

Electronic Supporting Information

Exciton coupling in molecular salts of 2-(1,8-naphthalimido)ethanoic acid and cyclic amines: modulation of the solid-state luminescence.

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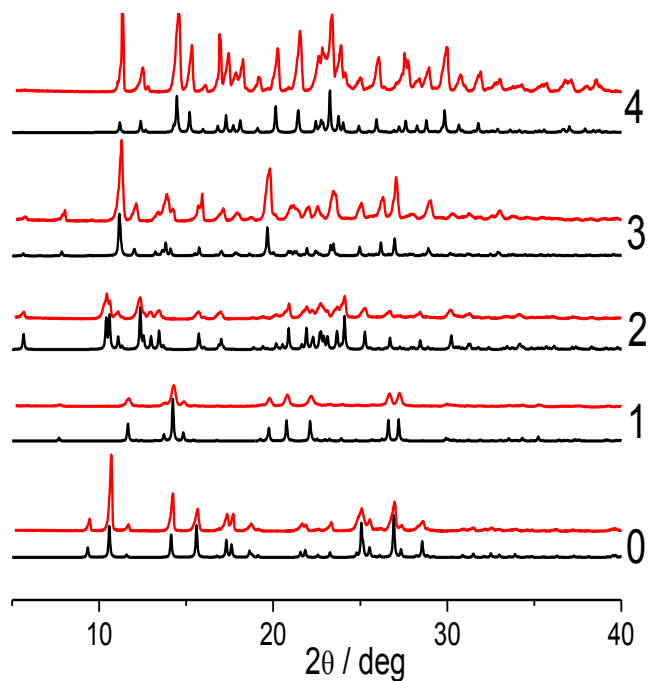


Figure ESI1. Comparison between calculated (black) and experimental (red, obtained from the kneading experiments) diffraction patterns for compounds **0-4**.

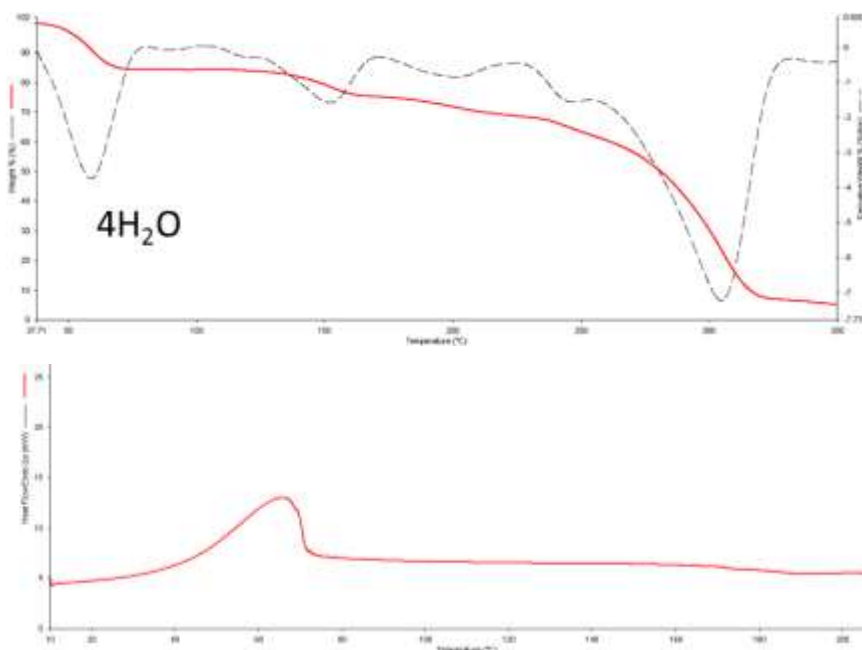


Figure ESI2. TGA (top) and DSC traces (bottom) for crystalline **2**.

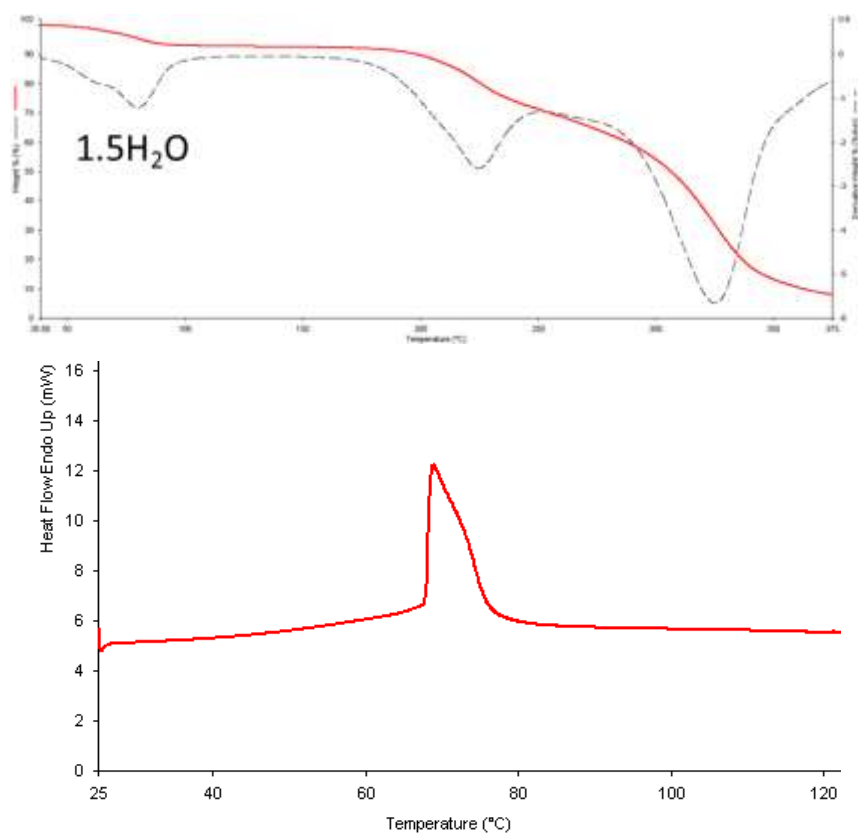


Figure ESI3. TGA (top) and DSC traces (bottom) for crystalline **3**.

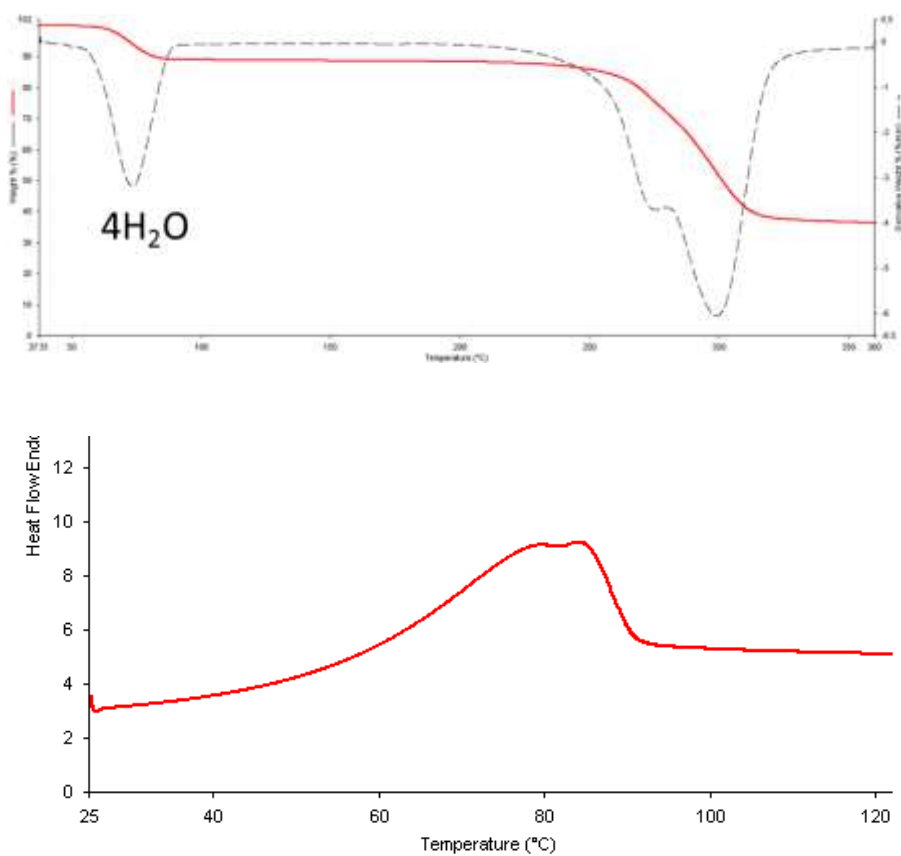


Figure ESI4. TGA (top) and DSC traces (bottom) for crystalline **4**.

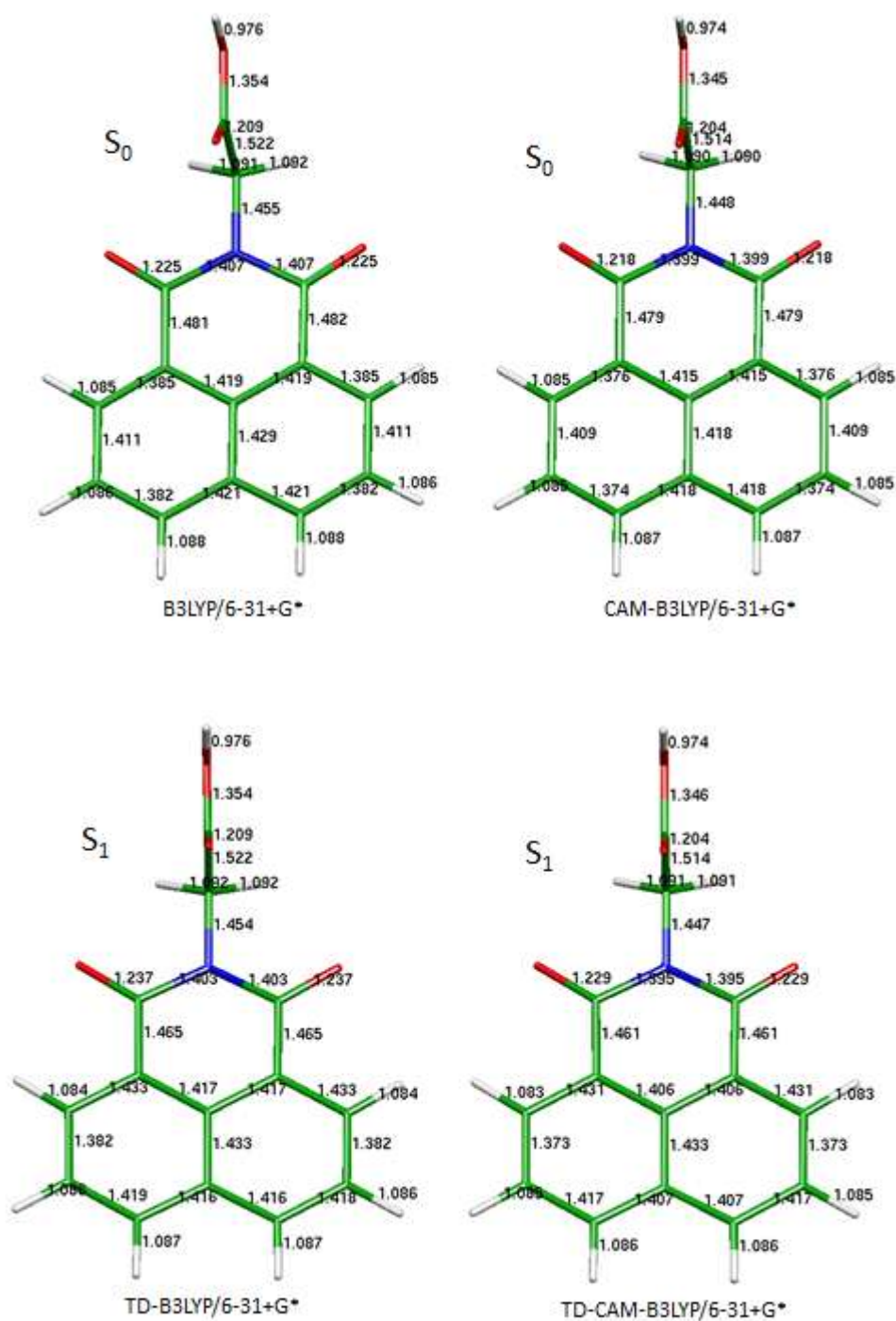


Figure ESI5. Equilibrium structures of the S_0 (top) and S_1 (bottom) electronic states of NEaH at B3LYP/6-31+G* (left) and CAM-B3LYP/6-31+G* (right) levels of theory.

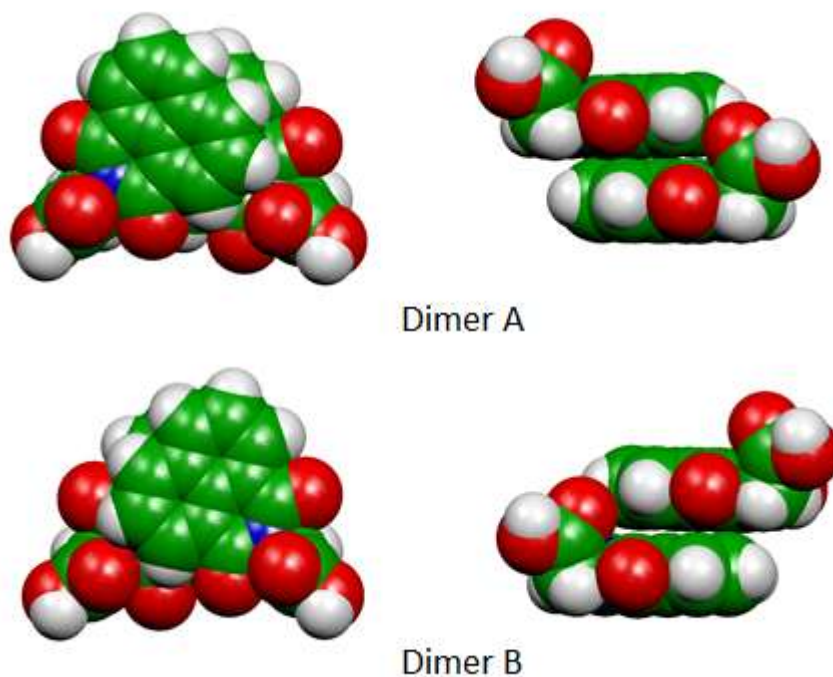


Figure ESI6. The dimers of compound **0** with the shortest intramolecular distance between centers of mass.

Table ESI1. Absolute energies of the ground and excited states of NEaH employed to evaluate the reorganization energies according to the AP method, computed reorganization energies and SS between absorption and emission spectra.

	<i>B3LYP/6-31+G*</i>	<i>CAM-B3LYP/6-31+G*</i>
$E_{excited}^{geo-gr}$ / a.u.	-894.526054	-894.094831
$E_{excited}^{geo-ex}$ / a.u.	-864.532754	-894.104349
E_{ground}^{geo-ex} / a.u.	-864.658479	-894.235773
E_{ground}^{geo-gr} / a.u.	-864.661567	-894.245196
$\lambda_{excited}$ / eV	0.18	0.26
λ_{ground} / eV	0.18	0.26
Computed SS	0.36	0.52

Table ESI2. Codes for the dimers employed to calculate excitonic interactions, intermolecular distances and angles between transition dipole moment directions and distance vector computed at TDHF/6-31+G* level of theory.

Dimer	Distance between centers of mass/ Å	Angle between transition dipole moment directions ^a	compound	Angle between μ_1 and r_{12}	Angle between μ_2 and r_{12}
A	4.8523	129	0	56	135
B	4.9168	129	0	45	123
A	4.5969	0	1	63	63
B	5.6200	0	1	55	55
C	6.2498	0	1	73	73
A	4.3202	0	2	87	87
B	5.0556	0	2	39	39

^a The discrepancy between the angles in **1** and **2** dimers (this table) and those reported Table 2 (main manuscript) is due to the fact that the *orientation* (not the direction) of the transition moments is arbitrary, and depends on the orbitals sign.

Table ESI3. Excitation energies (E) and oscillator strengths (f) of Frenkel exciton states from the supramolecular approach (TDHF/6-31+G* calculations on dimers).

Dimer	$E(S_1)/eV$ and f	$E(S_2)/eV$ and f	compound
A	4.26 (0.04)	4.42 (0.25)	0
B	4.29 (0.04)	4.43 (0.26)	0
A	4.36 (0.00)	4.41 (0.34)	1
B	4.38 (0.00)	4.42 (0.38)	1
C	4.41 (0.00)	4.44 (0.39)	1
A	4.43 (0.00)	4.48 (0.40)	2
B	4.27 (0.00)	4.50 (0.43)	2

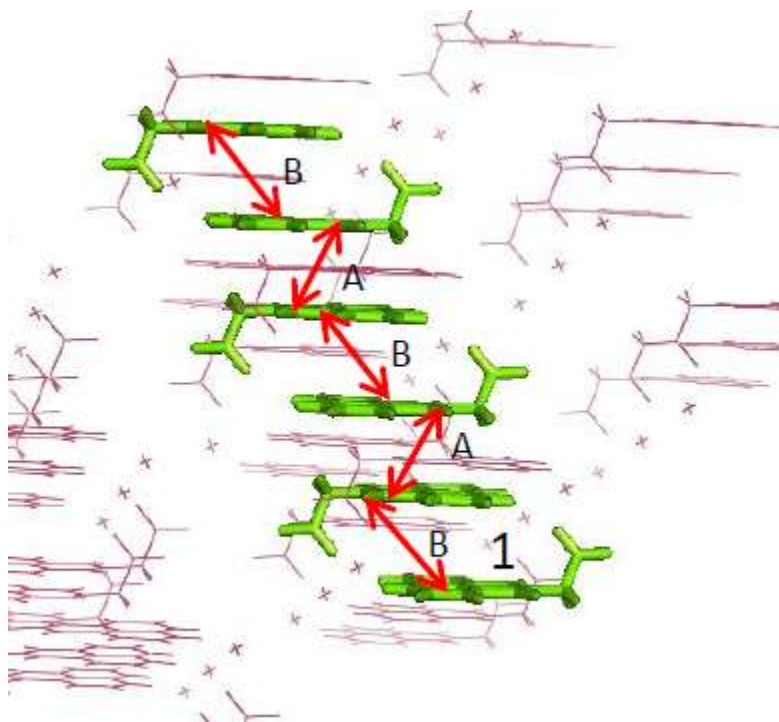


Figure ESI7. Sequences of dimers (A and B) detected along columns of naphthalimide moieties in crystalline **2**.

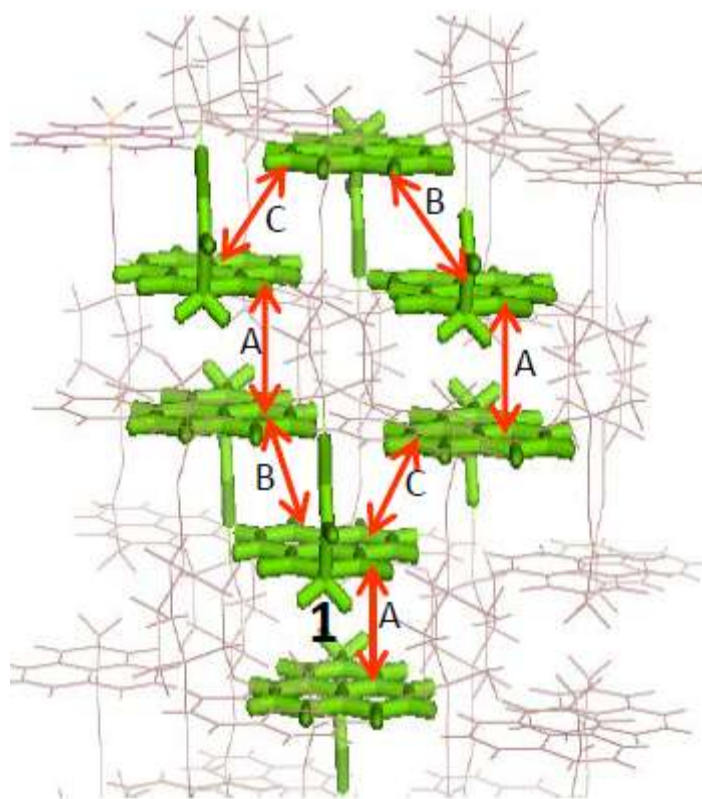


Figure ESI8. Sequences of dimers (A, B and C) detected along columns of naphthalimide moieties in crystalline **1**.

Table ESI4. Transition dipole moments (TDHF/6-31+G*) of the monomers forming the molecular dimers and displacement vectors r_{12} employed to evaluate exciton couplings within the PDA approximation.

Dimer (compound)	<i>vector</i>	<i>x, y, z components</i>
A (0)	μ_1	0.6237 -1.3460 0.1841
	μ_2	0.6161 1.3503 0.1818
	r_{12}	0.1196 -3.4002 -3.4596
B (0)	μ_1	0.6237 -1.3460 0.1841
	μ_2	0.6161 1.3503 0.1818
	r_{12}	-0.1227 -3.4002 -3.5495
A (1)	μ_1	-0.1144 -0.2164 -1.4302
	μ_2	-0.1137 -0.2245 -1.4254
	r_{12}	-3.8777 -0.4061 2.4351
B (1)	μ_1	-0.1144 -0.2164 -1.4302
	μ_2	-0.1145 -0.2242 -1.4251
	r_{12}	2.8316 4.1996 2.4351
C (1)	μ_1	-0.1144 -0.2164 -1.4302
	μ_2	-0.1145 -0.2242 -1.4251
	r_{12}	2.8316 -5.0112 2.4351
A (2)	μ_1	-0.6618 0.1741 -1.2923
	μ_2	-0.6618 0.1741 -1.2923
	r_{12}	3.6523 1.1892 -1.9776
B (2)	μ_1	-0.6618 0.1741 -1.2923
	μ_2	-0.6618 0.1741 -1.2923
	r_{12}	-4.4982 1.1892 -1.9776

Table ESI5. Crystallographic data and details of measurements for compounds **1** – **4**.

	1	2	3	4
Formula	C ₃₄ H ₃₀ O ₈ N ₄	C ₂₁ H ₃₀ O ₈ N ₂	C ₂₁ H ₂₅ N ₂ O _{6.5}	C ₃₂ H ₃₆ N ₄ O ₁₂
fw	622.62	438.47	409.44	668.64
Cryst. System	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	C2/c	P-1	P-1	P2 ₁ /c
Z	8	2	2	4
a (Å)	13.4187(6)	8.1505(6)	9.2171(8)	16.048(2)
b (Å)	9.2108(4)	8.9476(8)	13.770(1)	6.7332(6)
c (Å)	23.0093(9)	16.122(1)	16.195(1)	14.503(2)
α (deg)	90	75.732(7)	78.083(7)	90
β (deg)	94.022(4)	85.986(6)	79.755(7)	100.00(1)
γ (deg)	90	77.938(7)	81.159(7)	90
V (Å ³)	2836.9(2)	1114.1(2)	1964.52	1543.3(3)
D _{calc} (Mg/m ³)	1.458	1.307	1.384	1.439
μ (mm ⁻¹)	0.105	0.100	0.103	0.111
Measured reflns	7015	8797	15331	6682
indep. reflns	3326	5585	8908	3518
R1[onF ₀ ² , I > 2σ(I)]	0.0552	0.0574	0.0984	0.0642
wR2 (all data)	0.1355	0.1345	0.2268	0.1411
Residual electron density	0.164	0.184	0.418	0.216