Molecular insights into solid-state photochromism in bulk and confined *N*-salicylidenes

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Supporting Information

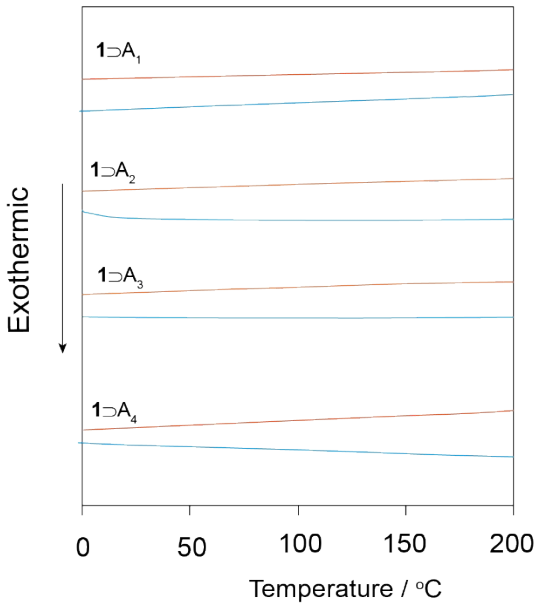

Figure S1. Differential scanning calorimetry traces of **1**⊃A_n. Heating curves are shown in orange; cooling curves are shown in blue. No endothermic or exothermic features are observed which would be characteristic of melting or crystallisation of the crystalline *N*-salicylidenes. It can be assumed that excess *N*-salicylidene has been removed via vacuum treatment.

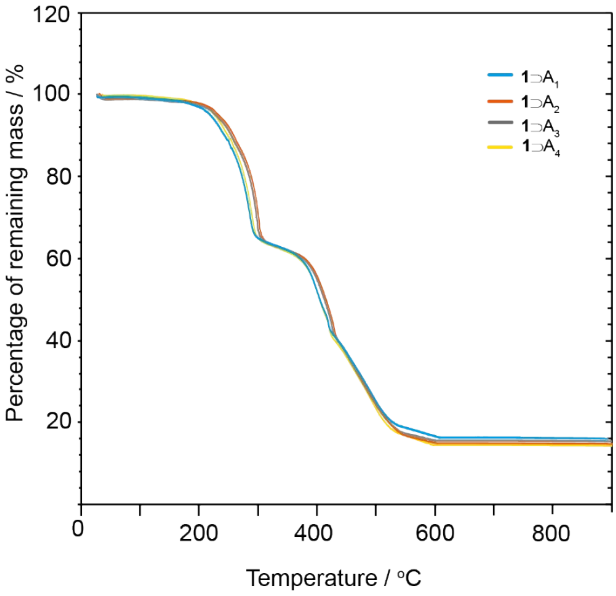

Figure S2. Thermogravimetric analysis traces of **1**⊃A_n. Expected final mass for the general formula **1**⊃$A_{n(0.5)}$ was calculated to be 15%-16% based on Al_2O_3. **1**⊃A_1 (16.1%), **1**⊃A_2 (15.8%), **1**⊃A_3 (15.6%), and **1**⊃A_4 (14.9%).

Table S1. Crystallographic and calculated geometry optimised parameters for other reported polymorphs of A_n compounds not used in this study.

	A_1	A_1	A_2
Crystal System	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$Pbc2_1$	$P2_1/c$
Z	4	4	4
Photochromic	Yes	No	No
Experimental torsion angle / °	45.4	6.6	2.3

Table S2. Comparison between calculated and experimental ^{13}C imine chemical shifts at the experimental torsion angle.

Structure	Experimental torsion angle / °	Experimental ^{13}C imine chemical shift (ppm)	Calculated ^{13}C imine chemical shift at experimental torsion angle (ppm)
A_1	47.1	162.1	161.4
A_2	47.0	161.9	161.0
A_3	3.5	155.4	153.2
A_4	5.7	155.2	155.8

Table S3. Torsional angles for anil structures A_1-A_4, calculated by geometry optimisations with four methods. Fixed and unfixed refer to whether the unit cell parameters were allowed to relax during the geometry optimisation.

Method	A_1	A_2	A_3	A_4
Experimental	47.1	47.0	3.5	5.7
PBE-D3 Fixed	45.6	43.9	10.7	7.8
PBE-D3 Unfixed	45.6	4.2	10.1	8.6
rSCAN Fixed	46.1	45.7	10.1	8.7
rSCAN Unfixed	46.0	45.7	11.4	9.0

Table S4. Calculated values of V_{free} for A_1-A_4 and **1**⊃A_1 - **1**⊃A_4

Molecule	Volume of Molecule / Å^3	Crystalline Unit Cell Volume / Å^3	Z	V_{free} per molecule / Å^3	V_{free} per molecule occluded within **1**

A_1	186.73	1023.38	4	69.1	279.4032
A_2	200.27	1132.607	4	82.9	265.8632
A_3	200.27	1049.972	4	62.2	265.8632
A_4	266.13	2388.821	8	32.5	200.0032

Volume of the cavity of **1** = 233.06 A^3. V_{free} per molecule was calculated using:

$V_{free} = (V_{cell} - Z\,.\,V_{molecule})/Z$

where V_{cell} is the unit cell volume and $V_{molecule}$ is the volume of a single molecule.

Table S5. Calculated ^{13}C chemical shieldings for A_1 and A_3 determined from single-molecule DFT calculations performed on fully optimised structures carbon sites numbered as shown in Figure 2 (main text).

Site	A1 Calculated ^{13}C chemical shielding (ppm)	A3 Calculated ^{13}C chemical shielding (ppm)	Calculated ^{13}C chemical shielding difference (ppm)
C1	29.6	31.6	-2.0
C2	75.8	74.6	1.2
C3	59.9	59.9	0.0
C4	75.9	59.9	16.0
C5	60.3	61.6	-1.3
C6	72.8	72.2	0.6
C7	32.0	33.0	-1.0
C8	42.6	43.2	-0.6
C9	67.5	67.4	0.1
C10	64.1	64.0	0.1
C11	67.2	66.5	0.7
C12	63.8	63.7	0.1
C13	76.3	76.4	-0.1

Torsional angles for fully optimised molecular structures are 34.0° (A_1) and 33.4° (A_3)

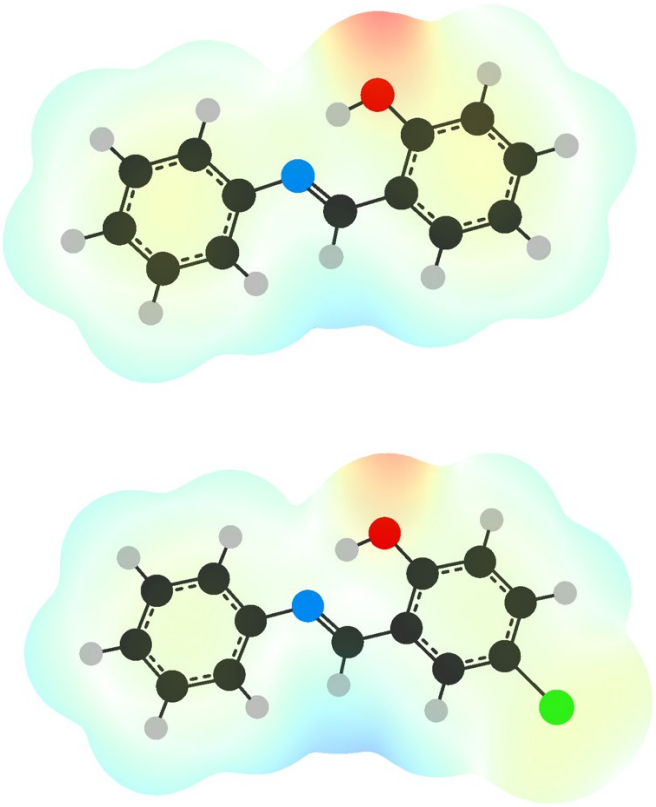

Figure S3. Electron density maps generated from single-molecule DFT calculations on A_1 (top) and A_3 (bottom). Atoms shown are carbon (black), nitrogen (blue), oxygen (red), hydrogen (grey) and chlorine (green).

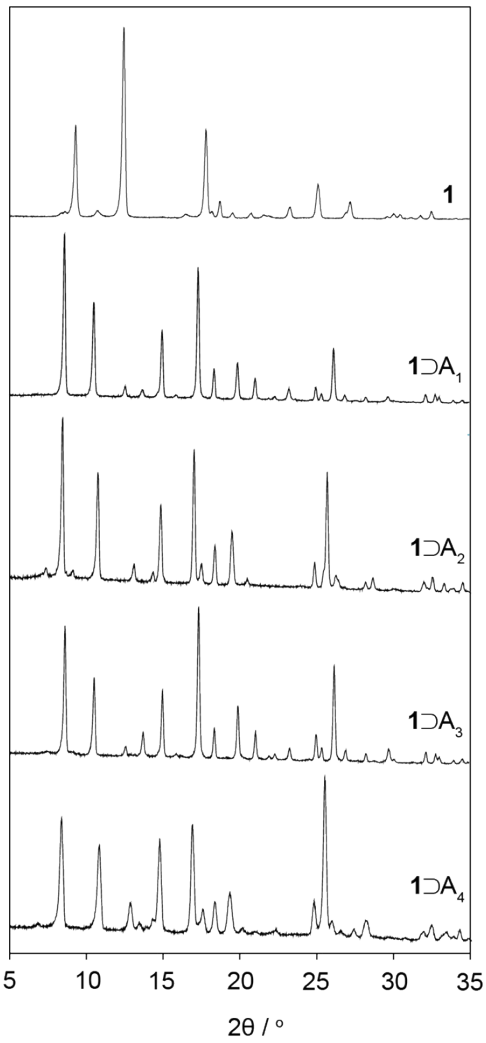

Figure S4a) Comparison of XRPD patterns of **1**⊃A_n.

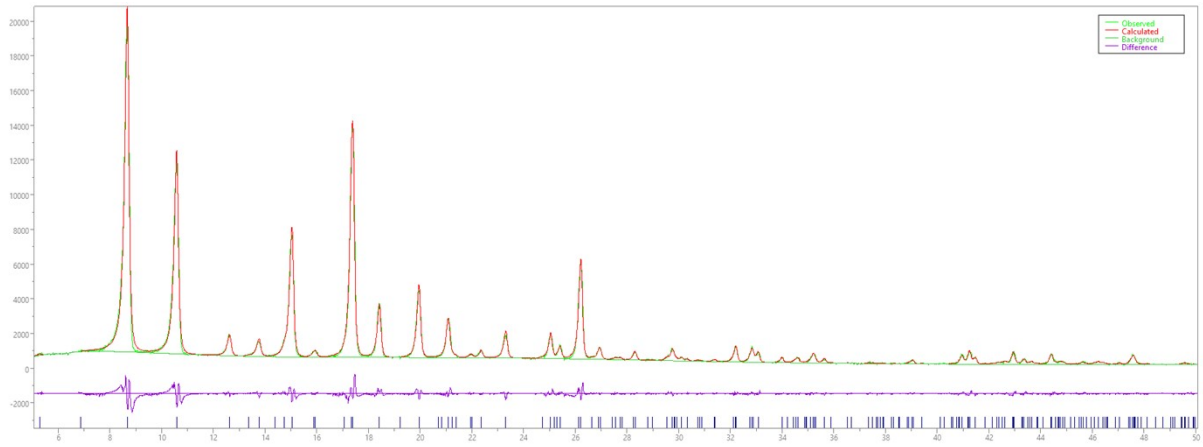

Figure S4b) Le Bail fit of **1**⊃A_1. Indexing was carried out by N-TREOR09 on EXPO2014. The crystal system was found to be orthorhombic. The lattice parameters were refined to be , a = 12.87 Å, b = 16.71 Å and c = 6.62 Å Å, $\alpha=\beta=\gamma=90^{\circ}$, V = 1423.7 Å^3. The space group was found to be *Imma*. General formula $AlC_{84}H_{68}N_4O_{20}$. The reliability (R) factor based on the powder profile was 5.122 %.

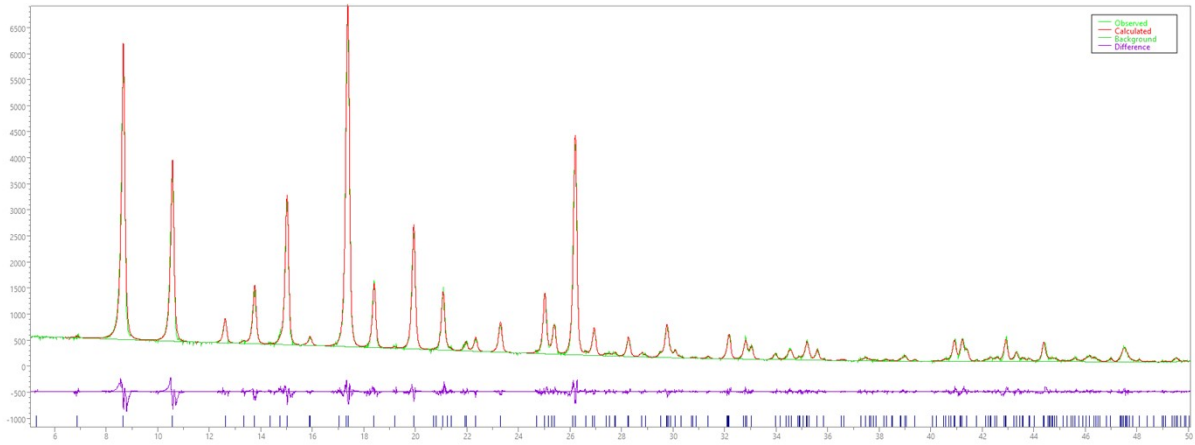

Figure S4c) Le Bail fit of **1**⊃A_3. Indexing was carried out by N-TREOR09 on EXPO2014. The crystal system was found to be orthorhombic. The lattice parameters were refined to be , a = 12.87 Å, b = 16.74 Å and c = 6.64 Å, $\alpha=\beta=\gamma=90^{\circ}$, V = 1430.5 Å^3. The space group was found to be *Imma*. General formula $AlC_{83}H_{68}N_4O_{20}Cl$. The reliability ($R$) factor based on the powder profile was 7.237 %.

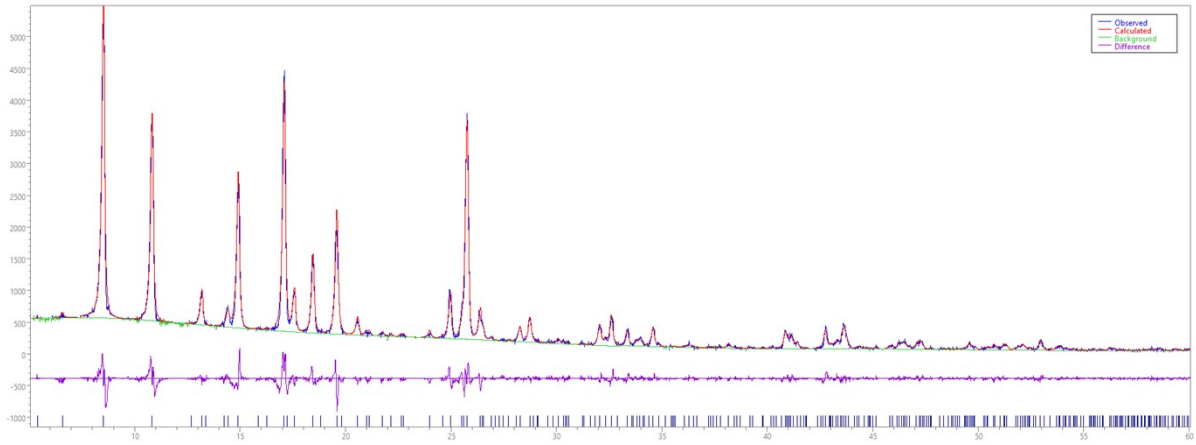

Figure S4d) Le Bail fit of **1**⊃A_2. Indexing was carried out by N-TREOR09 on EXPO2014. The crystal system was found to be orthorhombic. The lattice parameters were refined to be , a = 13.44 Å, b = 16.33 Å and c = 6.62 Å, $\alpha=\beta=\gamma=90^{\circ}$, V = 1452.9 Å^3. The space group was found to be *Imma*. General formula $AlC_{83}H_{68}N_4O_{20}Cl$. The reliability ($R$) factor based on the powder profile was 9.111 %.

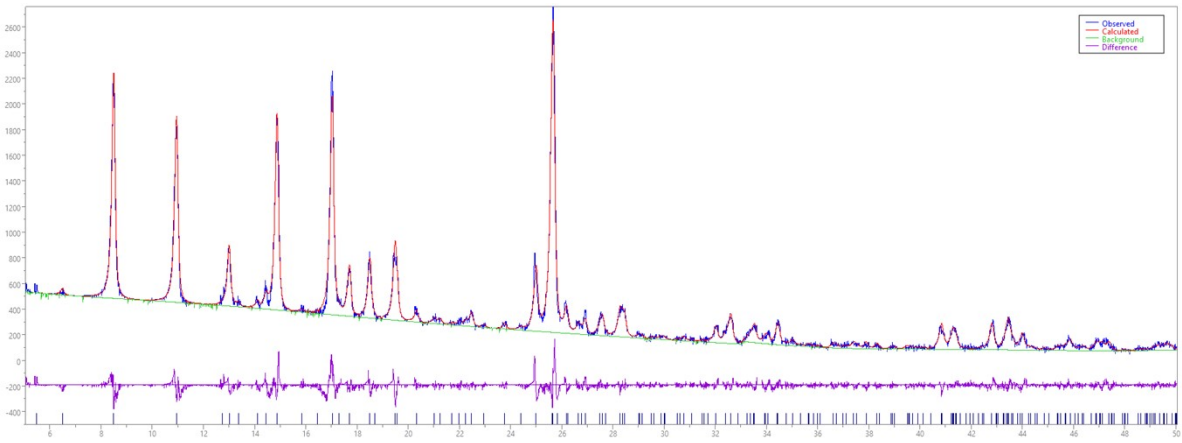

Figure S4e) Le Bail fit of **1**⊃A_4. Indexing was carried out by N-TREOR09 on EXPO2014. The crystal system was found to be orthorhombic. The lattice parameters were refined to be , a = 13.63 Å, b = 16.16 Å and c = 6.63 Å, $\alpha=\beta=\gamma=90^{\circ}$, V = 1460.3 Å^3. The space group was found to be *Imma*. General formula $AlC_{83}H_{68}N_4O_{20}Cl$. The reliability ($R$) factor based on the powder profile was 10.265 %.

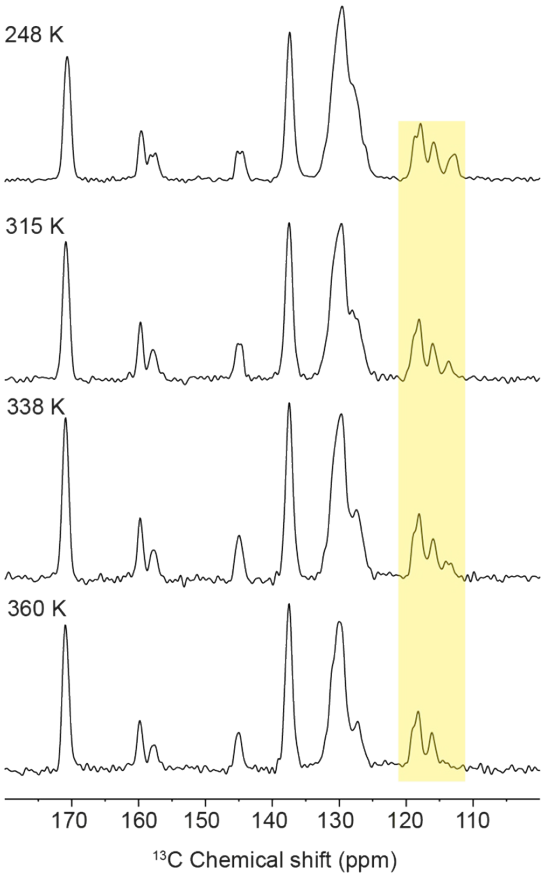

Figure S5. Variable-temperature ^{13}C CPMAS NMR spectra of **1**⊃A_1.

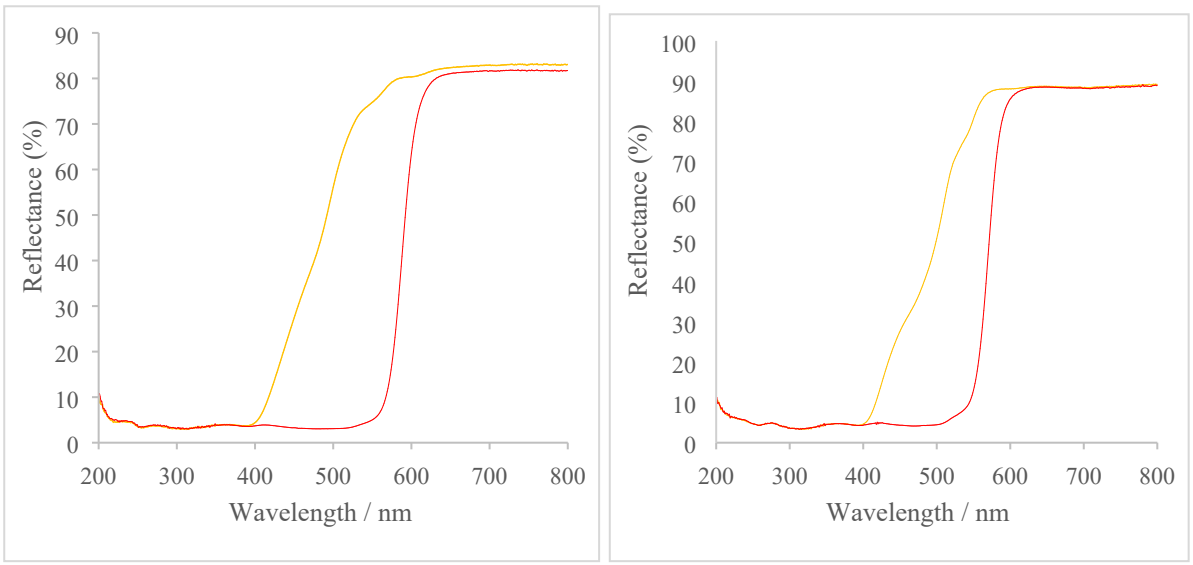

Figure S6. UV-vis reflectance spectra before irradiation (yellow) and after irradiation (red) of A_1 (left) and A_2 (right).

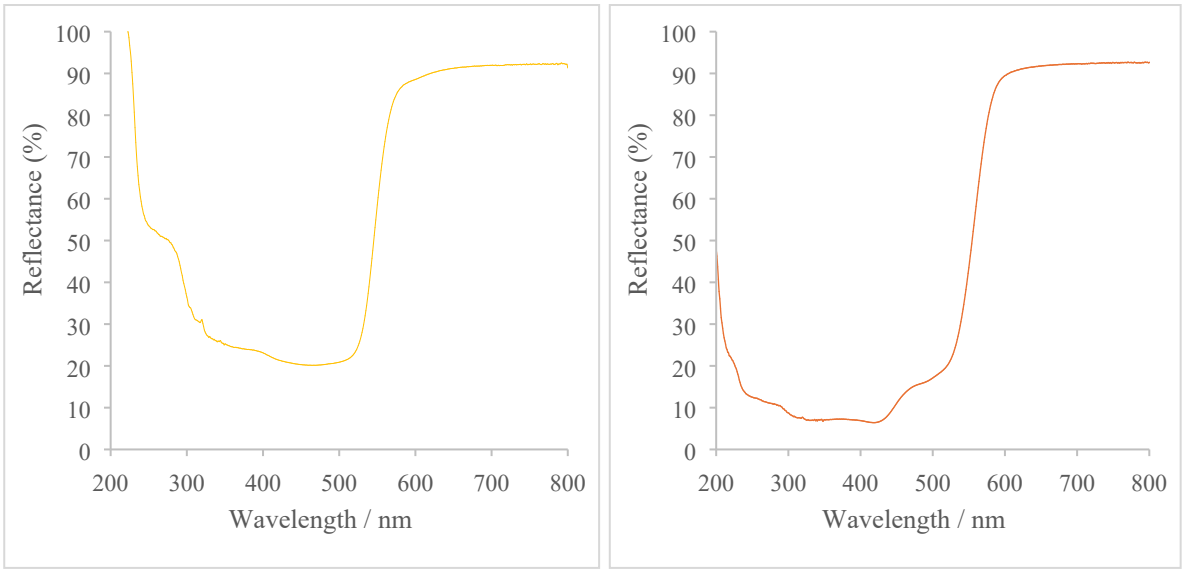

Figure S7. UV-vis reflectance spectra of bulk crystalline A_3 (left) and A_4 (right). UV-vis reflectance profiles remain the same after irradiation.

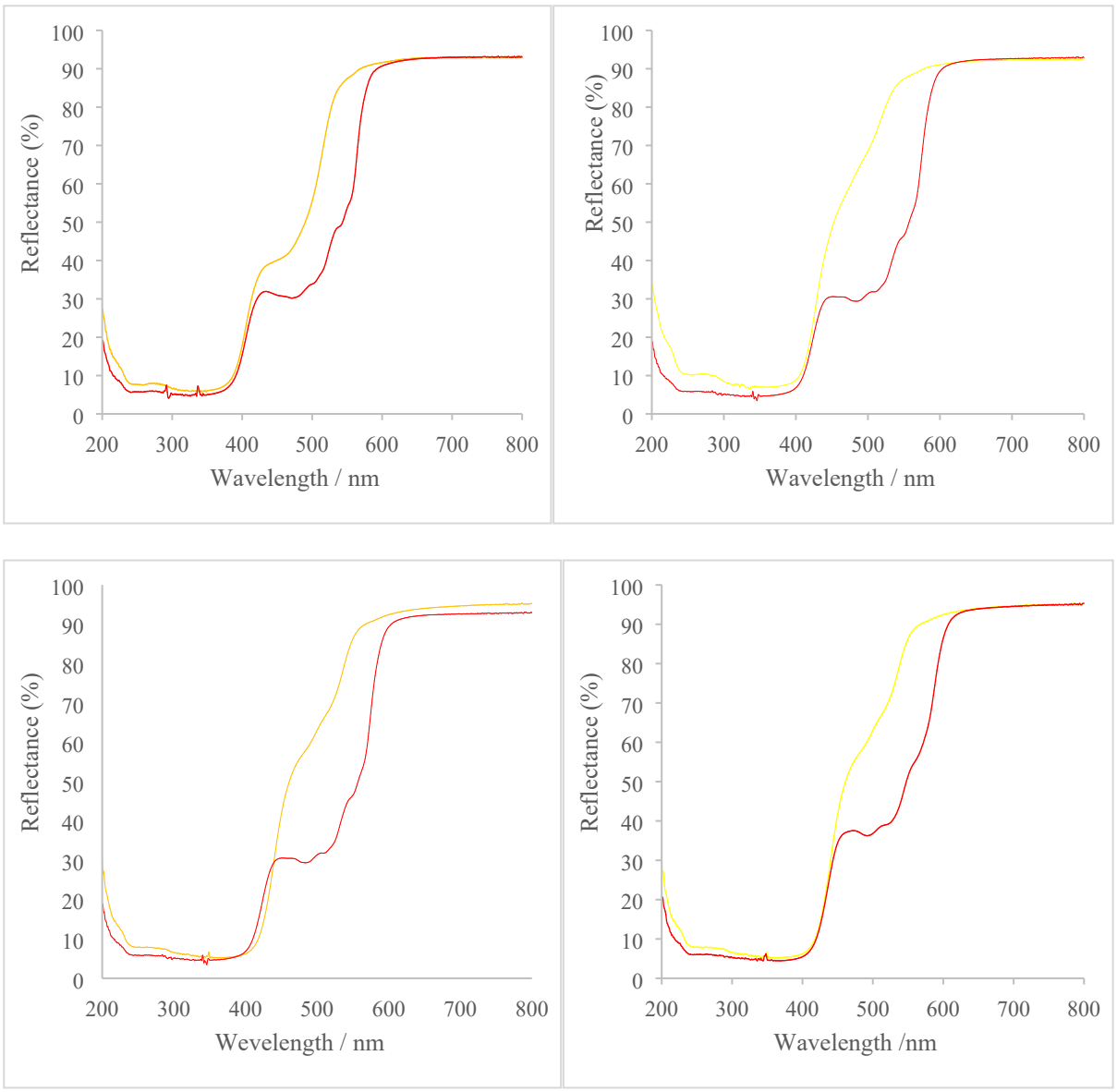

Figure S8. UV-vis reflectance spectra before irradiation (yellow) and after irradiation (red) of **1**⊃A_1 (upper left), **1**⊃A_2 (upper right), **1**⊃A_3 (lower left), and **1**⊃A_4 (lower right).

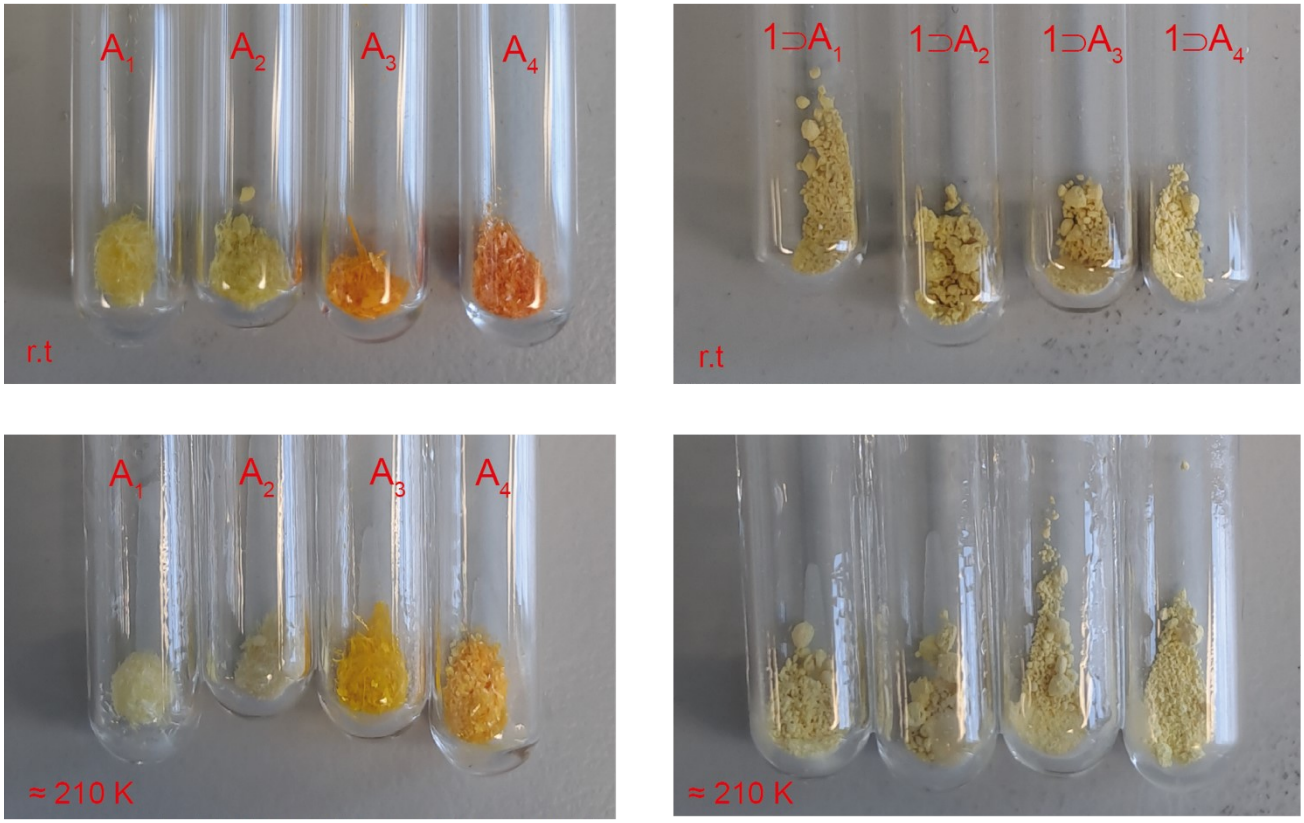

Figure S9. (Left) thermochromic properties of A_1-A_4 at room temperature (top) and 210 K (bottom). (Right) thermochromic properties of **1**⊃A_1-**1**⊃A_4 at room temperature (top) and 210 K (bottom).