

Supporting Information

Electronic, vibrational, and optical properties of fullerene-S₈ co-crystals

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Table S1. Largest electronic couplings (in meV) between the LUMOs of the fullerene and S_8 components in the $C_{60} - 2S_8$ co-crystal, as calculated at the PBE/6-31G (d,p) and B3LYP/6-31G (d,p) levels of theory.

Method	Orbitals	t_e
PBE	LUMO, LUMO	4
	LUMO, LUMO+1	16
	LUMO, LUMO+2	101
B3LYP	LUMO, LUMO	5
	LUMO, LUMO+1	22
	LUMO, LUMO+2	114

Table S2. Largest electronic couplings (in meV) between the LUMOs of the fullerene and S_8 components in the $C_{70} - 2S_8$ co-crystal, as calculated at the PBE/6-31G (d,p) and B3LYP/6-31G (d,p) levels of theory.

Method	Orbitals	t_e
PBE	LUMO-LUMO	65
B3LYP	LUMO-LUMO	76

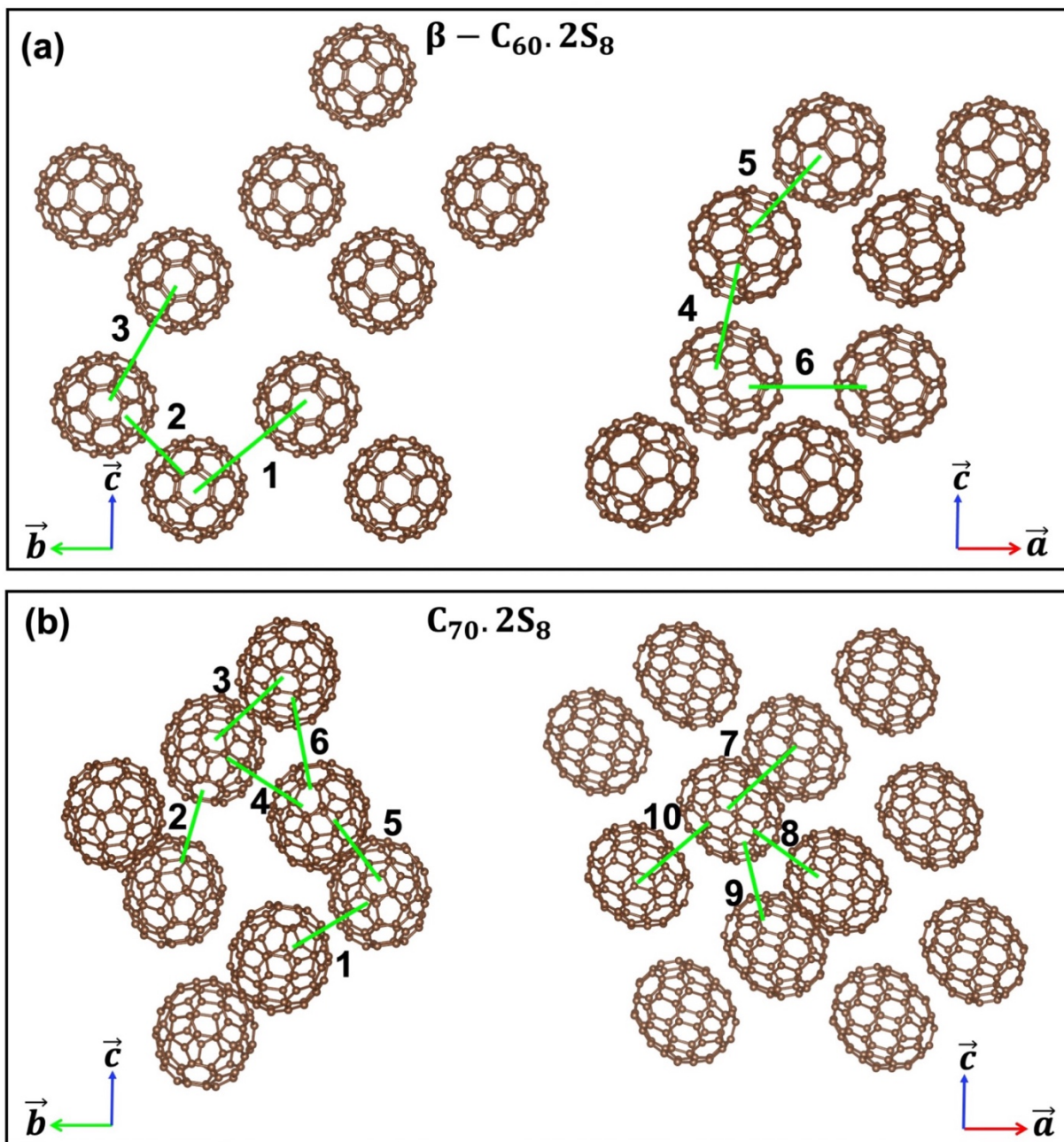


Figure S1. Fullerene pairs used for the calculations of the transfer integrals.

Table S3. Transfer integrals for holes (t_h) and electrons (t_e) between the fullerene pairs shown in Figure S1, as computed at the PBE/6-31G (d,p) and B3LYP/6-31G (d,p) (in parentheses) levels of theory. All energies are in meV.

Pair	$C_{60}2S_8$		$C_{70}2S_8$	
	t_h	t_e	t_h	t_e
1	37 (41)	32 (45)	40 (35)	27 (29)
2	48 (55)	41 (47)	6 (6)	2 (2)
3	33 (38)	48(55)	12 (9)	19 (25)
4	48 (55)	40 (47)	40 (35)	27 (29)
5	50 (57)	17 (19)	12 (9)	19 (25)
6	33 (37)	13 (15)	6 (6)	2 (2)
7			40 (35)	27 (29)
8			17 (20)	13 (15)
9			6 (6)	2 (2)
10			12 (9)	19 (25)

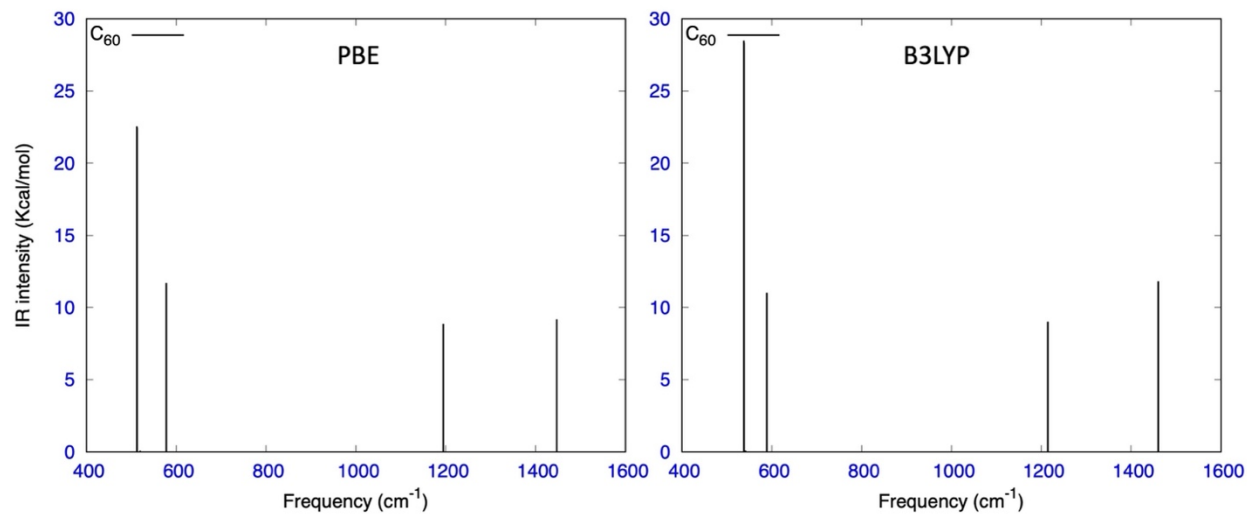


Figure S2. Comparison of the IR spectra of C_{60} obtained at the PBE/6-31G (d,p) and B3LYP/6-31G (d,p) levels of calculation.

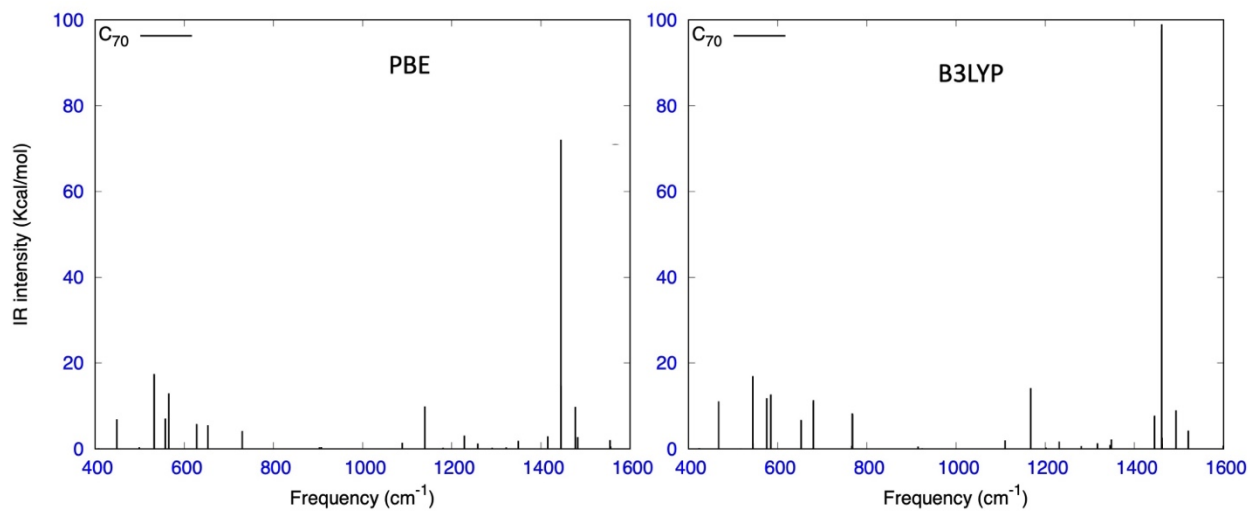


Figure S3. Comparison of the IR spectra of C_{70} obtained at the PBE/6-31G (d,p) and B3LYP/6-31G (d,p) levels of calculation.

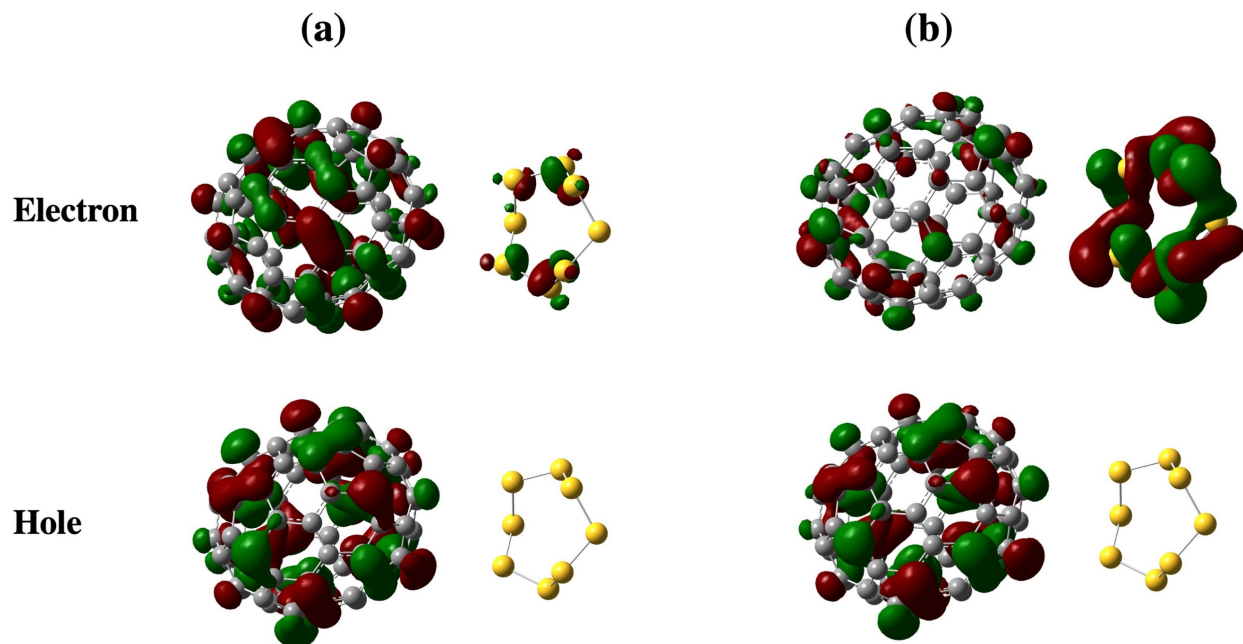


Figure S4. Comparison of the natural transition orbitals (NTOs) in the $C_{70} - S_8$ complex for the mixed charge transfer-local exciton states with energies of: (a) 2.70 eV (S_{23} state; λ for the NTO shown is 0.64; the other major contributing NTOs correspond to transitions among fullerene frontier molecular orbitals); (b) 2.77 eV (S_{27} state; λ for the NTO shown is 0.55; the other major contributing NTOs correspond to transitions among fullerene frontier molecular orbitals).

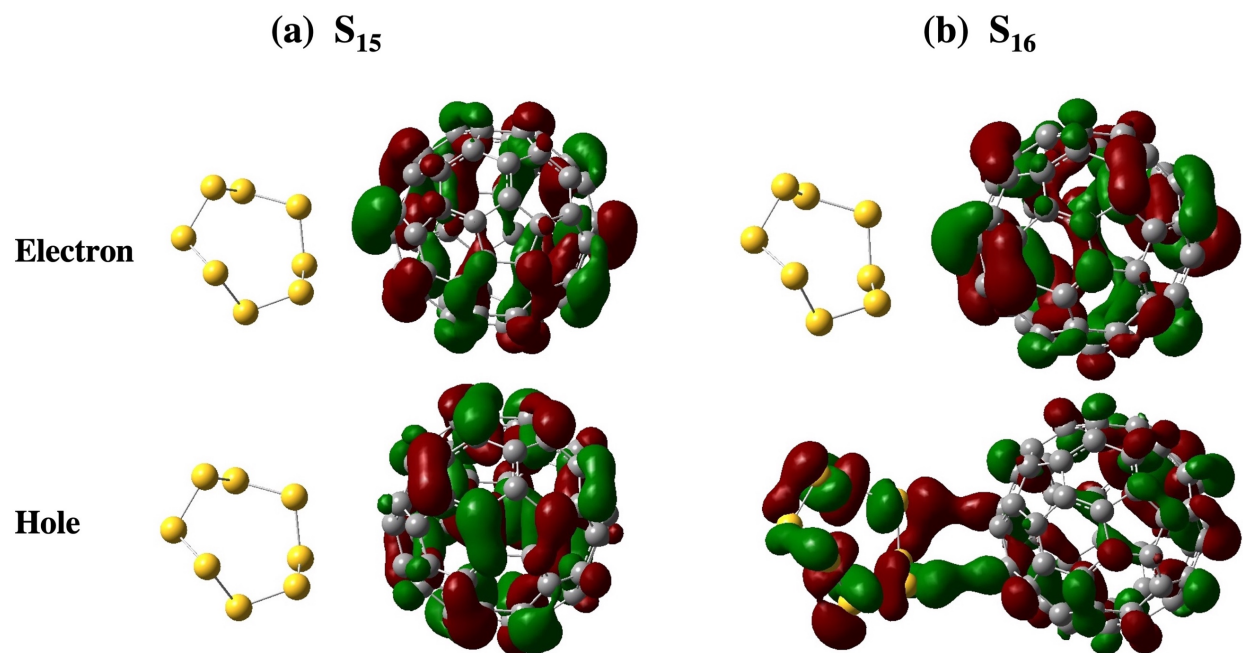


Figure S5. Comparison of the LC- ω HPBE/6-31G (d,p) natural transition orbitals (NTOs) in the $C_{60} - S_8$ complex between (a) the C_{60} singlet local excited state S_{15} (λ value for the NTO shown is 0.66; the other relevant NTOs involve additional fullerene frontier molecular orbitals) and (b) the lowest singlet charge-transfer state ($\lambda(\text{NTO}) = 0.81$), i.e., the S_{16} state.

Table S4. Singlet TD-DFT excitation energies [eV] in S₈-C₆₀ and S₈-C₇₀ model complexes, as calculated at the B3LYP/6-31G (d,p) level of theory. The lowest CT states in each system are indicated in bold.

Transition	S ₈ -C ₆₀ complex (eV)	S ₈ -C ₇₀ complex (eV)
S ₀ → S ₁	2.10	2.10
S ₀ → S ₂	2.10	2.11
S ₀ → S ₃	2.10	2.15
S ₀ → S ₄	2.10	2.16
S ₀ → S ₅	2.11	2.17
S ₀ → S ₆	2.11	2.17
S ₀ → S ₇	2.11	2.19
S ₀ → S ₈	2.11	2.34
S ₀ → S ₉	2.11	2.34
S ₀ → S ₁₀	2.11	2.40
S ₀ → S ₁₁	2.28	2.40
S ₀ → S ₁₂	2.28	2.49
S ₀ → S ₁₃	2.28	2.55
S ₀ → S ₁₄	2.28	2.56
S ₀ → S ₁₅	2.28	2.58
S₀ → S₁₆	2.84	2.58
S ₀ → S ₁₇	2.85	2.59
S ₀ → S ₁₈	2.85	2.59
S ₀ → S ₁₉	2.86	2.67
S ₀ → S ₂₀	2.86	2.67
S ₀ → S ₂₁	2.87	2.69
S ₀ → S ₂₂	2.87	2.69
S₀ → S₂₃	2.87	2.70
S ₀ → S ₂₄	2.88	2.70
S ₀ → S ₂₅	2.88	2.72
S ₀ → S ₂₆	3.16	2.77
S₀ → S₂₇	3.16	2.77

Table S5. Singlet TD-DFT excitation energies [eV] in S₈, C₆₀, and an S₈-C₆₀ model complex, as calculated at the LC- ω HPBE/6-31G (d,p) level of theory. The lowest CT state in the latter system is indicated in bold.

Transition	S ₈ (eV)	C ₆₀ (eV)	S ₈ -C ₆₀ complex (eV)
S ₀ → S ₁	4.03	2.18	2.17
S ₀ → S ₂	4.03	2.18	2.17
S ₀ → S ₃	4.10	2.18	2.17
S ₀ → S ₄	4.14	2.18	2.17
S ₀ → S ₅	4.15	2.18	2.17
S ₀ → S ₆	4.22	2.18	2.18
S ₀ → S ₇	4.33	2.18	2.18
S ₀ → S ₈	4.50	2.18	2.18
S ₀ → S ₉	4.50	2.18	2.18
S ₀ → S ₁₀	4.52	2.18	2.18
S ₀ → S ₁₁	4.53	2.38	2.36
S ₀ → S ₁₂	4.59	2.38	2.37
S ₀ → S ₁₃	4.59	2.38	2.37
S ₀ → S ₁₄	4.62	2.38	2.37
S ₀ → S ₁₅	4.68	2.38	2.37
S₀ → S₁₆	4.68	3.32	3.25
S ₀ → S ₁₇	4.83	3.32	3.27
S ₀ → S ₁₈	4.98	3.32	3.28
S ₀ → S ₁₉	4.98	3.32	3.28
S ₀ → S ₂₀	5.02	3.32	3.29
S ₀ → S ₂₁	5.02	3.32	3.30
S ₀ → S ₂₂	5.31	3.32	3.30
S ₀ → S ₂₃	5.41	3.32	3.31
S ₀ → S ₂₄	5.41	3.41	3.33
S ₀ → S ₂₅	5.42	3.41	3.34
S ₀ → S ₂₆	5.42	3.41	3.34
S ₀ → S ₂₇	5.46	3.41	3.36

Reference

1. Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J.; Golden, W. G.; Seki, H.; Brown, C. A.; de Vries, M. S., Vibrational Raman and infrared spectra of chromatographically separated C₆₀ and C₇₀ fullerene clusters. *Chemical Physics Letters* **1991**, *179* (1-2), 181-186.