Electronic Supplementary Information

Electronic, vibrational, and charge-transport properties of benzothienobenzothiophene-TCNQ co-crystals

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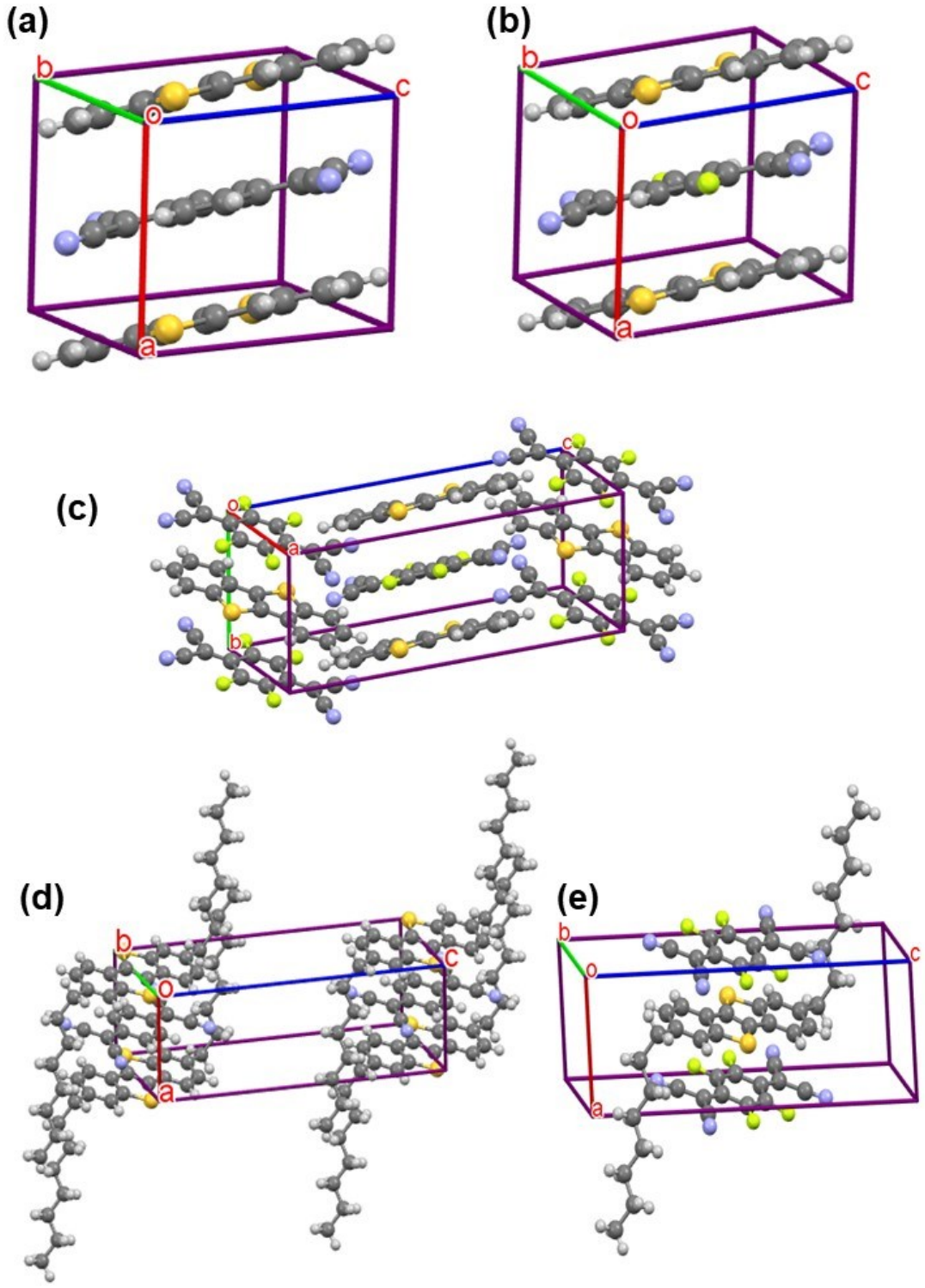
1. Experimental crystal structures



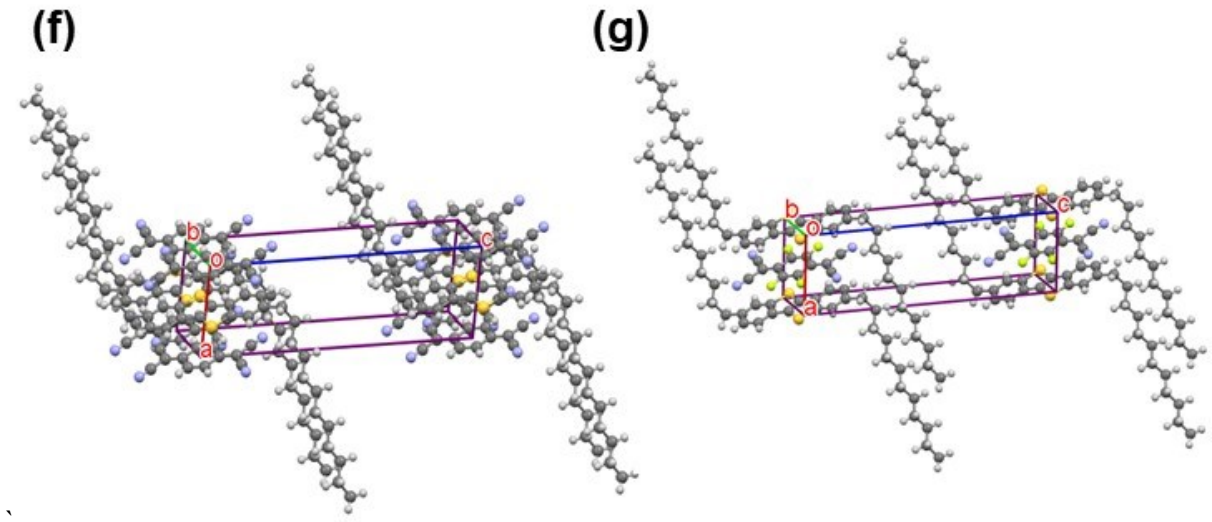


Figure S1. Experimental crystal structures of: (a) BTBT-TCNQ, (b) BTBT-F_2TCNQ, (c) BTBT-F_4TCNQ, (d) diC_8BTBT-TCNQ, (e) diC_8BTBT-F_4TCNQ, (f) diC_{12}BTBT-TCNQ, and (g) diC_{12}BTBT-F_4TCNQ. The stacking directions are represented in red for the (a, b, d, e, f, and g) cases and in green for the (c) case.[1, 2]

Table S1. Unit-cell parameters of co-crystals.[1, 2]

	BTBT-TCNQ	**BTBT-F_2TCNQ**	**BTBT-F_4TCNQ**	**diC_8BTBT-TCNQ**	**diC_8BTBT-F_4TCNQ**	**diC_{12}BTBT-TCNQ**	**diC_{12}BTBT-F_4TCNQ**
a (Å)	7.1933	7.1608	7.9628	7.1829	7.1030	7.2075	7.096
b (Å)	8.0044	7.9489	7.062	7.7361	8.077	7.7416	8.053
c (Å)	9.0183	9.1084	19.111	17.946	17.592	21.258	21.148
α (deg)	81.181	80.928	90.00	86.554	85.90	82.579	83.20
β (deg)	89.310	89.567	99.328	80.529	82.020	88.358	86.85
γ (deg)	87.721	87.878	90.00	73.518	72.443	73.252	72.50

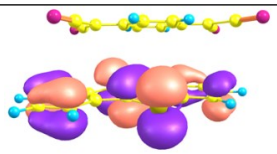
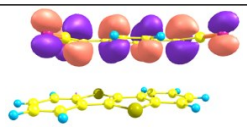
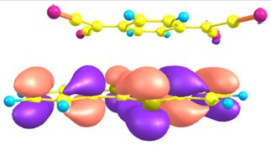
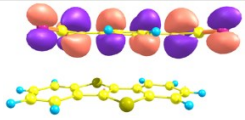
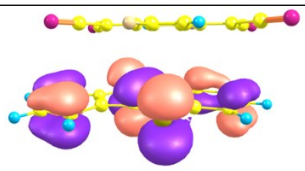
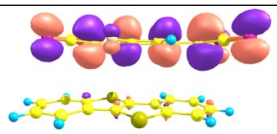
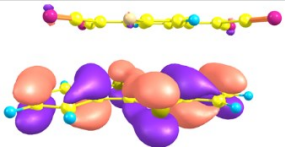
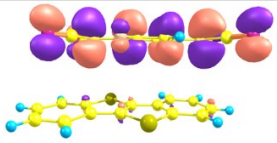
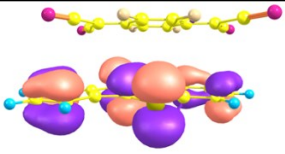
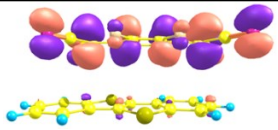
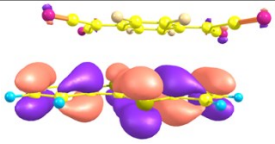
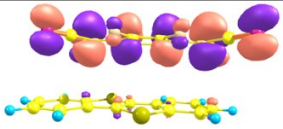
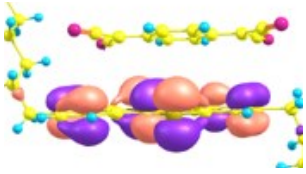
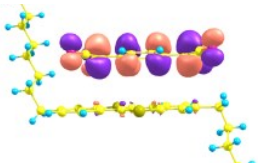
2. Effective masses

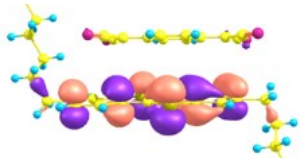
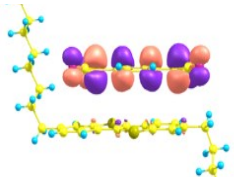
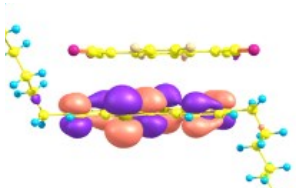
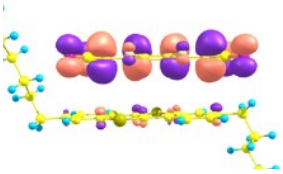
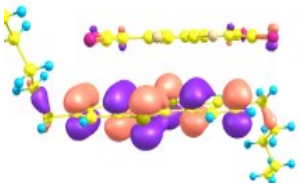
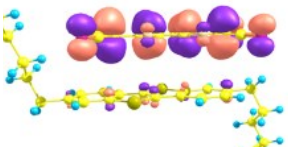
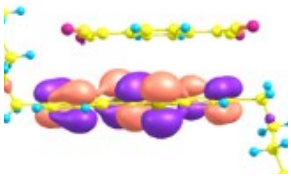
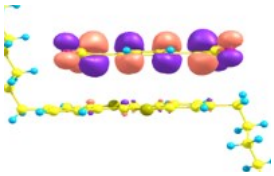
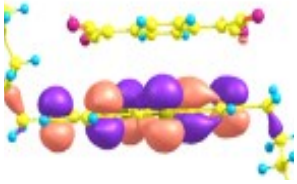
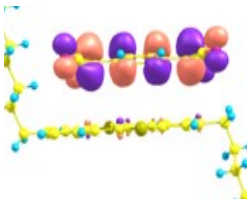
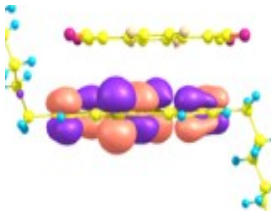
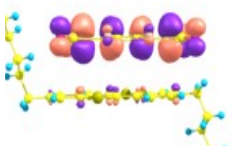
Table S2. Hole and electron effective masses, m (in units of the free electron mass at rest, m_0).

Crystal		m / m_0	Parallel to
BTBT-TCNQ	Holes at Γ (0, 0, 0)	1.3	b-0.09a-0.71c
		4.7	c+0.45a+0.87b
		10.7	a-0.11b-0.19c
	Electrons at T (0, 0.5, 0.5)	1.07	a-0.03b+0.01c
		3.2	c-0.03a-0.79b
		13.4	b-0.02a+0.55c
BTBT-F_2TCNQ	Holes at Γ (0, 0, 0)	1.03	b-0.13a-0.77c
		3.41	b+0.45a+0.96c
		4.91	a-0.09b-0.19c
	Electrons at T (0, 0.5, 0.5)	0.8	a-0.07b+0.05c
		1.5	b+0.1a-0.7c
		4.3	c-0.04a+0.8c
BTBT-F4TCNQ	Holes at Γ (0, 0, 0)	2.1	a+0.17c
		2.3	b
		5.2	c-0.65a
	Electrons at Γ (0, 0, 0)	0.83	b
		3.62	a+0.31c
		5.73	a-0.61c
di-C_8BTBT-TCNQ	Holes at Γ (0, 0, 0)	3.06	a+0.011b-0.002c
		33.76	b-0.27a-0.09c
		358.06	c-0.56a+0.51b
	Electrons at Γ (0, 0, 0)	1.0	a-0.007b
		26.9	b-0.29a
		240.0	c-0.4a-0.03b
di-C_8BTBT-F_4TCNQ	Holes at Y (0, 0.5, 0)	1.5	a-0.04b+0.00098c
		61.66	c-0.6b+0.7c
		308.26	b-0.23b-0.16c
	Electrons at T (0, 0.5, 0.5)	0.73	a+0.02b+0.003c
		15.80	b-0.4a+0.09c
		327.9	c-0.14a-0.56c
di-C_{12}BTBT-TCNQ	Holes at Γ (0, 0, 0)	3.9	a-0.07b-0.04c
		13.7	b+0.03a+0.82c
		18.9	b-0.26a-0.18c
	Electrons at Γ (0, 0, 0)	1.25	a-0.09b-0.03c
		7.54	b-0.001a+0.71c
		14.91	b-0.24a-0.20c

di-C_{12}BTBT-F_4TCNQ	Holes at Y (0, 0.5, 0)	3.56	a-0.17b-0.03c
		21.06	b+0.017a+0.63c
		30.92	b-0.15a-0.24c
	Electrons at (0, 0.5, 0.010)	1.11	a-0.009b-0.043c
		6.0	b-0.03a+0.7c
		11.54	b-0.27a-0.22c

3. Orbital representations of singlet excited states

Co-crystal	Excited State	Hole	Electron
BTBT-TCNQ	S1		
	S2		
BTBT-F_2TCNQ	S1		
	S2		
BTBT-F_4TCNQ	S1		
	S2		
di-C_8BTBT-TCNQ	S1		

	S2		
di-C_8BTBT-F_4TCNQ	S1		
	S2		
di-C_{12}BTBT-TCNQ	S1		
	S2		
di-C_{12}BTBT-F_4TCNQ	S1		

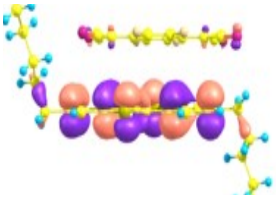
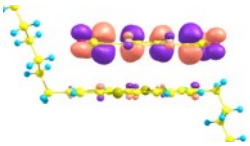
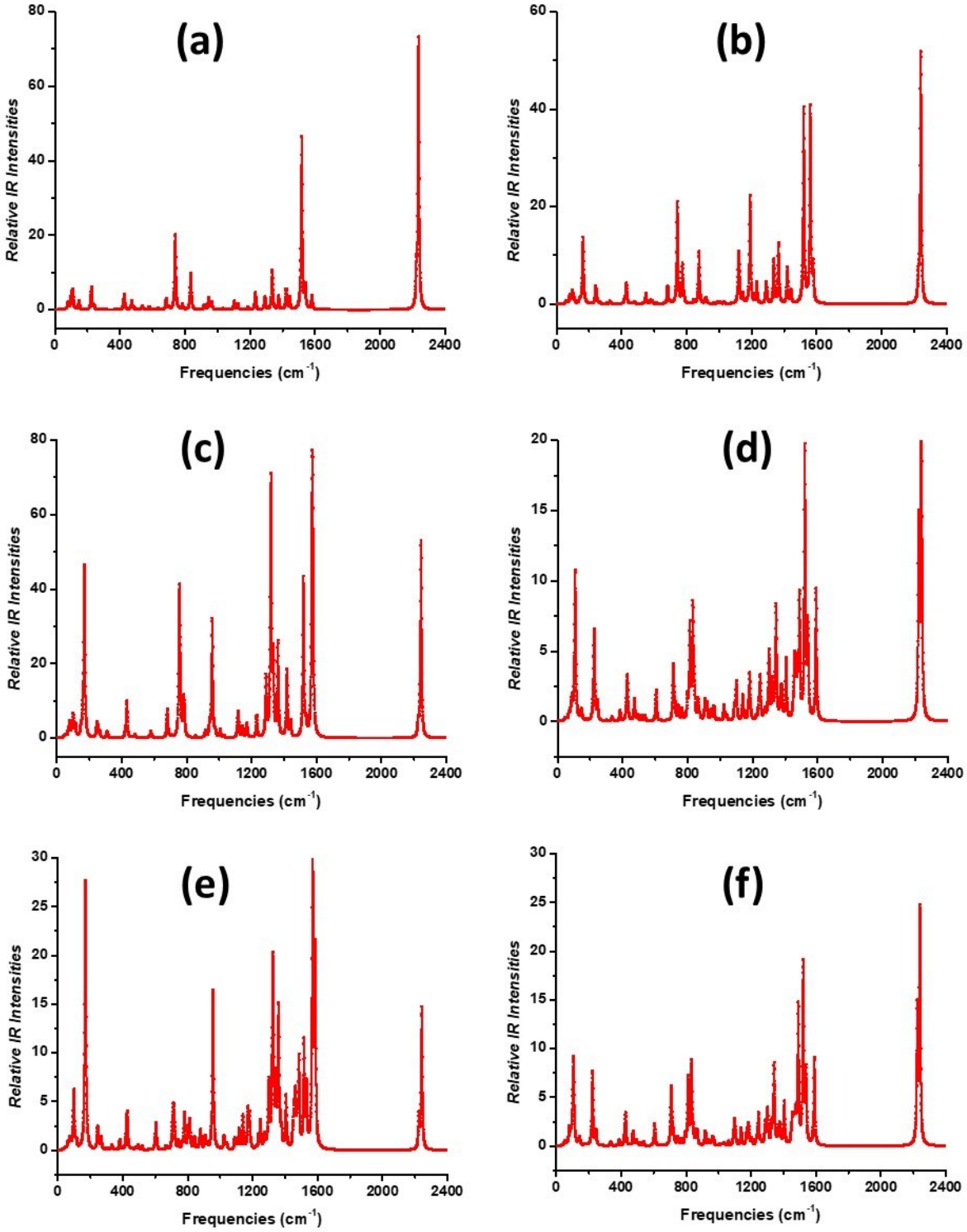
	S2		

Figure S2. Natural Transition Orbitals[3] for the lowest excited states calculated at the TDDFT B3LYP/6-31G (d, p) level.

Table S3. B3LYP/6-31G (d,p) estimates of the DA electronic-coupling contributions to hole superexchange coupling in the BTBT-TCNQ co-crystal.

Orbitals	**Electronic Coupling (in meV)**
$HOMO_D$-$HOMO\text{-}3_A$	20.3
$HOMO_D$-$HOMO\text{-}2_A$	-108.3
$HOMO_D$-$HOMO\text{-}1_A$	54.3
$HOMO_D$-$HOMO_A$	-52.1
$HOMO_D$-$LUMO_A$	160.3
$HOMO_D$-$LUMO+1_A$	-45.9
$HOMO_D$-$LUMO+2_A$	120.1
$HOMO_D$-$LUMO+3_A$	-45.9

4. Calculated IR spectra of the co-crystals



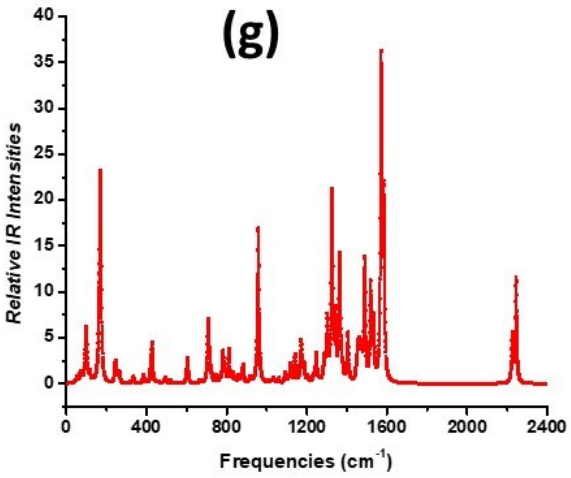
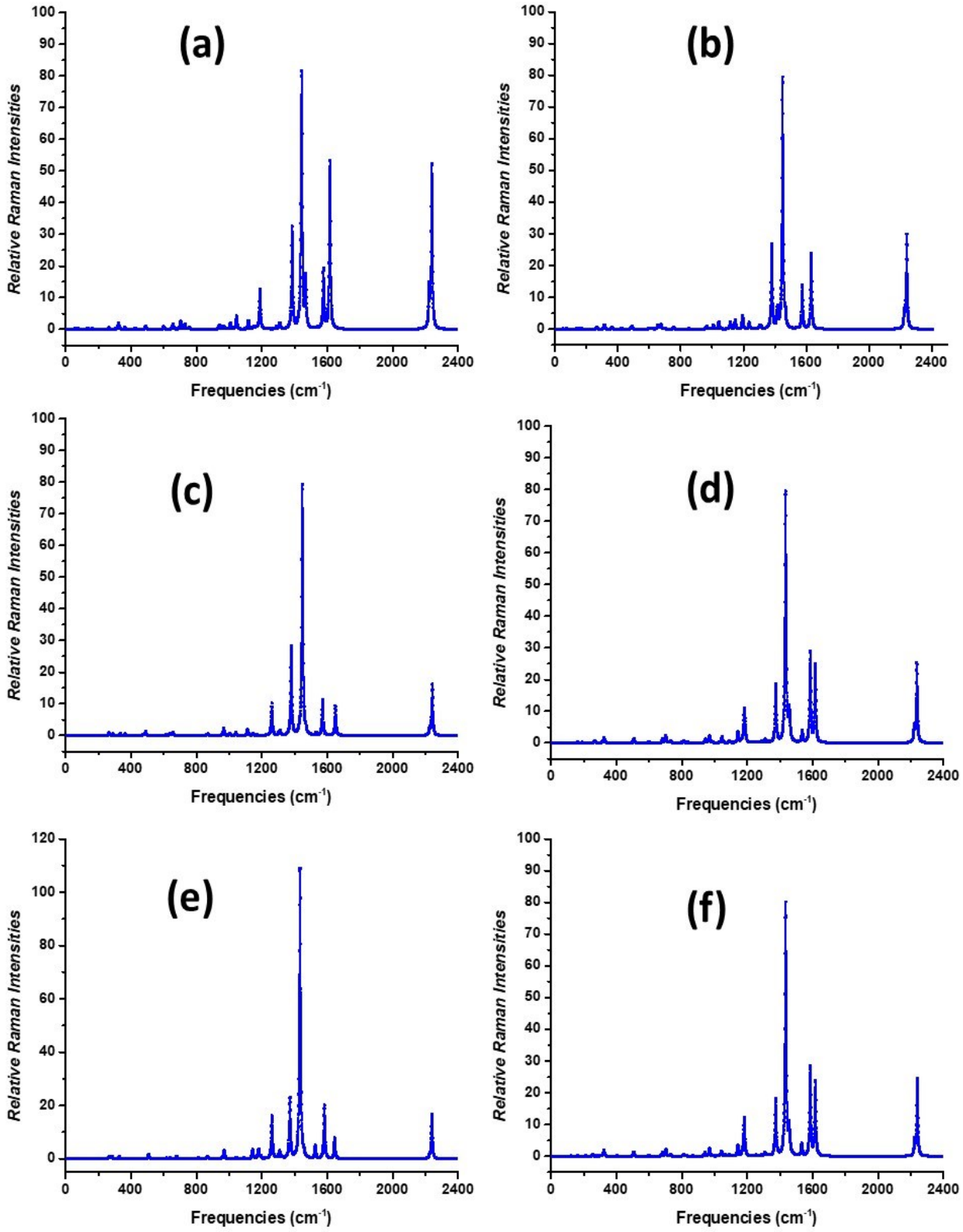


Figure S3. B3LYP/6-31G(d,p)-calculated IR spectra of the co-crystals: (a) BTBT-TCNQ; (b) BTBT-F2TCNQ; (c) BTBT-F4TCNQ; (d) diC8BTBT-TCNQ; (e) diC8BTBT-F4TCNQ; (f) diC12BTBT-TCNQ; (g) diC12BTBT-F4TCNQ.

5. Calculated Raman spectra of the co-crystals



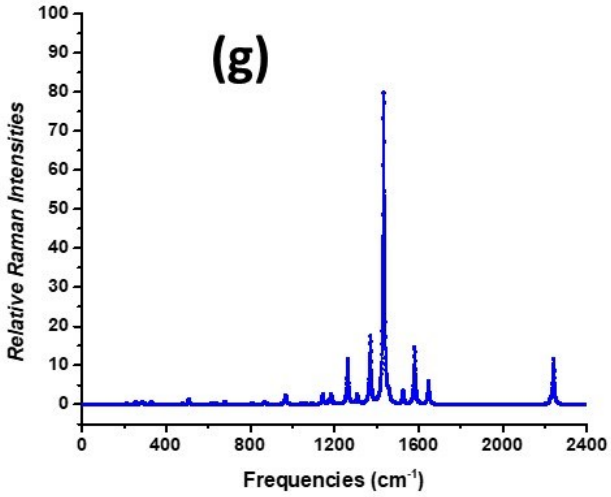


Figure S4. B3LYP/6-31G(d,p)-calculated Raman spectra of the co-crystals: (a) BTBT-TCNQ; (b) BTBT-F2TCNQ; (c) BTBT-F4TCNQ; (d) diC8BTBT-TCNQ; (e) diC8BTBT-F4TCNQ; (f) diC12BTBT-TCNQ; (g) diC12BTBT-F4TCNQ.

Table S4. B3LYP/6-31G (d,p) estimates of the Dushinsky matrix for the mixing between the vibrational modes of the neutral and radical-anion states of F_2TCNQ molecule.[4] All frequencies were scaled by a factor of 0.9614.

Frequency/ cm^{-1} (neutral state)	% of mixing	Frequency / cm^{-1} (radical-anion state)
1524	15.3	1001
	10.3	1267
	18.8	1443
	20.5	1501
1567	10.2	1267
	34.6	1443
	23.5	1501
2233	12.2	252
	28.3	1167
	21.8	2175
2250	79.9	2207

References

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