Electronic Supplementary Information

Spontaneous resolution of silver double helicates consisting of achiral ligands with several aromatic rings

Qiaozhen Sun, Yan Bai, Guangjie He, Chunying Duan*, Zhihua Lin and Qingjin Meng*

Experiment:

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Intensities of all complexes were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs.[1] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL *version* 5.1.[2] The elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 analyzer.

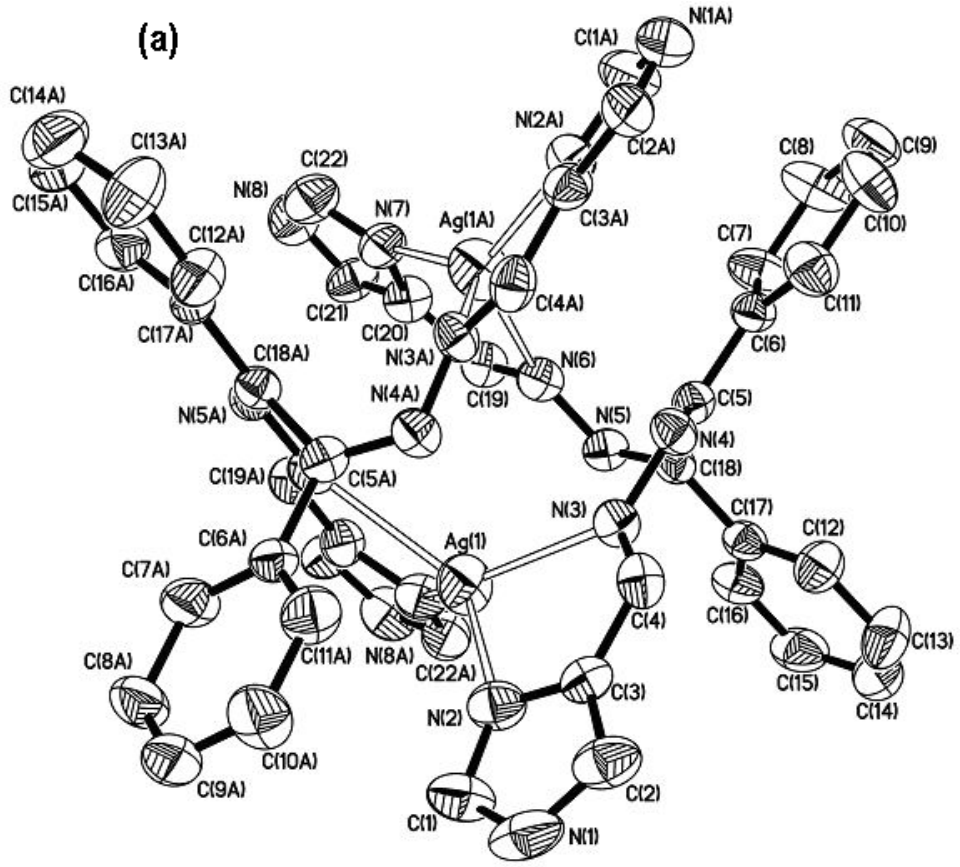
The CD spectra were measured on the resulting complexes as crystal in 100 mg of oven-dried KBr. 10-mm diameter disks were made in a standard disk press. The baseline correction was performed with the spectrum of a pure KBr disk, prepared in the same conditions. The displayed absorption spectra result from subtraction of spectrum of a standard KBr disk. Spectra were recorded for the wavelength range 200-600 nm for all the disks with the pathlength was 3nm. The experimental arrangements for measuring the nonlinear optical properties utilized an M200 high-power mode-locked Nd:YAG laser with 200 *ps* pulse at a repetition rate of 5 Hz.

Preparation of L^1: Benzil dihydrazone (0.98 g, 4.1 mmol) was dissolved in 10mL methanol, then added to a solution of 4-formylimidazole (0.79g, 8.2mmol) in 20mL of methanol. The mixture was refluxed for 4 hrs. Yellow power of the ligand L^1 was filtered out and dried under vacuum.

Preparation of the compound 1: The ligand L^1 (0.1 mmol, 0.039 g) and $AgNO_3$ (0.2 mmol, 0.034 g) were mixed in methanol (30 mL), and after refluxing for 2 h the yellow solution was obtained. And a yellow solid was formed which was isolated by filtration and dried over P_2O_5 under vacuum. Yield: 52%. $[(C_{22}H_{18}N_8)_2Ag_2]_3(NO_3)_6(CH_3OH)_6(H_2O)_3$ C, 45.6; H, 3.7; N, 20.8%. Found: C, 45.2; H, 3.4; N, 20.5%. Crystals suitable for X-ray structure analyses were obtained by slowly evaporating the yellow solution of methanol at room temperature.

Preparation of the compound 2: The ligand L^2 (0.2 mmol, 0.083 g) and $AgNO_3$ (0.2 mmol, 0.034 g) were mixed in methanol (40 mL), and after refluxing for 2 h the yellow solution was obtained. The resultant solution was then added to a saturated solution (5 mL) of $NaClO_4 \cdot H_2O$. And a yellow solid was formed which was isolated by filtration and dried over P_2O_5 under vacuum. Yield: 72%. Anal. calc. for $[(C_{26}H_{20}N_6)_2Ag_2]_3(ClO_4)_5(NO_3)$: C, 50.7; H, 3.3; N, 14.0%. Found: C, 50.5; H, 3.2; N, 13.9%. Crystals suitable for X-ray structure analyses were obtained by slowly evaporating the yellow solution of methanol at room temperature.

1. SMART and SAINT, Area Detector Control and Integration Software; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1996.
2. Sheldrick, G. M. *SHELXTL V5.1, Software Reference Manual*; Bruker, AXS, Inc.: Madison, WI, 1997.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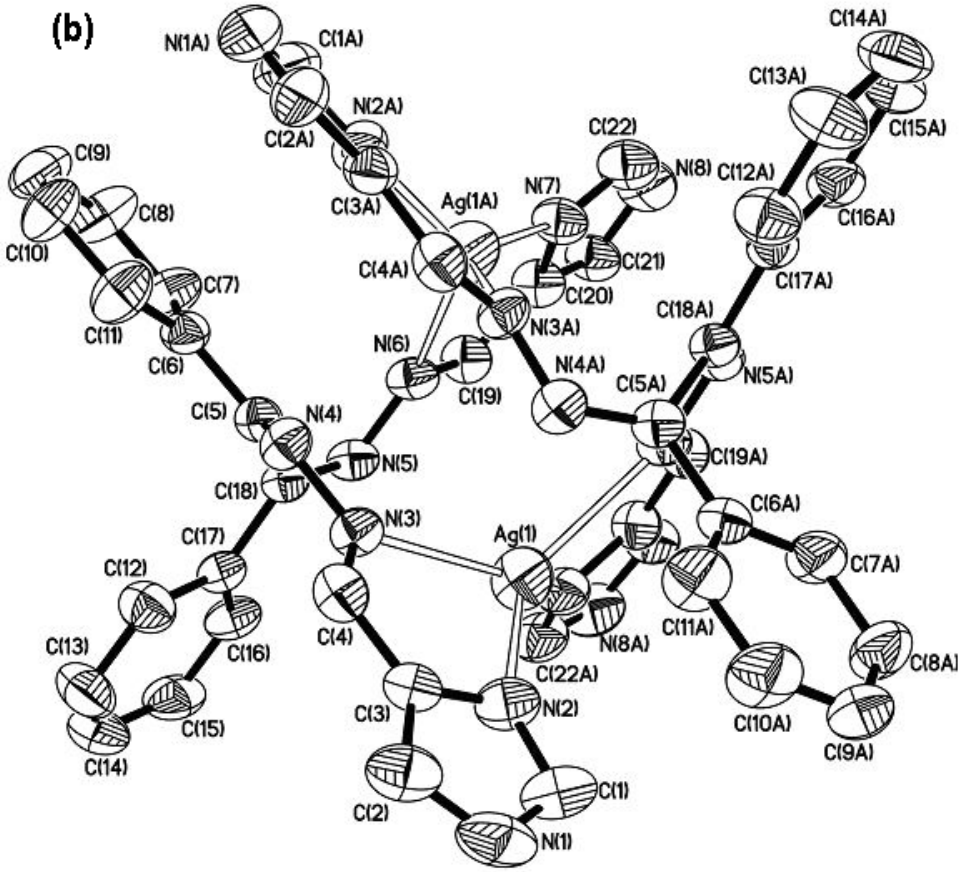
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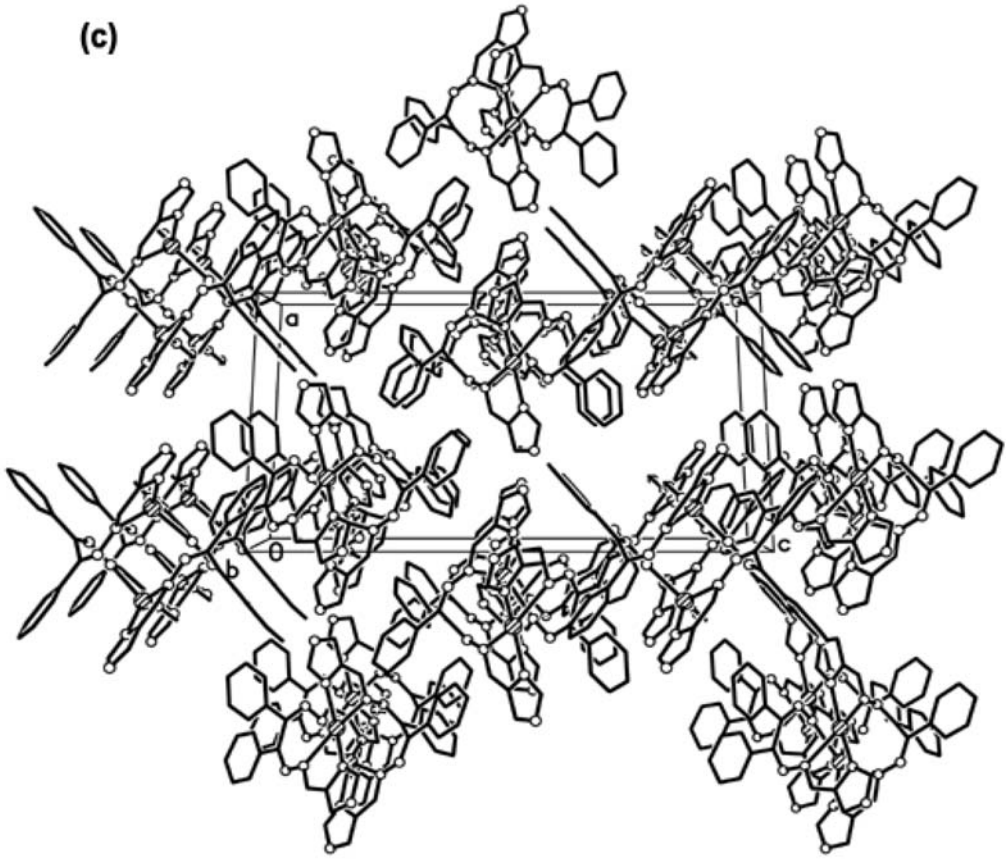


Figure S1. Molecular structure of compound **1** with 30% thermal ellipsoids showing *Δ* (a) and *Λ* (b) absolute configurations of the $Ag_2L^1_2$ species. (c) The packing diagram of compound **1** along b axis. The hydrogen atoms and the anions are omitted for clarity.

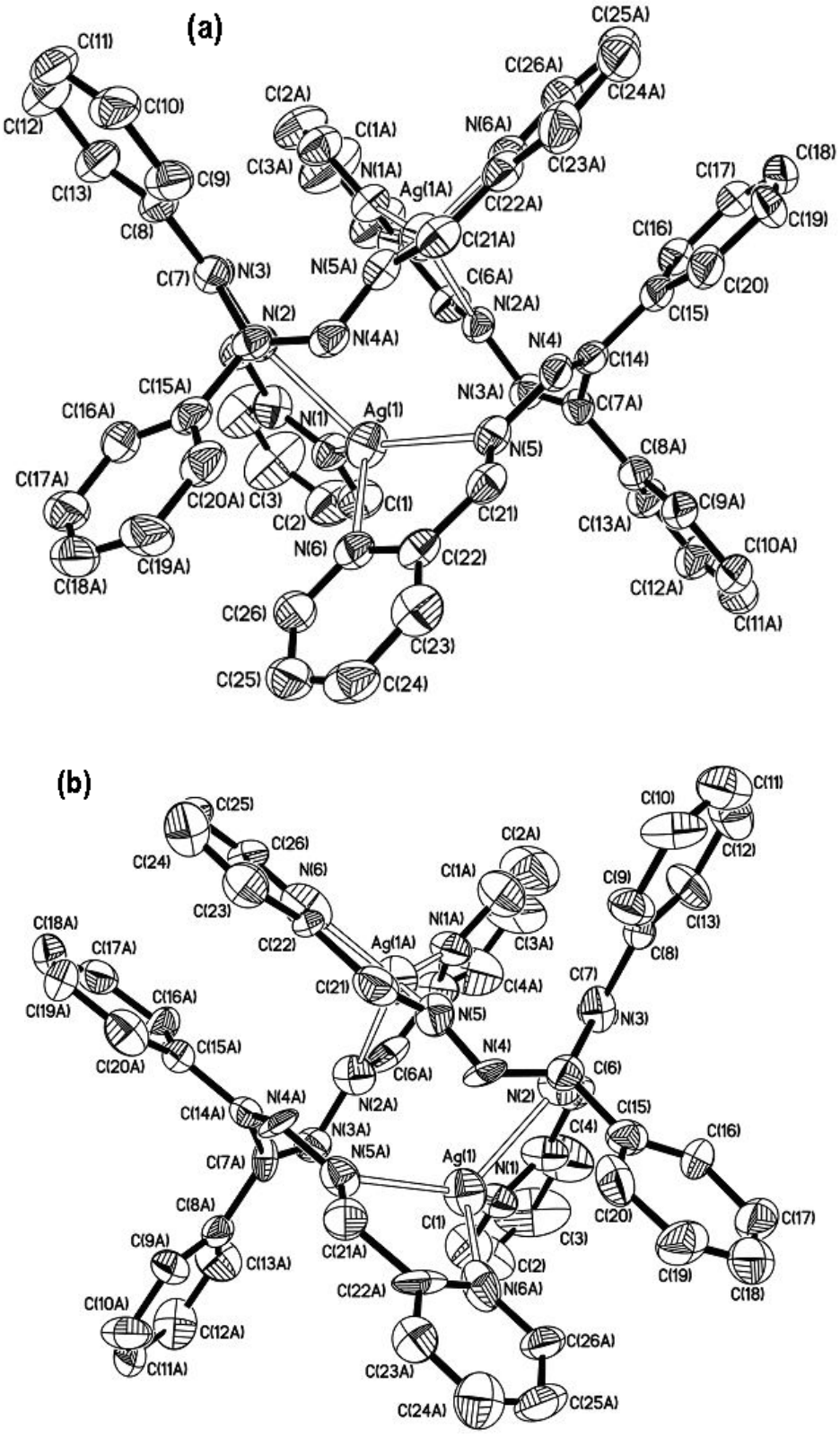


Figure S2 Molecular structure]of compound **2** with 30% thermal ellipsoids showing *Δ* (a) and *Λ* (b) absolute configurations of the $Ag_2L^1_2$ species. The hydrogen atoms and the anions are omitted for clarity.

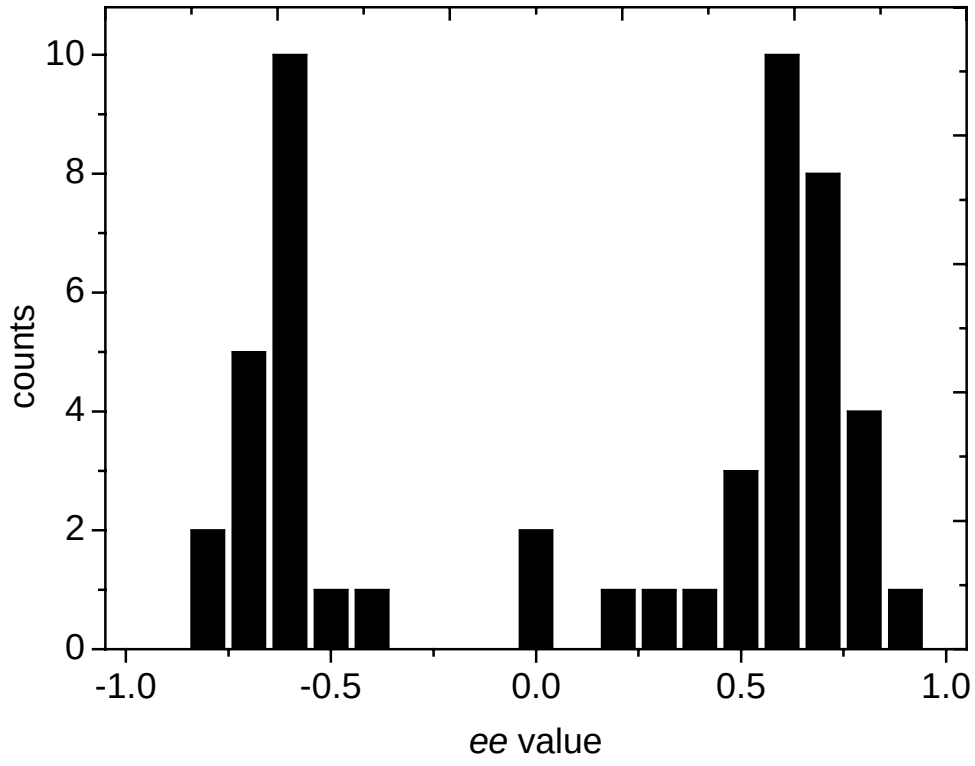


Figure S3 Spontaneous chiral symmetry breaking in compound **2** crystallization showing the corresponding histogram of crystal enantiomeirc excess (*ee* = (*M*-*P*)/(*M*+*P*) calculated from crystals obtained in 50 independent crystallizations

Table S1 Solid state CD spectra of compound **1** (20 crystals measured with ee=0)

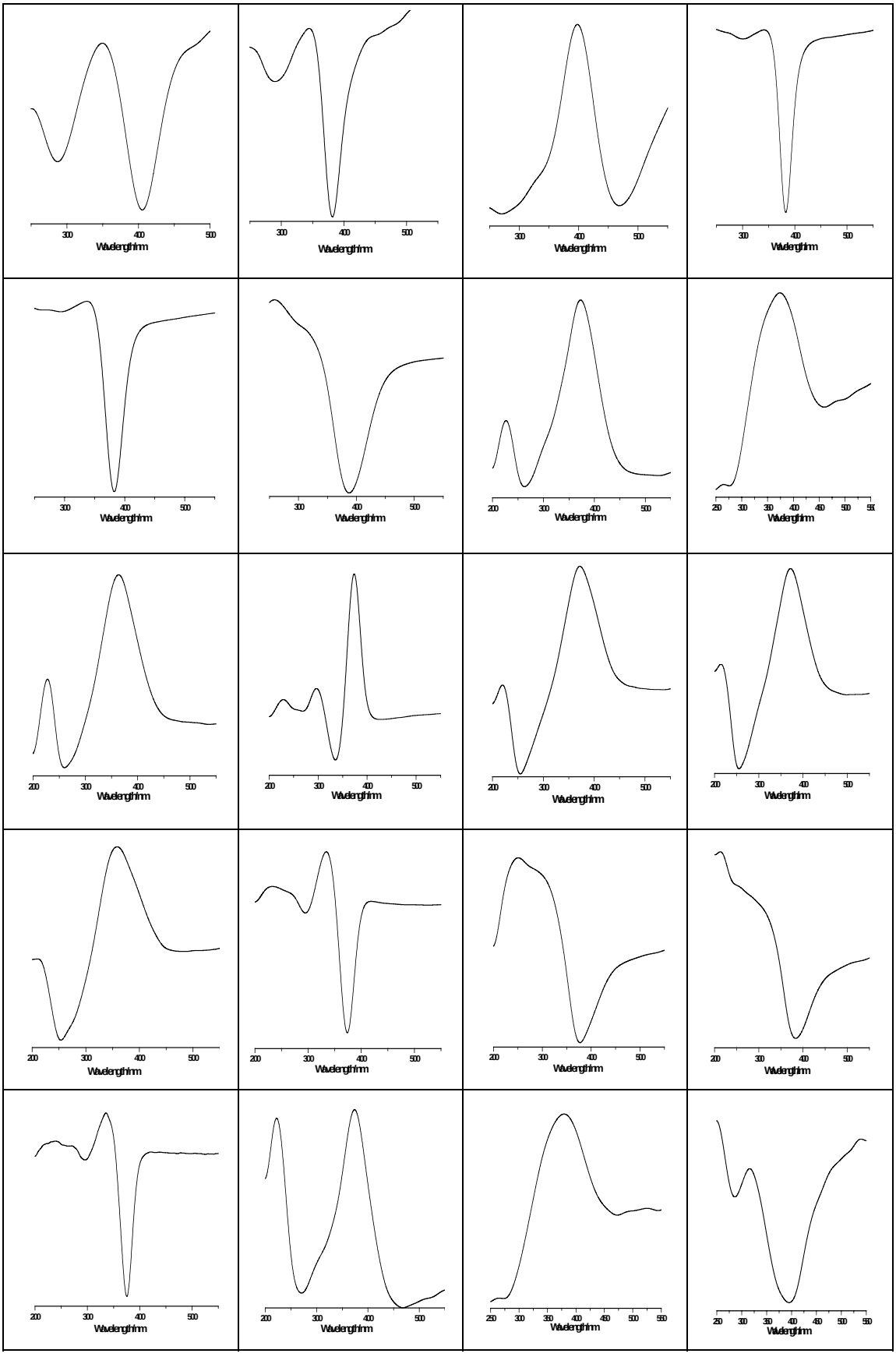
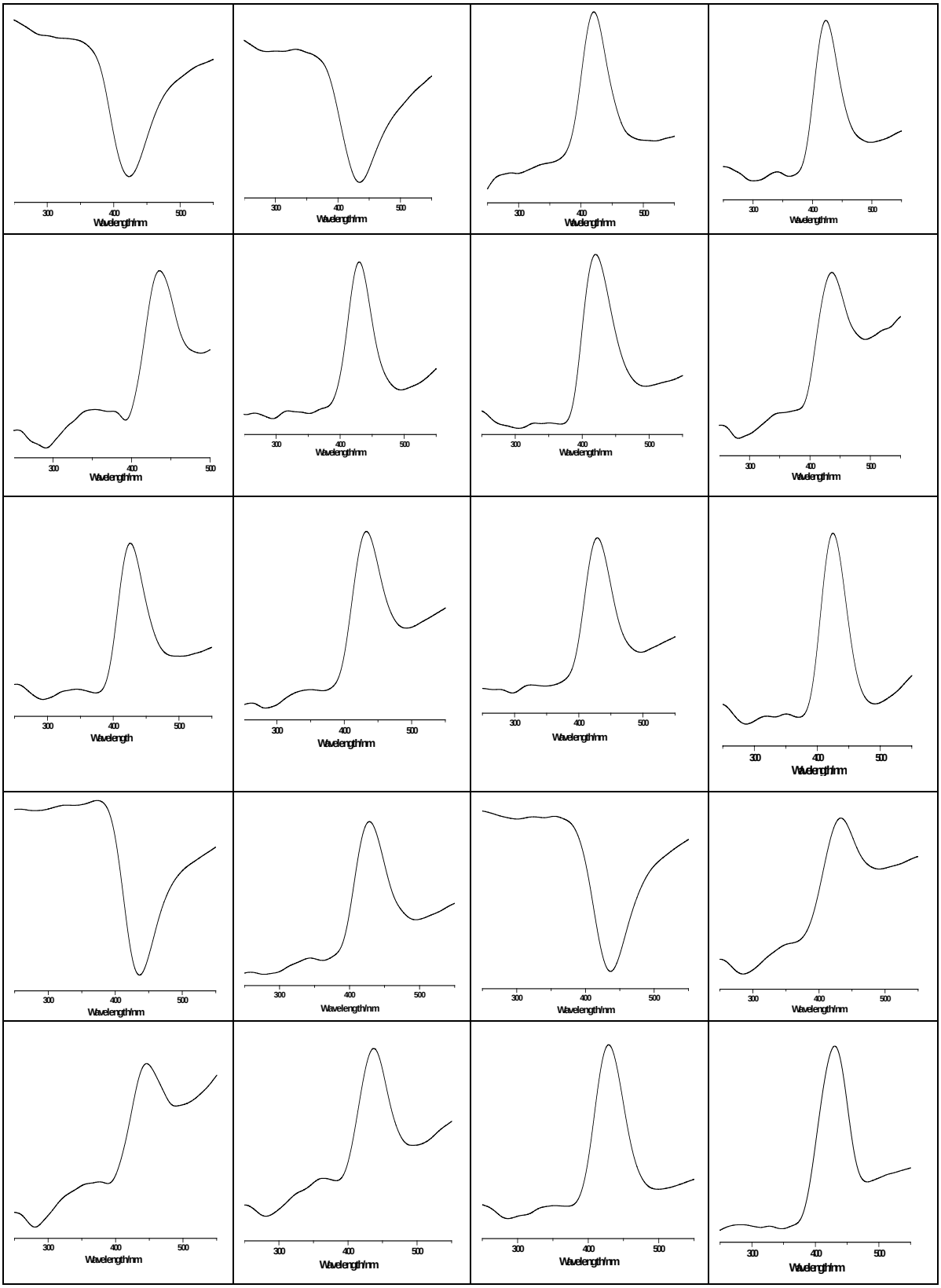
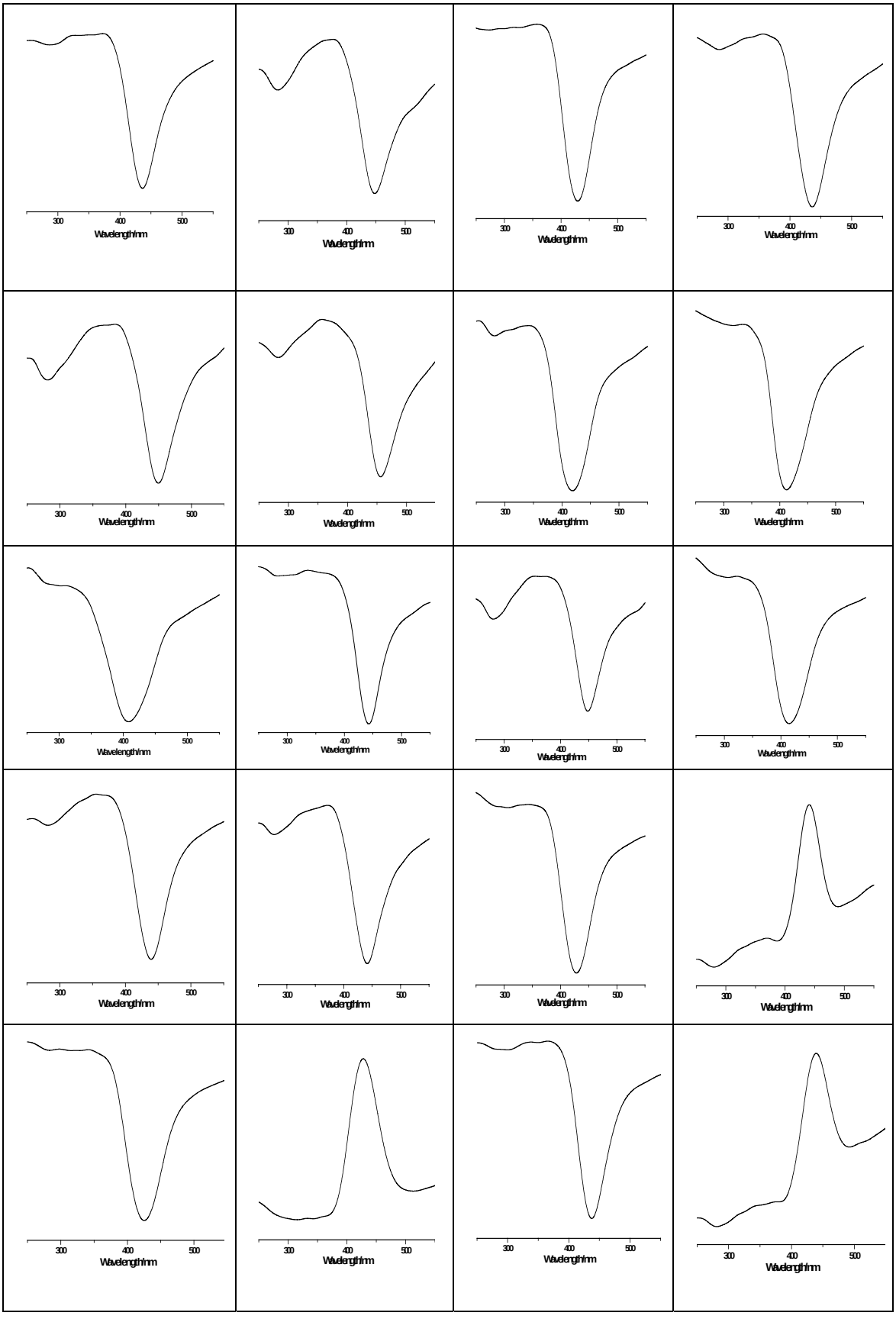


Table S2 Selected solid-state CD spectra of compound **2** (100 crystals from first t- fifth independent crystallizations)

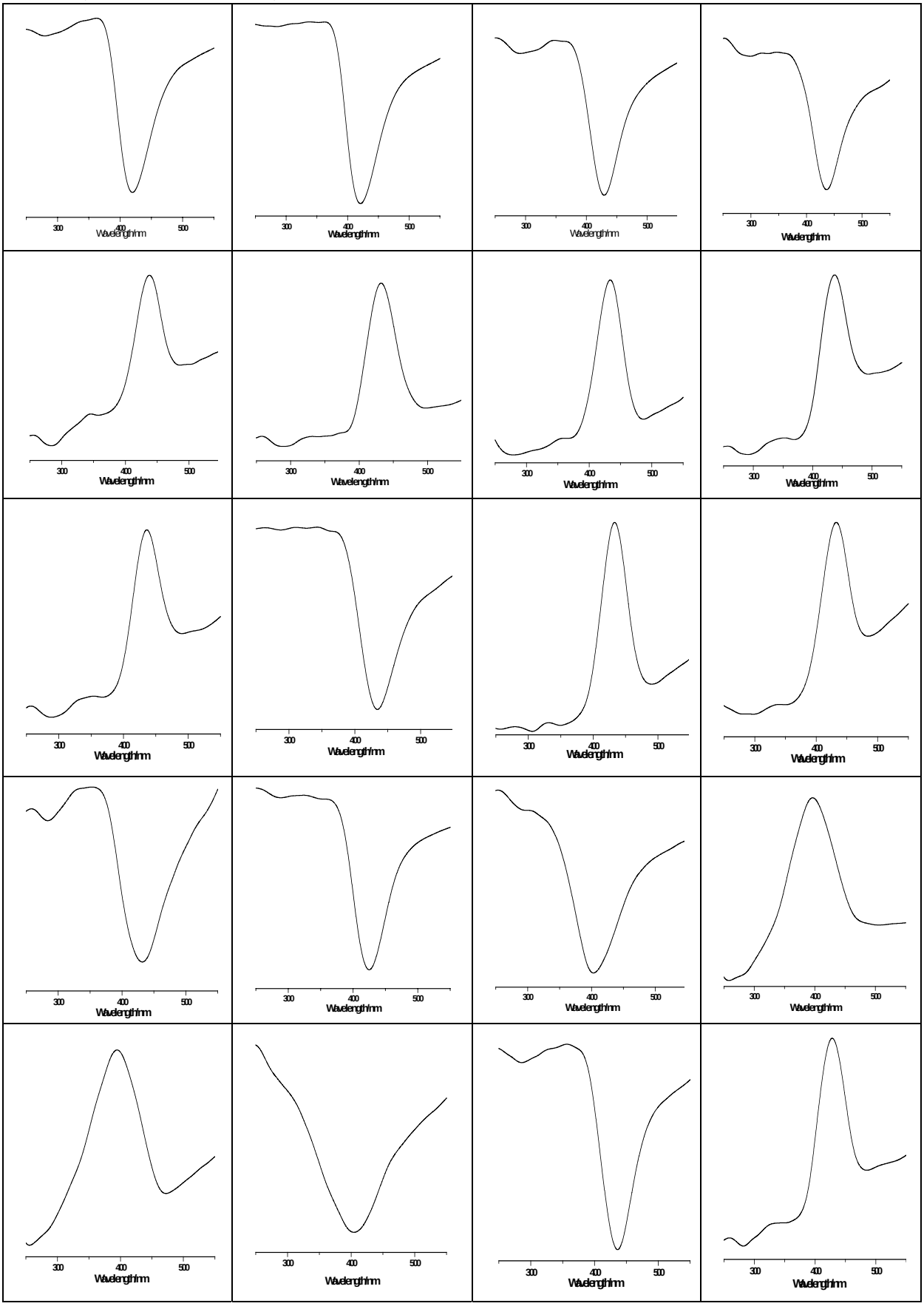
(a) 20 crystals from the first crystallization (calculated *ee* = 60%)



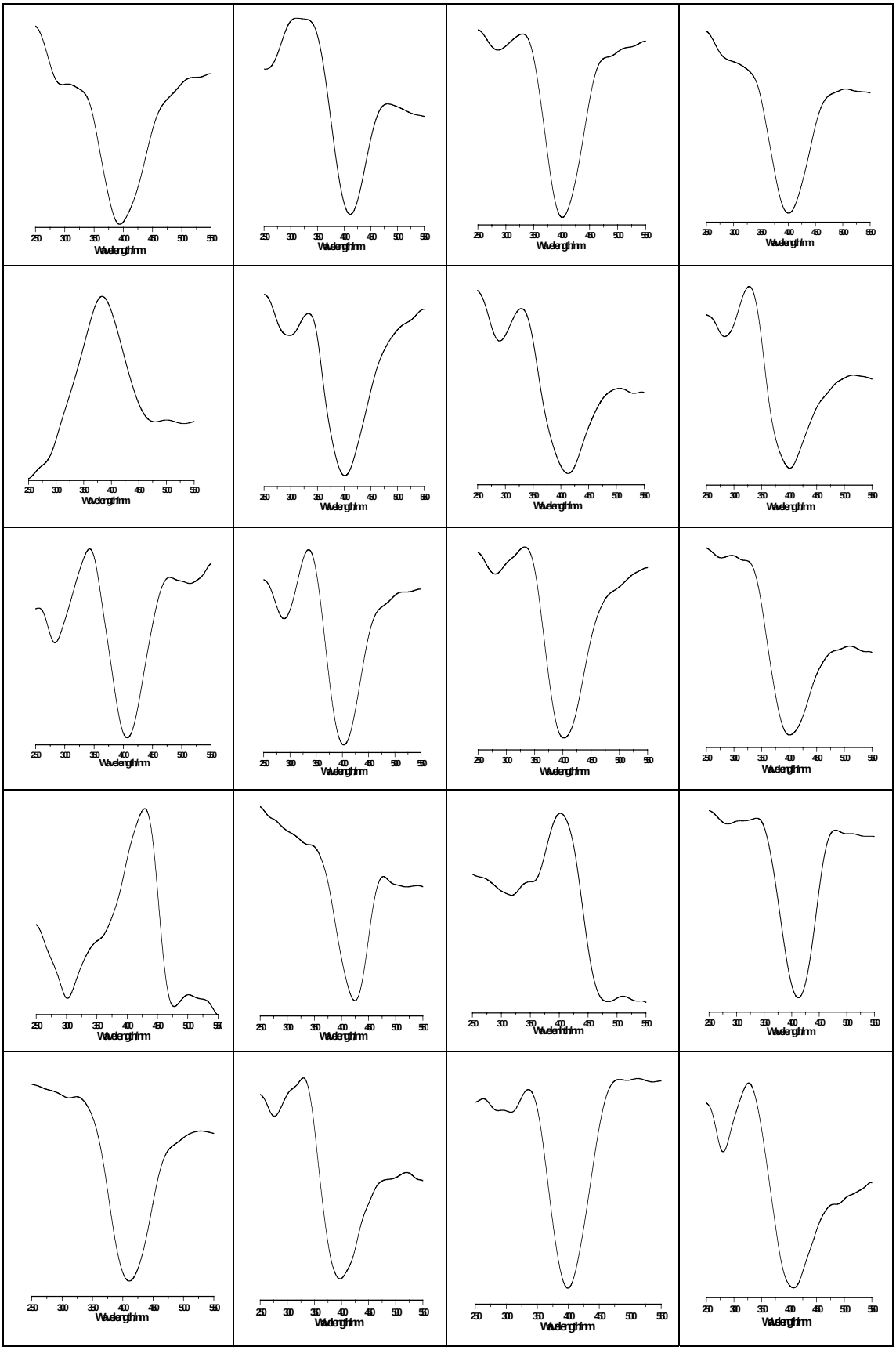
(b) 20 crystals from the second crystallization (calculated *ee* = -70%)



(c) 20 crystals from the third crystallization (calculated *ee* = 0)



(d) 20 crystals from the fourth crystallization (calculated *ee* = -70%)



(e) 20 crystals from the fifth crystallization (calculated *ee* = 80%)