SUPPLEMENTARY INFORMATION

Substituent Effects in Weak Charge-Transfer Cocrystals of Benzene Derivatives with Classical TCNQ Acceptors: Experimental and Theoretical Study

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Table S1. Crystallographic data and structure refinement details for cocrystals.

Crystal	*o*-Xylol/F_1TCNQ (**1**)	*o*-Xylol/F_2TCNQ (**2**)	*o*-Xylol/F_4TCNQ (**3**)	p-Xylol/F_1TCNQ (**4**)
Formula	$C_{28}H_{21}FN_4$	$C_{20}H_{12}F_2N_4$	$C_{28}H_{20}F_4N_4$	$C_{20}H_{11}FN_4$
CCDC number	2295405	2295404	2295403	2295406
Color	Dark red	Dark red	Dark red	Dark red
Habitus	Prism	Plate	Plate	Plate
Size (mm)	0.140 x 0.193 x 0.406	0.058 x 0.142 x 0.321	0.046 x 0.201 x 0.401	0.080 x 0.193 x 0.456
Formula weight	432.49	346.34	488.48	432.49
T (K)	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P-1*	*P2₁/n*	*P2₁/c*	*Pc*
a (Å)	7.2356(12)	8.9555(13)	12.481 (3)	8.6765(8)
b (Å)	12.6475(19)	7.1481(11)	7.2128(19)	7.1797(5)
c (Å)	12.7998(18)	27.308(4)	13.381 (4)	13.6918(11)
α (deg)	98.572(5)	90	90	90
β (deg)	90.470(5)	99.089(5)	96.757 (7)	103.851(5)
γ (deg)	92.882(5)	90	90	90
V (Å^3)	1156.6(3)	1726.1(5)	1196 (5)	828.12(12)
Z	2	4	2	2
D Calcd (g m^{-3})	1.242	1.333	1.356	1.317
μ (mm−1)	0.080	0.097	0.103	0.089
Reflection collected	8458	55367	9467	22299
Unique reflections	8458	4504	3080	3881
Reflections observed	5332	2667	1528	2195
θ min, θ max (◦)	1.609, 28.862	1.510, 28.926	3.268, 28.772	2.837, 28.739
Goodness-of-fit (GOF) on F^2	1.110	1.076	1.026	1.010
R1, *wR2* (I >2σ(I)	0.0784, 0.1758	0.0607, 0.1339	0.0649, 0.1216	0.0501, 0.0981
R1, *wR2* (all data)	0.1377, 0.2127	0.1216, 0.1656	0.1595, 0.1632	0.1136, 0.1234
Largest peak and hole (e Å^{-3})	0.350 and -0.407	0.263 and -0.237	0.255 and -0.250	0.188 and -0.172

Figure S1. Fragments of crystal packing of cocrystal *p*-xylol/F_1TCNQ (1:1) showing D-A mixed stacks and the arrangement of molecules within the stacks.

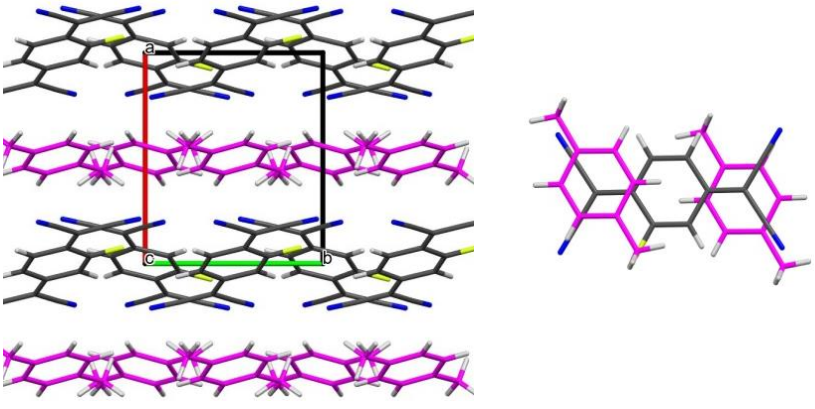


Table S2. The energies (hartree) of HOMO for some benzene derivatives by different methods.

Donor	PBE0/6-31+G(d)	wB97XD/6-31+G(d)
Benzene	-0.26623	-0.33070
Toluene	-0.25372	-0.31772
o-xylol	-0.24714	-0.31099
m-xylol	-0.24662	-0.31057
p-xylol	-0.24268	-0.30624

Table S3. The energy (E, hartree) of intermolecular pairwise interactions and counterpoise corrected complexation energies (ΔE_{cor}, kcal/mol) for the title dimeric CT complexes in different isomeric forms based on optimizations by different methods (6-31G+(d)).

Donor = *o-xylol*

Donor	Coordination type	isomer	PBE0	PBE0	wB97XD	wB97XD	MP2	MP2
Acceptor			E	ΔE_{cor}	E	ΔE_{cor}	E	ΔE_{cor}
TCNQ	Exo	1	-988.3195142	**-2.98**	-989.1428264	**-11.2**	-986.4842445	-9.27
	Endo	1	-988.3186952	**-2.56**	-989.1449728	**-12.78**	-986.4851368	-9.54
	Endo	2	-988.3186206		-989.1423364	**-11.26**		
	T	1	-988.3202069	**-3.82**	-989.1383697	**-8.85**		
F_1TCNQ	Exo	1	**-1087.464646**	**-3.47**	-1088.3499431	**-12.08**	-1082.0621208	-10.23
	Exo	2	-1087.4641579					
	Endo	1	-1087.4633474					
	Endo	2	-1087.4635418	**-2.77**	-1088.3512937	**-13.21**		
	T	1	-1087.4648105	**-4.02**	-1088.3442519	**-9.00**		
F_2TCNQ	Exo	1	**-1186.6083909**	**-3.78**	-1187.5551311	**-12.47**	-1184.5260806	-10.81
	Endo	1	-1186.6073856	**-3.23**	-1187.5545846	**-12.53**		
F_4TCNQ	Exo	1	**-1384.8788118**	**-4.61**	-1385.9483995	**-13.80**	-1382.5487413	-12.52
	Exo	2	-1384.8780529					
	Exo	3	-1384.8775469					
	Exo	4	-1384.8774907					
	Exo	5	-1384.877486					
	Exo	6	-1384.877945					
	Exo	7	**-1384.878812**					
	Endo	1	-1384.8780371	-4.21	-1385.9480589	-14.08		
	Endo	2	-1384.8779284					
	Endo	3	-1384.8779668					
	Endo	4	-1384.8779667					
	Endo	5	-1384.8777633					
	Endo	6	-1384.877602*					
	Endo	7	-1384.8777641					
	Endo	8	-1384.877676*					
	Endo	9	-1384.8779289					

Table S3. (Continued)

Donor = *m-xylol*

Donor	Coordination type	isomer	PBE0	PBE0	wB97XD	wB97XD	MP2	MP2
Acceptor			E	ΔE_{cor}	E	ΔE_{cor}	E	ΔE_{cor}
TCNQ	Exo	1	-988.319260	**-2.78**	-989.1428802	**-11.52**		
	Exo	2	-988.319407	**-2.86**	-989.1438275	**-12.09**		
	Endo	1	-988.3192323	**-2.79**	-989.1449129	**-12.87**		
	Endo	2	Not stable		-989.1434405	**-12.12**		
	T	1	-988.3204205	**-3.92**	**Not stable**	**Not stable**		
F_1TCNQ	Exo	1	**-1087.4644365**	**-3.18**	-1088.3500821	**-12.45**		
	Exo	2	-1087.4638334					
	Exo	3	-1087.4645618	**3.35**	-1088.3507532	**-12.86**	-1085.5069926	-10.24
	Endo	1	-1087.4636739		-1088.3513455			
	Endo	2	-1087.46404	**-3.03**	-1088.3514599	**-13.42**		
	T	1	-1087.4650213	**-4.10**	**Not stable**	**Not stable**		
F_2TCNQ	Exo	1	**-1186.6080551**	**-3.45**	-1187.5552281	**-12.83**		
	Exo	2	-1186.6081002	**3.55**	-1187.5557796	**-13.14**		
	Endo	1	-1186.6077415	**-3.33**	-1187.5541958	**-12.12**		
F_4TCNQ	Exo	1	-1384.8784747	-	-1385.9484841	**-14.19**		
	Exo	2	-1384.878570					
	Exo	3	-1384.8785729					
	Exo	4	**-1384.8785737**	4.36	-1385.949211	**14.51**		
	Exo	5	-1384.8779328					
	Exo	6	-1384.878556					
	Exo	7	**-1384.878585**	**4.49**	-1385.9475773	**13.63**		
	Exo	8	-1384.878401					
	Endo	1	-1384.8783268	-4.25	-1385.9489626	**-14.75**		

Table S3. (Continued)

Donor = *p-xylol*

	Coordination type	isomer	PBE0	PBE0	wB97XD	wB97XD	MP2	MP2
Acceptor			E	ΔE_{cor}	E	ΔE_{cor}	E	ΔE_{cor}
TCNQ	Exo	1	-988.3192674	**-2.80**	**-989.1441452**	**--12.43**	-986.4862448	-9.82
	Exo	2	-988.3190197					
	Endo	1	-988.3186304	**-2.60**	**-989.1429479**	**-11.76**	-986.4843512	-9.20
	T	1	-988.3202702	**-3.90**	**-989.1376659**	**-8.83**	No stable	
F_1TCNQ	Exo	1	**-1087.4645328**	**-3.37**	-1088.3513131	**-13.32**	-1085.5082144	-10.78
	Exo	2	-1087.463923					
	Endo	1	-1087.4634066	**-2.81**				
	Endo	2	-1087.4635013	**-4.09**	-1088.3497406	**-12.46**		
	T	1	-1087.4649261		**Not stable**	**Not stable**		
F_2TCNQ	Exo	1	**-1186.6080267**	**-3.55**	-1187.556302	**-13.56**	-1382.5502914	-11.19
	Endo	1	-1186.6074522	**-3.24**	-1187.5554367	**-13.30**		
F_4TCNQ	Exo	1	**-1384.8785207**	**-4.43**	-1385.9495563	**-14.84**	-1382.5502914	-12.86
	Exo	2	-1384.8782244					
	Exo	3	-1384.878186					
	Endo	1	-1384.8779319	-4.11				
	Endo	2	-1384.878194	**-4.24**	-1385.9491074	**-14.72**		

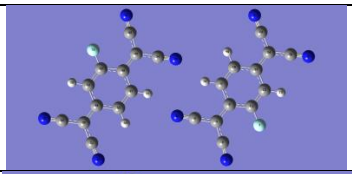
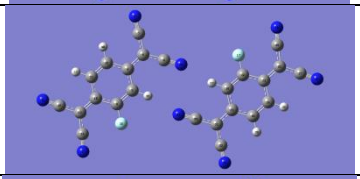
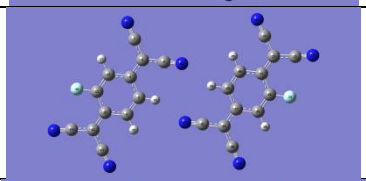
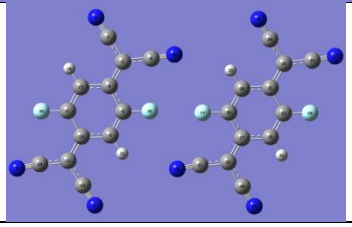
Table S4. The energy (E, hartree) of intermolecular pairwise interactions and counterpoise corrected complexation energies (ΔE_{cor}, kcal/mol) for xylene dimeric complexes in different isomeric forms based on optimizations by different methods (6-31G+(d)).

		PBE0	PBE0	wB97XD	wB97XD	MP2	MP2
Aryl	Dimer	E	ΔE_{cor}	E	ΔE_{cor}	E	ΔE_{cor}
o-xylol	CH/π Di-stack	**-621.025638**	**-1.52**	-621.587353	**-8.23**	**-619.6498541**	**-4.83**
	π-π stack	Not stable	Not stable	Not stable	Not stable		
	CH/π Mono-stack	-621.024118	-0.79	-621.5836192	-6.06		
m-xylol	CH/π Di-stack	-621.0250963	-1.19	-621.584020	-6.89	-619.6475941	-3.91
	π-π -stack	Not stable	Not stable	-621.5856053	-7.84		
	CH/π Mono-stack	Not stable	Not stable	Not stable	Not stable		
p-xylol	CH/π Di-stack	-621.024840	-1.20	-621.5827467	-6.34	-619.6466235	-3.72
	π-π -stack	Not stable	Not stable	-621.5827244	-6.29		
	CH/π Mono-stack	Not stable	Not stable	Not stable	Not stable		

Table S5. The energy (E, hartree) of intermolecular pairwise interactions and counterpoise corrected complexation energies (ΔE_{cor}, kcal/mol) for toluene dimeric complexes in different isomeric forms based on optimizations by different methods (6-31G+(d)).

	PBE0	PBE0	wB97XD	wB97XD	MP2	MP2
	E	ΔE_{cor}	E	ΔE_{cor}	E	ΔE_{cor}
CH/π Di-stack	-542.486176	**-1.28**	-542.9687369	**-6.21**	**-541.301746**	**-3.53**
π-π -stack side	Not stable	Not stable	-542.965648	**-4.93**	**-541.3017153**	**-2.90**
π-π stack	Not stable	Not stable	-542.9639882	**-3.26**	**-541.2983596**	**-1.68**
CH/π mono-stack	Not stable	Not stable	-542.9665078	**-4.91**	**-541.3004881**	**-2.82**
T-shaped	-542.4853318	**-0.89**	-542.9646261	**-3.74**	**-541.2978621**	**-2.18**

Table S6. The counterpoise corrected complexation energies (ΔE_{cor}, kcal/mol) of intermolecular Side-On interactions for the dimeric F_n-TCNQ (n = 0÷4) complexes based on optimizations by different methods (6-31G+(d)).

	PBE0	wB97XD	MP2	Isomeric pair
TCNQ/TCNQ	-5.38	-7.01		
F_1TCNQ/F_1TCNQ (1)	-5.45	-7.03		
F_1TCNQ/F_1TCNQ (2)	-4.81	-6.30		
F_1TCNQ/F_1TCNQ (3)	-5.62	-7.33	6.50	
F_2TCNQ/F_2TCNQ (1)	-4.78	-6.29		
F_2TCNQ/F_2TCNQ (2)	-2.99	**Not stable**		
F_4TCNQ/F_4TCNQ	Not stable	**Not stable**		