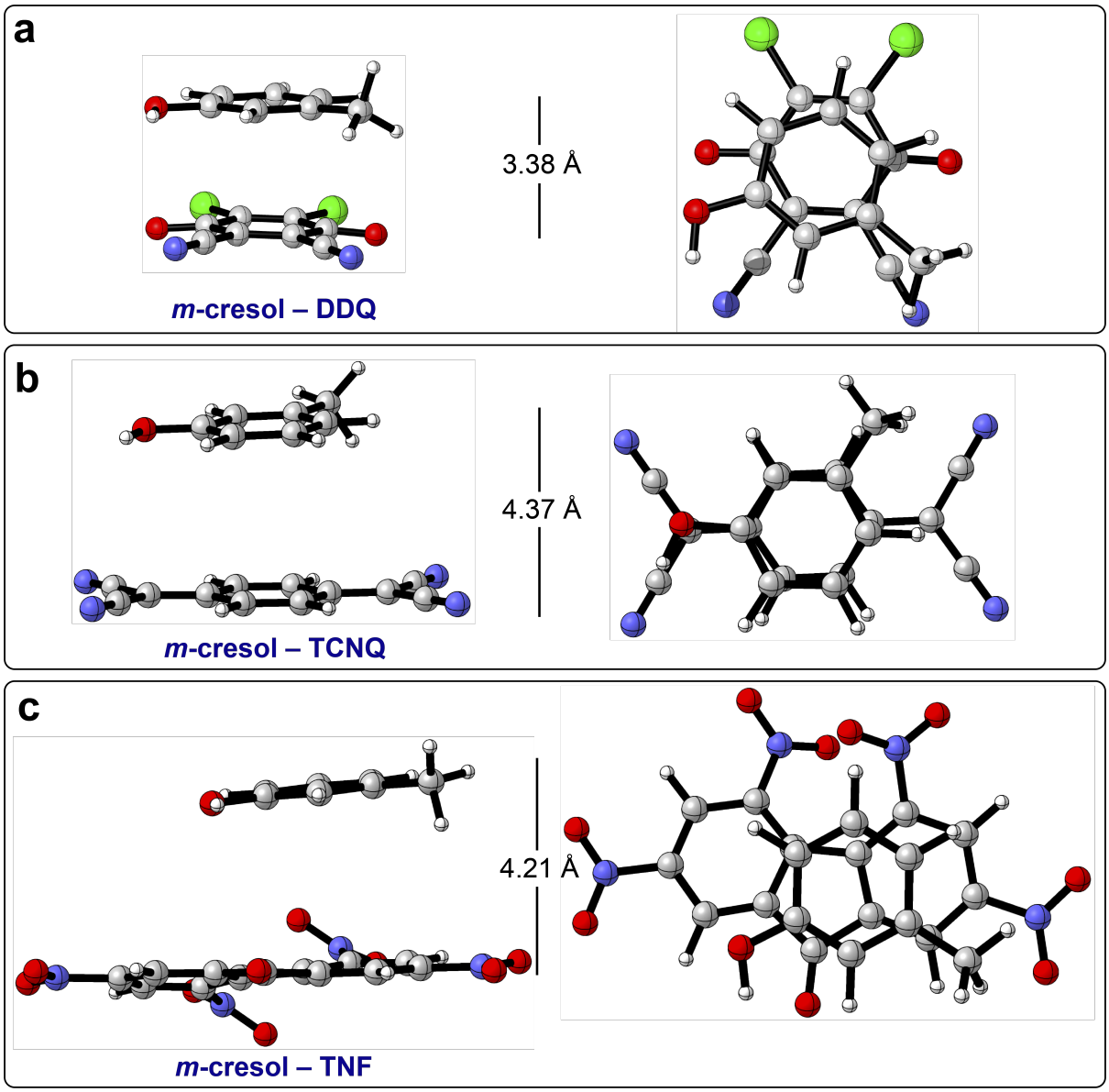

Figure S8. Conformations of *m*-cresol–DDQ (a), *m*-cresol–TCNQ (b), and *m*-cresol–TNF (c) charge-transfer complexes solvated in chloroform at PBE0/6-31+G(d,p) level.

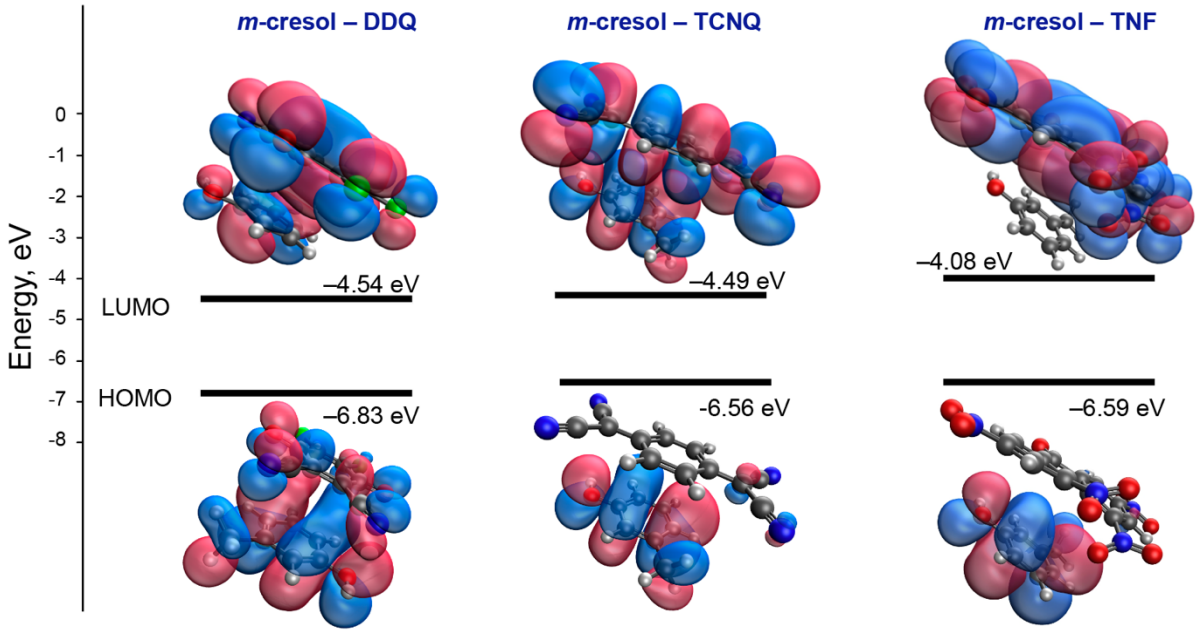

Figure S9. MO energy-level diagrams of CT complexes of *m*-cresol solvated in chloroform at PBE0/6-31+G(d,p) level.

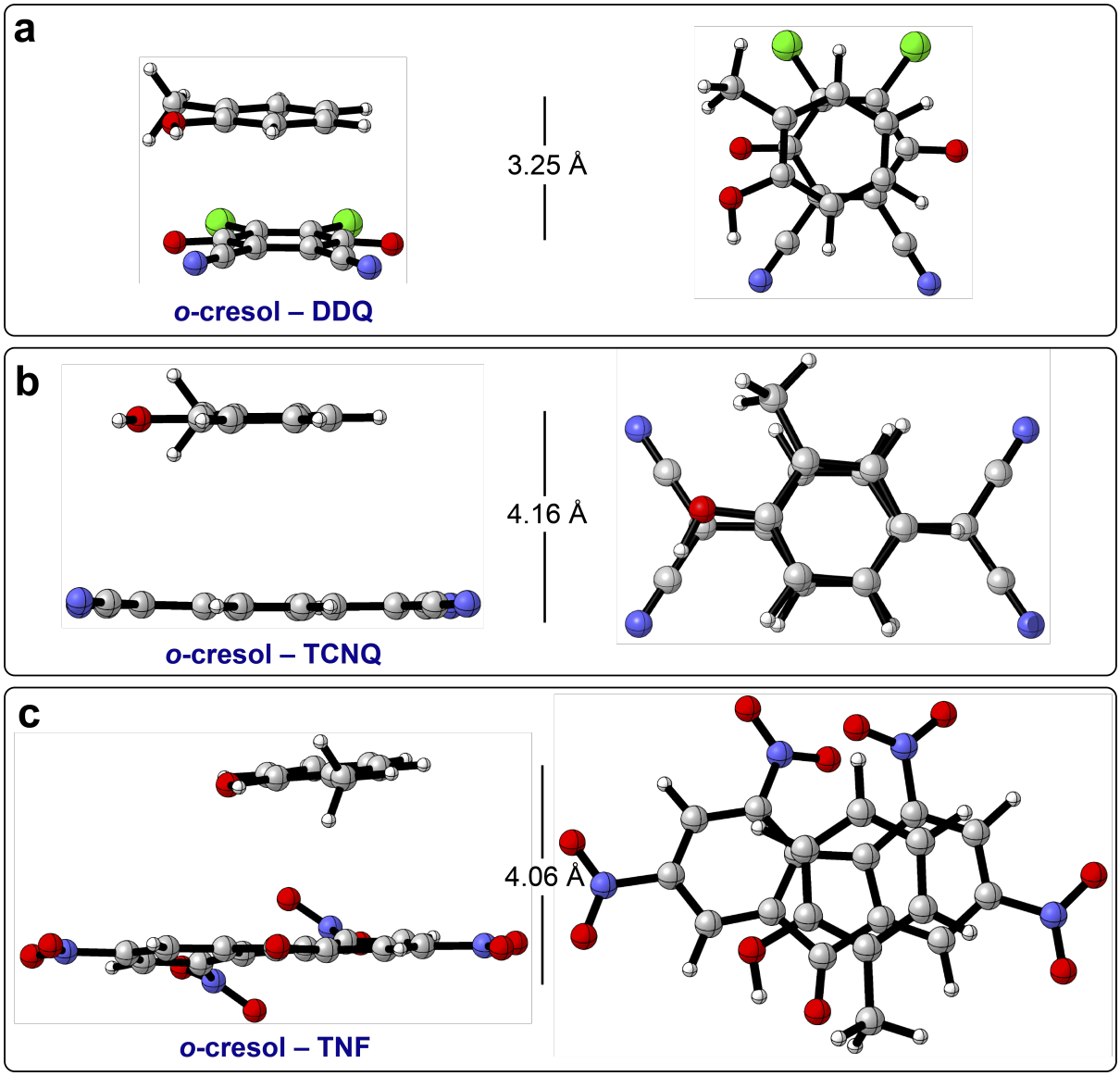

Figure S10. Conformations of *o*-cresol–DDQ (a), *o*-cresol–TCNQ (b), and *o*-cresol–TNF (c) charge-transfer complexes solvated in chloroform at PBE0/6-31+G(d,p) level.

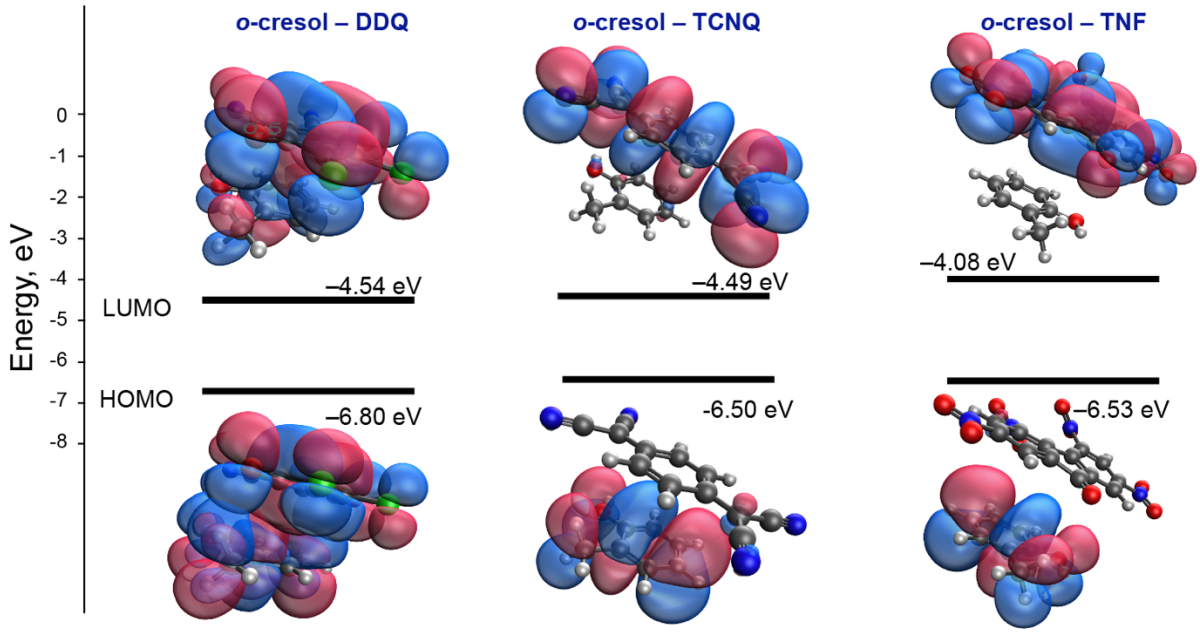

Figure S11. MO energy-level diagrams of CT complexes of *o*-cresol solvated in chloroform at PBE0/6-31+G(d,p) level.

2.4. Optimized geometry and MO of CTCs with xylenols

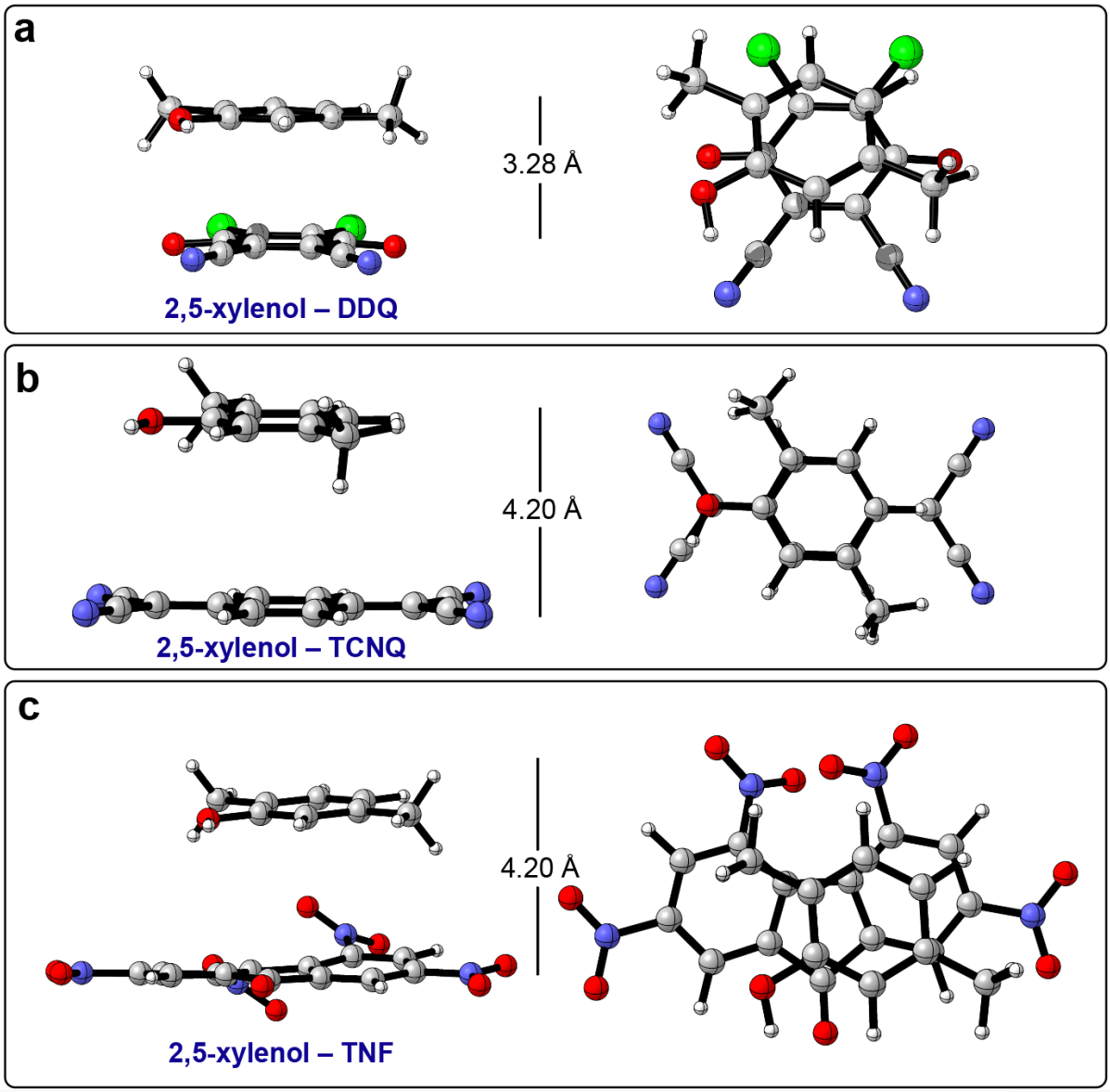

Figure S12. Conformations of 2,5-xylenol–DDQ (a), 2,5-xylenol –TCNQ (b), and 2,5-xylenol – TNF (c) charge-transfer complexes solvated in chloroform at PBE0/6-31+G(d,p) level.

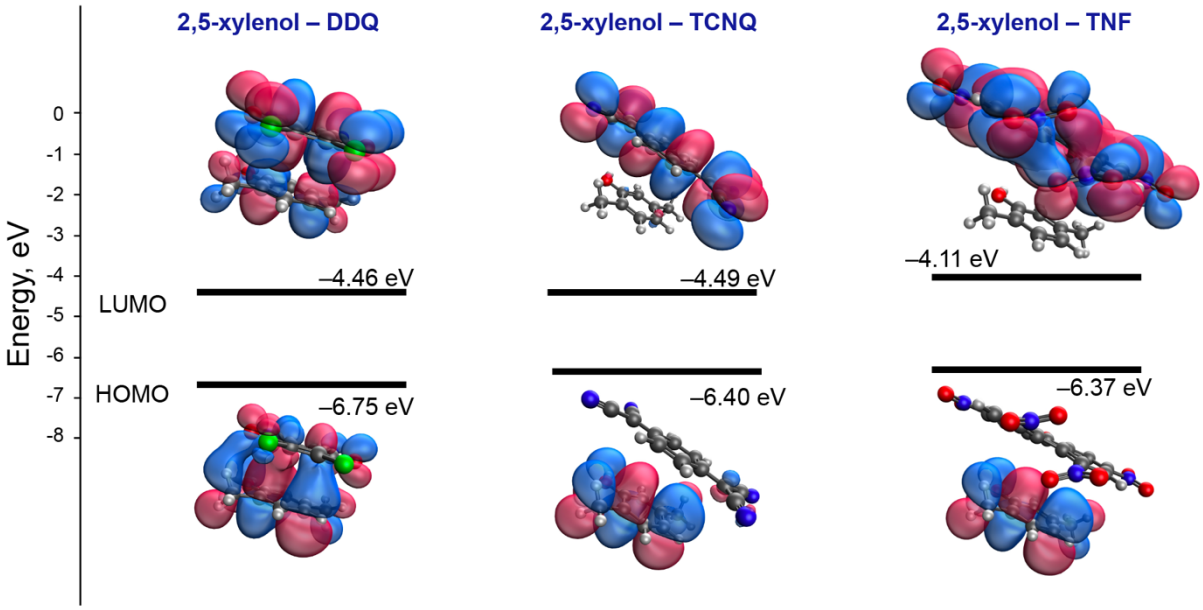

Figure S13. MO energy-level diagrams of CT complexes of 2,5-xylenol solvated in chloroform at PBE0/6-31+G(d,p) level.

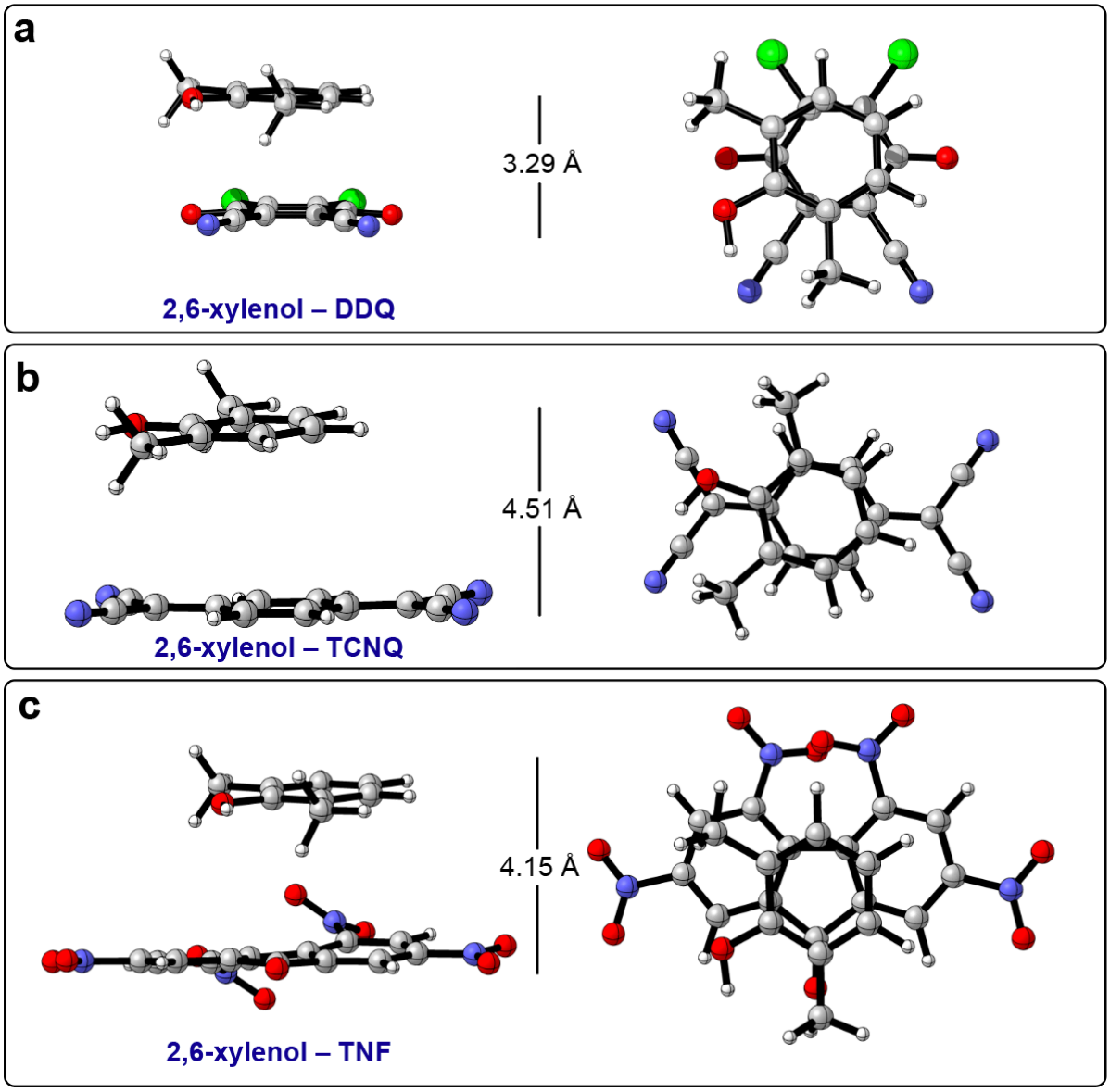

Figure S14. Conformations of 2,6-xylenol–DDQ (a), 2,6-xylenol –TCNQ (b), and 2,6-xylenol – TNF (c) charge-transfer complexes solvated in chloroform at PBE0/6-31+G(d,p) level.

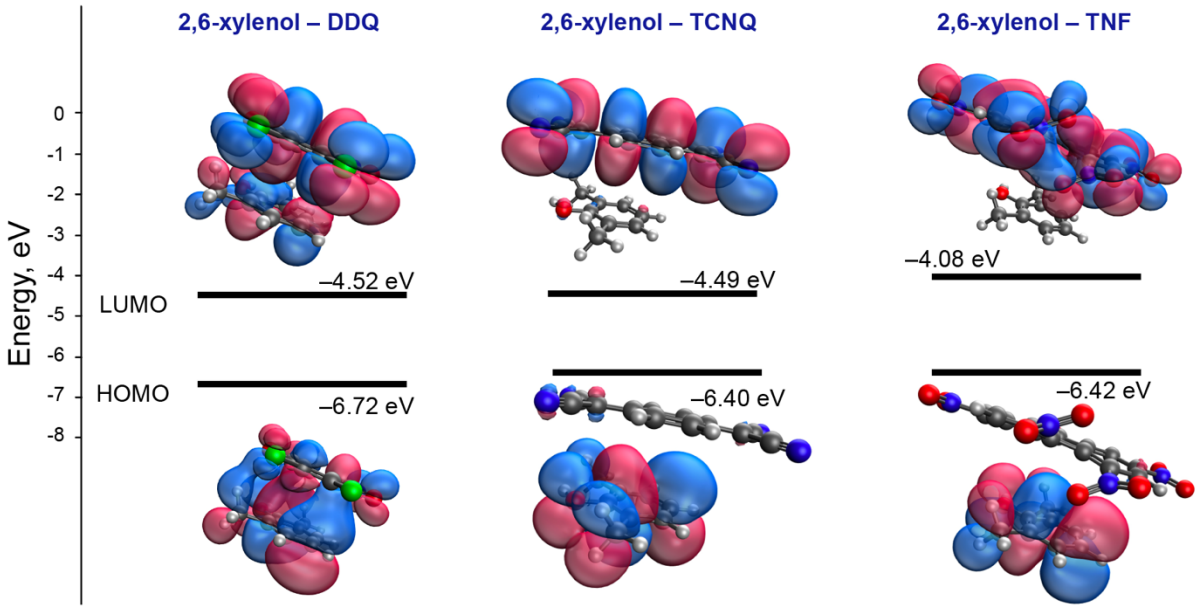

Figure S15. MO energy-level diagrams of CT complexes of 2,6-xylenol solvated in chloroform at PBE0/6-31+G(d,p) level.

3. Optical properties of charge-transfer complexes of phenolic compounds

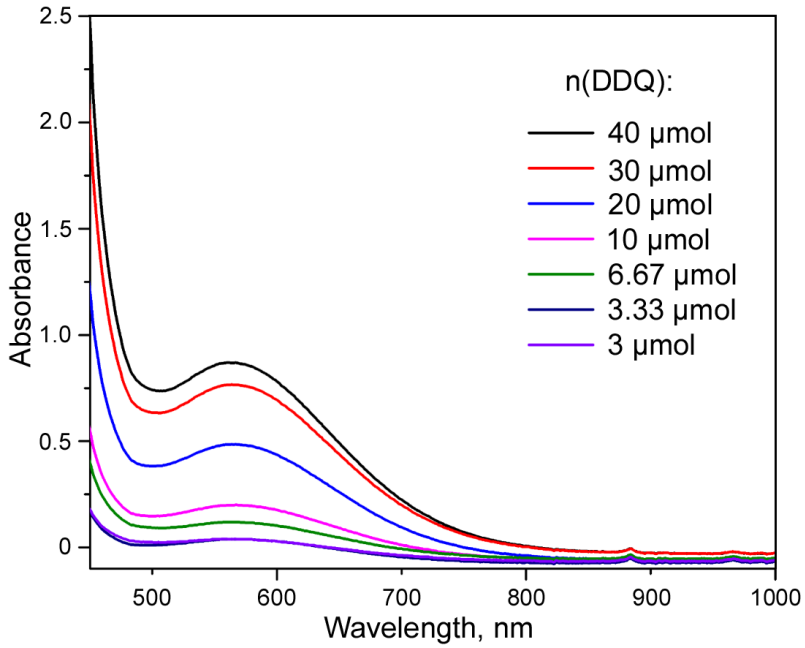

Figure S16. UV-vis spectra of mixtures of 40 µmol **phenol** with DDQ in various proportions in 1.8 mL $CHCl_3$. (Calculated stoichiometry 1:1, calculated stability constant K = 74 M^{-1}).

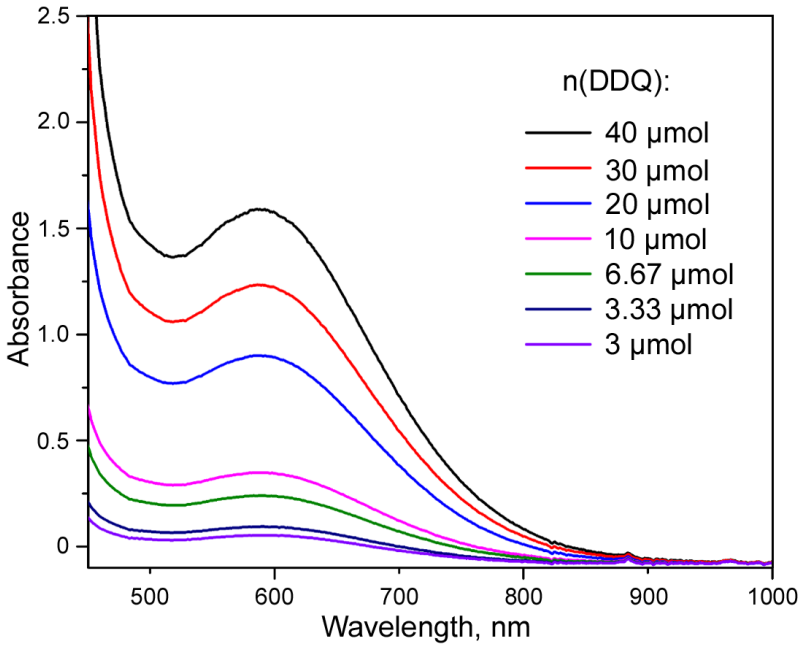

Figure S17. UV-vis spectra of mixtures of 40 µmol ***m*-cresol** with DDQ in various proportions in 1.8 mL $CHCl_3$. (Calculated stoichiometry 1:1, calculated stability constant K = 107 M^{-1}).

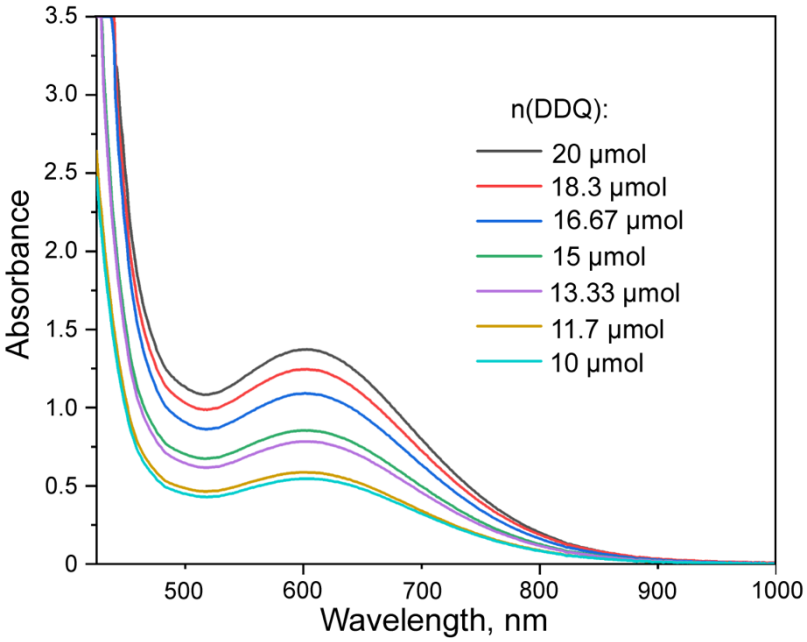

Figure S18. UV-vis spectra of mixtures of 20 µmol ***o*-cresol** with DDQ in various proportions in 1.5 mL $CHCl_3$. (Calculated stoichiometry 1:1).

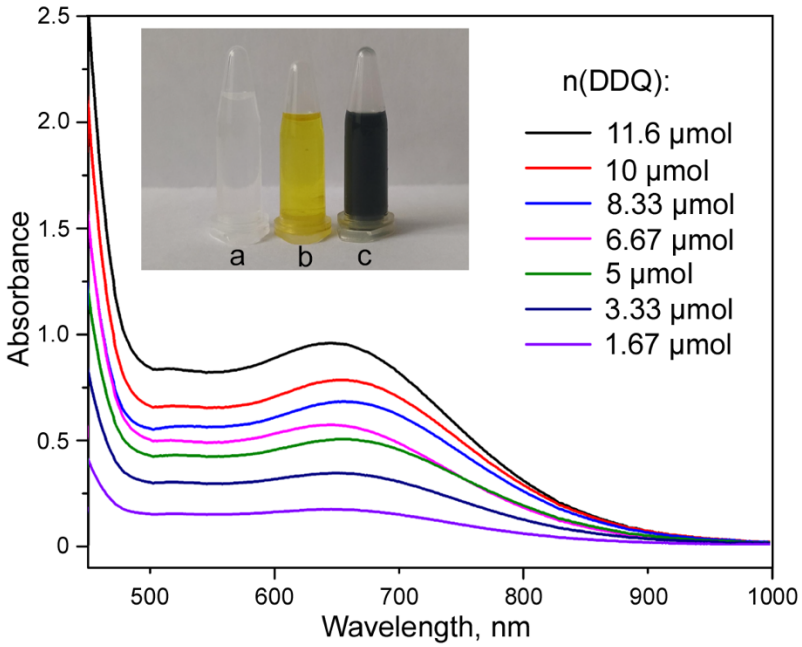

Figure S19. UV-vis spectra of mixtures of 20 µmol **2,5-xylenol** with DDQ in various proportions in 1.8 mL $CHCl_3$. (Calculated stoichiometry 1:1, calculated stability constant K = 40 M^{-1}). Photograph demonstrates colors of 2,5-xylenol (a), DDQ (b), and mixed 2,5-xylenol and DDQ (c) solutions in chloroform.

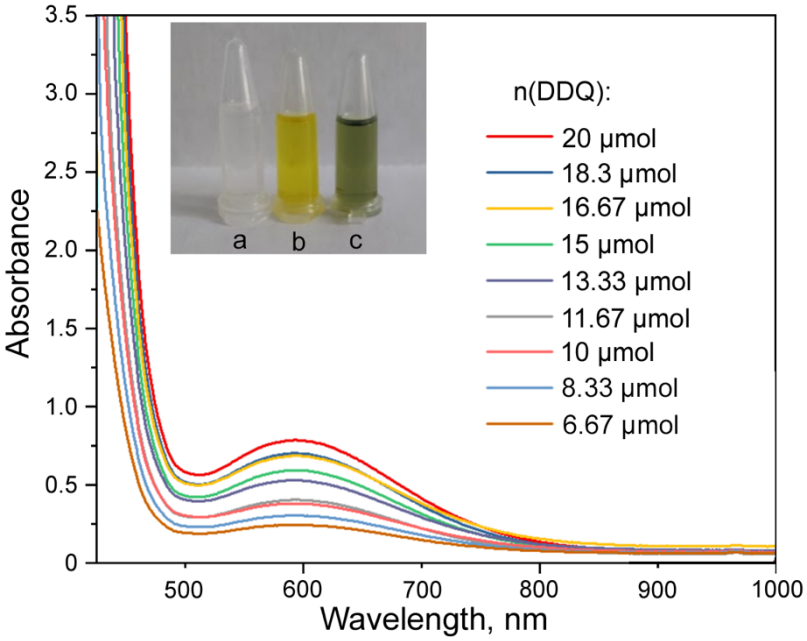

Figure S20. UV-vis spectra of mixtures of 20 µmol ***p*-chlorophenol** with DDQ in various proportions in 1.2 mL $CHCl_3$. (Calculated stoichiometry 1:1, calculated stability constant K = 102 M^{-1}). Photograph demonstrates colors of *p*-chlorophenol (a), DDQ (b), and mixed 2,5-xylenol and DDQ (c) solutions in chloroform.

Table S3. Optical properties (λ_{CT} and ε_{max}), stability constants (*K*), and stoichiometry (determined as *tgα* in a Bent-French plot of lg(Abs) vs. lg($c_{acceptor}$)) of the CTCs with phenolic compounds and DDQ in chloroform.

Phenolic compound	λ_{CT}, nm	ε_{max}, cm M^{-1}	*K*, M^{-1}	*tgα*
Phenol	562	63.4	74	1.07 ± 0.09
o-Chlorophenol	565	–	–*	–
p-Chlorophenol	588	40.7	102	1.21 ± 0.08
o-Cresol	605	94.4	–	1.13 ± 0.09
m-Cresol	588	104.9	107	1.4 ± 0.1
2,5-Xylenol	637	117.2	40	1.18 ± 0.08
2,6-Xylenol	666	–	–	1.2 ± 0.1

* complex was unstable in solution at high concentrations required for UV-vis detection.

4. SERS sensor characterization

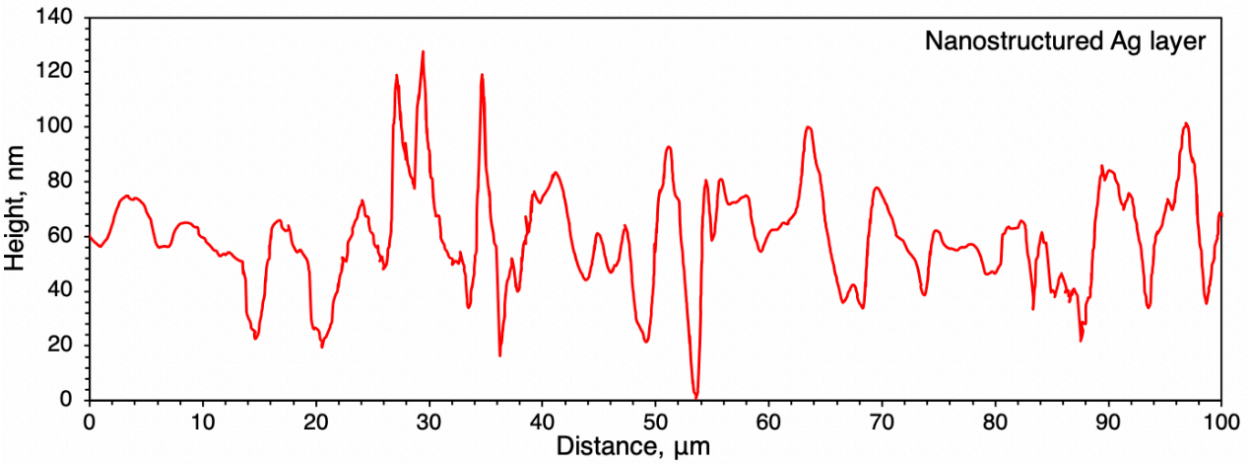

Figure S21. Characteristic contact profilometer image for nanostructured silver layer on the glass substrate.

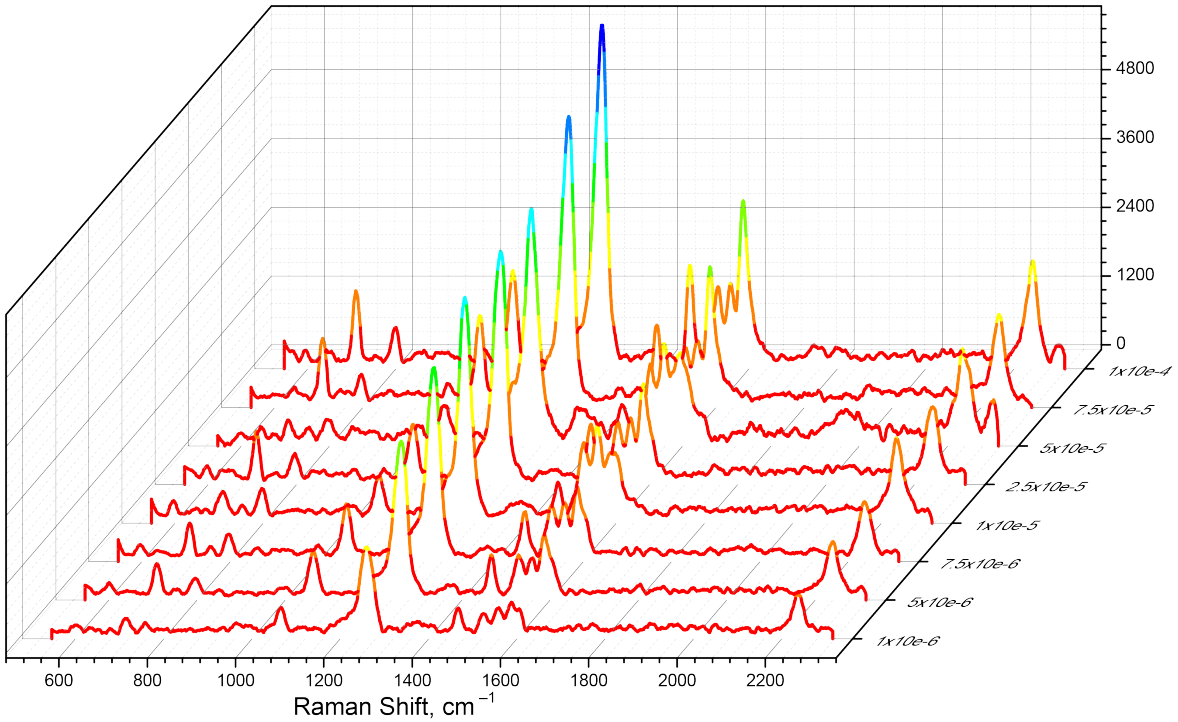

Figure S22. SERS spectra of different concentrations of *o*-chlorophenol applied on the USR sensor modified with DDQ.

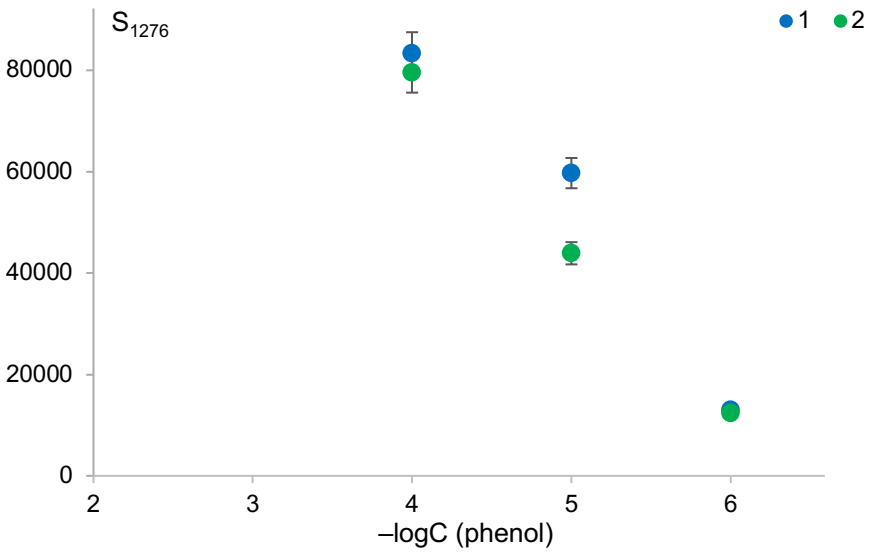

Figure S23. Dependence of the peak area of the CTC phenol:DDQ (5 mM) with a Raman shift of 1276 cm^{-1} on the concentration of phenol: (1) model solution; (2) extracted from an aqueous solution (P = 0.95; n = 10).

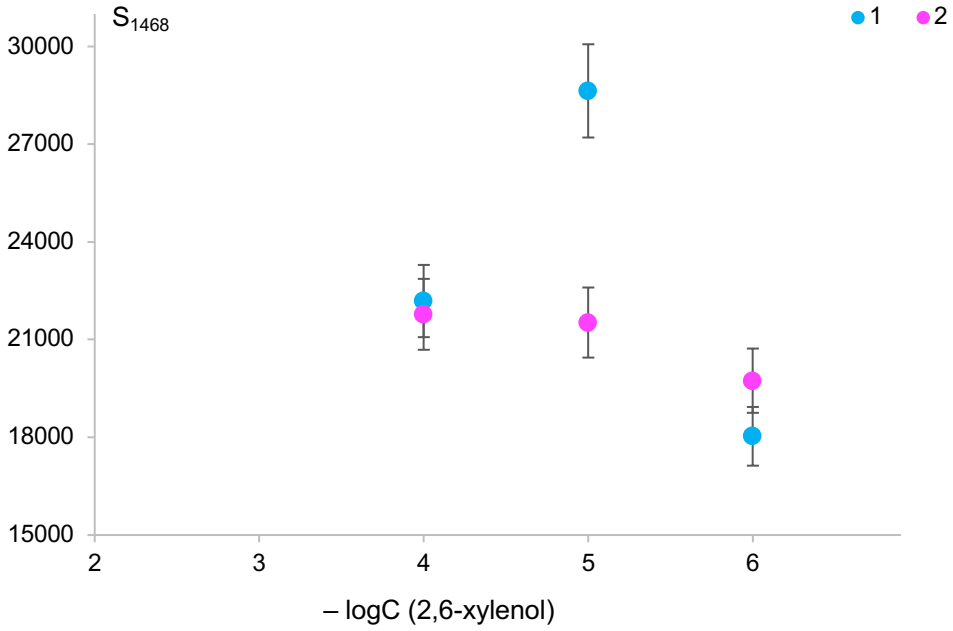

Figure S24. Dependence of the peak area of the CTC 2,6-xylenol:DDQ (5 mM) with a Raman shift of 1276 cm^{-1} on the concentration of 2,6-xylenol: (1) model solution; (2) extracted from an aqueous solution (P = 0.95; n = 10).

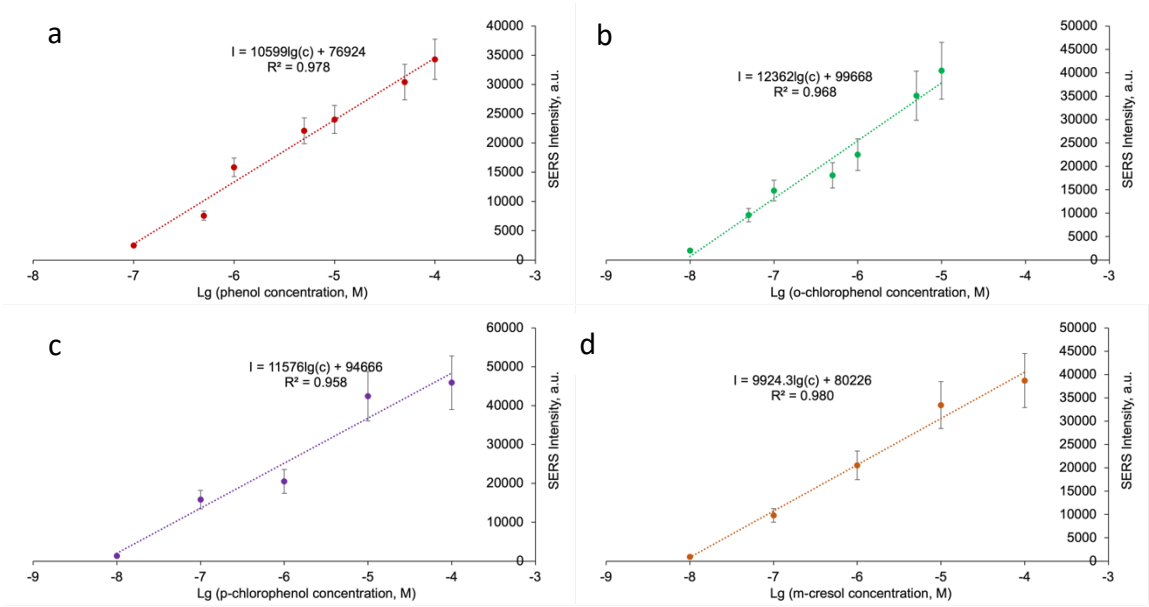

Figure S25. Calibration curves for determination of: (a) phenol with TCNQ-modified SERS sensor by peak intensity at 1605 cm^{-1}, (b) *o*-chlorophenol with DDQ-modified SERS sensor by peak intensity at 1465 cm^{-1} in the presence of 10 µM *p*-chlorophenol, (c) *p*-chlorophenol with TNF-modified SERS sensor by peak intensity at 1523 cm^{-1} in the presence of 10 µM *o*-chlorophenol, and (d) *m*-cresol with DDQ-modified SERS sensor by peak intensity at 1598 cm^{-1} in the presence of 10 µM *o*-cresol (n = 5; P = 0.95) (Raman instrument settings: 632.8 nm laser wavelength, 10% neutral density filter, 10 s acquisition time).

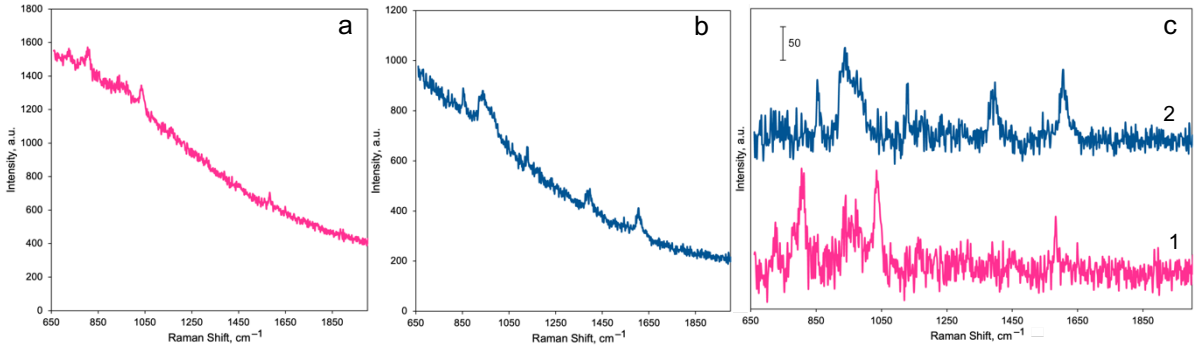

Figure S26. SERS spectra acquired from real objects: 10 µL of 10-fold diluted with chloroform gasoline fuel on the TNF-modified SERS sensor (a and c, spectrum 1) and 10 µL of 10-fold diluted with phosphate buffer to pH 7 lake freshwater on the TNF-modified SERS sensor (b and c, spectrum 2). SERS spectra before (a, b) and after (c) baseline subtraction. (n = 5; P = 0.95); (Raman instrument settings: 10%, 632.8 nm, 10 s).