Electronic Supplementary Information: Theoretical investigation of polymorph- and coformer-dependent photoluminescence in molecular crystals

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TABLE I: Absorption of the 8 ROY polymorphs: calculated triplet-excitation energies for the crystal ($\Delta E_{0\mathrm{T}}^{\mathrm{cryst}}$) and the excised 9-ACA molecule ($\Delta E_{0\mathrm{T}}^{\mathrm{mol}}$), along with the molecular singlet-triplet splittings ($\Delta E_{\mathrm{ST}}^{\mathrm{mol}}$). All values are in eV.

Species	$\Delta E_{0\mathrm{T}}^{\mathrm{cryst}}$	$\Delta E_{0\mathrm{T}}^{\mathrm{mol}}$	$\Delta E_{\mathrm{ST}}^{\mathrm{mol}}$
R	1.52	2.66	0.74
R05	1.40	2.61	0.77
ORP	1.44	2.62	0.76
OP	1.55	2.76	0.81
ON	1.50	2.52	0.78
YN	1.92	2.90	0.99
Y	1.92	2.97	0.96
YT04	1.84	2.93	0.96

TABLE II: Emission of 9-ACA (**A**) and its cocrystals (**A**·**B**–**A**·**E**): calculated triplet-excitation energies for the crystal ($\Delta E_{0\mathrm{T}}^{\mathrm{cryst}}$) and the excised 9-ACA molecule ($\Delta E_{0\mathrm{T}}^{\mathrm{mol}}$), along with the molecular singlet-triplet splittings ($\Delta E_{\mathrm{ST}}^{\mathrm{mol}}$). All values are in eV.

Species	$\Delta E_{0\mathrm{T}}^{\mathrm{cryst}}$	$\Delta E_{0\mathrm{T}}^{\mathrm{mol}}$	$\Delta E_{\mathrm{ST}}^{\mathrm{mol}}$
A	1.47	1.62	1.59
A·**B**	1.38	1.57	1.58
A·**C**	1.39	2.07	1.43
A·**D**	1.48	1.59	1.60
A·**E**	1.01	2.07	1.44

TABLE III: Band structures of the 8 ROY polymorphs: calculated valence band edges (maximum, $E_{\mathrm{val}}^{\mathrm{max}}$) and conduction band edges (minimum, $E_{\mathrm{cond}}^{\mathrm{min}}$), along with the corresponding valence-conduction band gaps (ΔE_{BG}). All values are in eV.

Species	$E_{\mathrm{val}}^{\mathrm{max}}$	$E_{\mathrm{cond}}^{\mathrm{min}}$	ΔE_{BG}
R	2.12	3.24	1.12
R05	0.95	2.21	1.25
ORP	1.92	3.28	1.37
OP	1.96	3.34	1.38
ON	2.02	3.32	1.30
YN	1.68	3.30	1.62
Y	1.73	3.57	1.84
YT04	1.86	3.53	1.67

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TABLE IV: Band structures of 9-ACA (**A**) and its cocrystals (**A**·**B**–**A**·**E**): calculated valence band edges (maximum, $E_{\rm val}^{\rm max}$) and conduction band edges (minimum, $E_{\rm cond}^{\rm min}$), along with the corresponding valence-conduction band gaps ($\Delta E_{\rm BG}$). All values are in eV.

Species	$E_{\rm val}^{\rm max}$	$E_{\rm cond}^{\rm min}$	$\Delta E_{\rm BG}$
A	1.78	3.52	1.74
A·**B**	2.03	3.68	1.65
A·**C**	1.83	3.41	1.58
A·**D**	1.98	3.79	1.81
A·**E**	1.62	2.42	0.80

TABLE V: The ROY molecule: calculated values of molecular triplet-excitation energies ($\Delta E_{\rm 0T}^{\rm mol}$) and molecular S_1-T_1 splittings (H_{12}), across the 0-180° range of $\theta_{\rm thio}$.

$\theta_{\rm thio}$ (°)	$\Delta E_{\rm 0T}^{\rm mol}$ (eV)	H_{12} (eV)
0	3.69	0.68
10	3.73	0.65
20	3.78	0.68
30	3.85	0.73
40	3.95	0.79
50	4.06	0.85
60	4.17	0.92
70	4.26	0.98
80	4.31	1.01
90	4.33	1.02
100	4.30	1.01
110	4.24	0.97
120	4.16	0.93
130	4.08	0.89
140	4.00	0.84
150	3.93	0.79
160	3.87	0.73
170	3.83	0.68
180	3.80	0.62

TABLE VI: ROY polymorphs: internal rotation angles (in degrees) calculated using fixed-cell ($\theta_{\rm thio}^{\rm fc}$) and variable-cell optimization ($\theta_{\rm thio}^{\rm vc}$) of the ground-state crystal geometries, compared to experiment ($\theta_{\rm thio}^{\rm exp}$). The mean absolute percent errors (MAPE's) are also given.

Species	$\theta_{\rm thio}^{\rm exp}$	$\theta_{\rm thio}^{\rm fc}$	$\theta_{\rm thio}^{\rm vc}$
R	21.7	22.1	19.8
R05	34.0/44.9	42.5	23.3
ORP	39.4	36.4	29.0
OP	46.1	43.1	37.7
ON	52.6	50.5	42.2
YN	104.1	106.2	113.0
Y	104.7	106.4	112.0
YT04	112.8	114.4	119.9
MAPE	-	3.8%	15.8%

TABLE VII: 9-ACA (**A**) and its cocrystals (**A**·**B**–**A**·**E**): the amounts of absolute charge per 9-ACA molecule (e^-) in S_0 and T_1.

Species	S_0	T_1
A	0.001	0.001
A·**B**	0.05	0.06
A·**C**	0.13	0.12
A·**D**	0.11	0.11
A·**E**	0.08	0.28

FIG. 1: The ROY molecule: calculated molecular singlet-excitation energies ($\Delta E_{0S}^{\mathrm{mol,rel.}}$), molecular S_1-T_1 splitting ($H_{12}^{\mathrm{rel.}}$), and S_0 and T_1 energies ($E_{S_0/T_1}^{\mathrm{rel.}}$), across the 0-180° range of θ_{thio}, all relative to their respective values at $\theta_{\mathrm{thio}} = 0°$.