Electronic Supplementary Information for Dalton Transactions

Supporting Information

Spontaneous Chiral Resolution, Nonlinear Optical and Luminescence of Eight-Coordinate Lanthanide(III) Complexes

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Materials and Methods:

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Elemental analyses of C, N, and H were carried out on a Vario EL III analyzer. Calcd (%) for $C_{32}H_{12}Cl_3DyN_{12}$: C, 46.12; H, 1.44; N, 20.16. Found: C, 45.47; H, 1.39; N, 19.83.

Solid-state CD spectra were recorded with a JASCO J-810 spectropolarimeter at room temperature. For each CD measurement *ca.* 0.3 mg sample was taken to be mixed with 40 mg of an oven-dried and well ground KCl powder in an agate mortar and subsequent pressing like those used for IR spectroscopy. The baseline correction was performed against the spectrum of a pure KCl disk, prepared under the same conditions. The displayed absorption spectra result from subtraction of this spectrum of a standard KCl disk.

The solid-state luminescence emission spectrum was recorded on a FluoroLog-3 spectrophotometer at room temperature with excitation and emission slits at 2.0 nm, increment 1.0 nm and integration time 0.1 s.

Synthesis of $[DyCl_3(dicnq)_2]_n$ (dicnq = 6,7-dicyanodipyridoquinoxaline) 1 and **1':**

A mixture of $DyCl_3 \cdot 6H_2O$ (190 mg, 0.52 mmol), dicnq (282 mg, 0.1 mmol), acetonitrile (6 mL) and methanol (2 mL) was sealed into a 25-mL polytetrafluoroethylene-lined stainless

steel container under autogenous pressure and then heated at 110 °C for 3 days and cooled at 2 °C h^{-1} to 30 °C. Pale yellow prismatic crystals of $[DyCl_3(dicnq)_2]_n$ were isolated in 53% yield based on $DyCl_3 \cdot 6H_2O$.

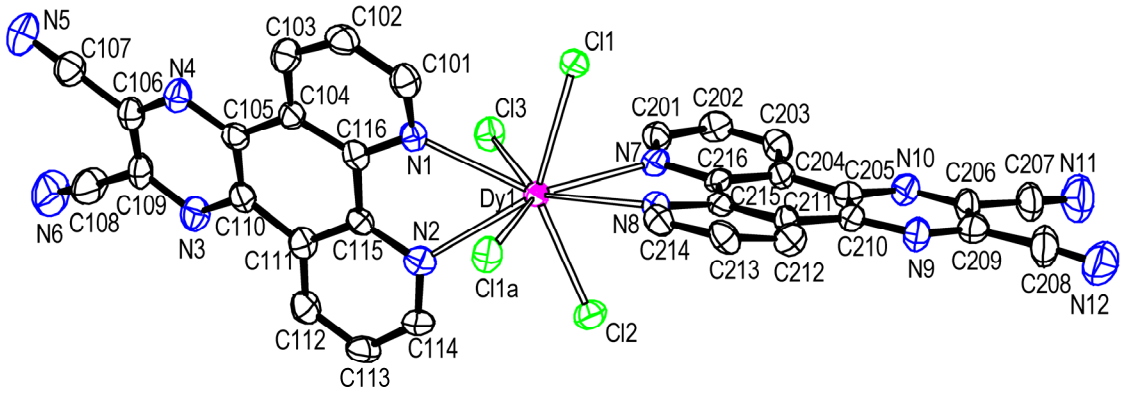


Figure S1. Molecular structure of **1'** with 50% probability displacement ellipsoids. The hydrogen atoms are omitted for clarity. Symmetry code: a = -x,y-1/2,-z+1.

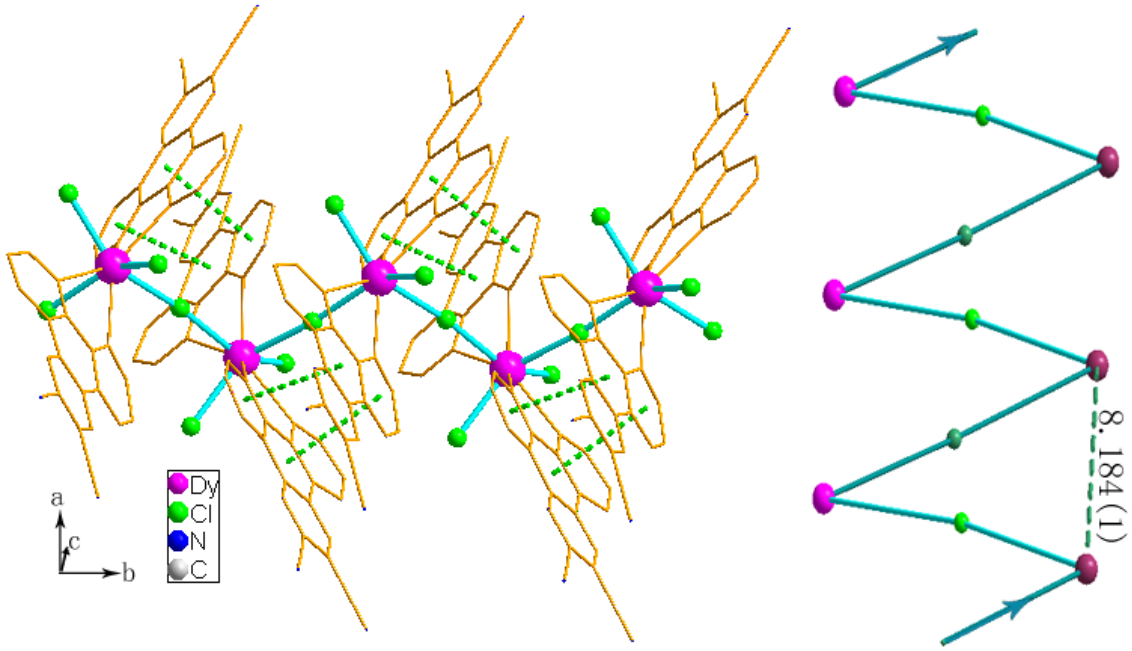


Figure S2. The 1-D chloro-bridging left-handed helical chain of **1'** along the *b* direction with intrachain π-π stacking shown as dashed lines.

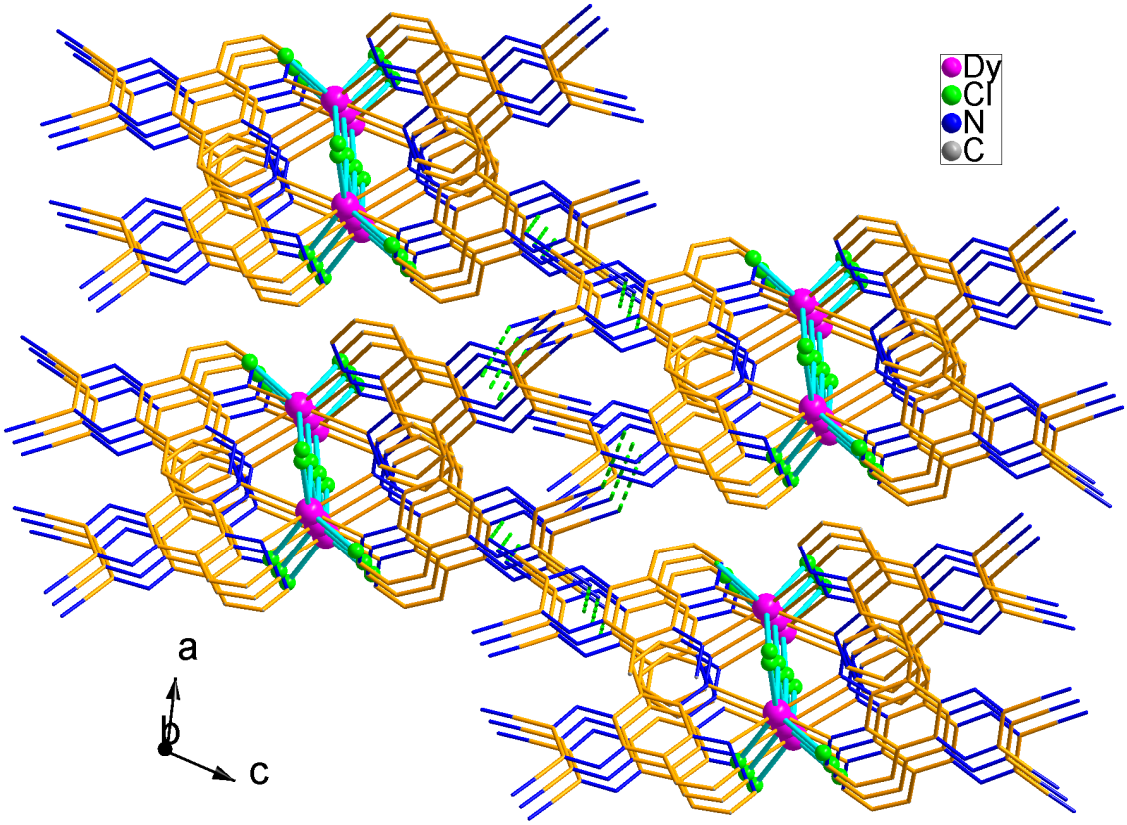


Figure S3. The 3-D supramolecular network of **1'** with C≡N···π close contacts being shown as green dashed lines.

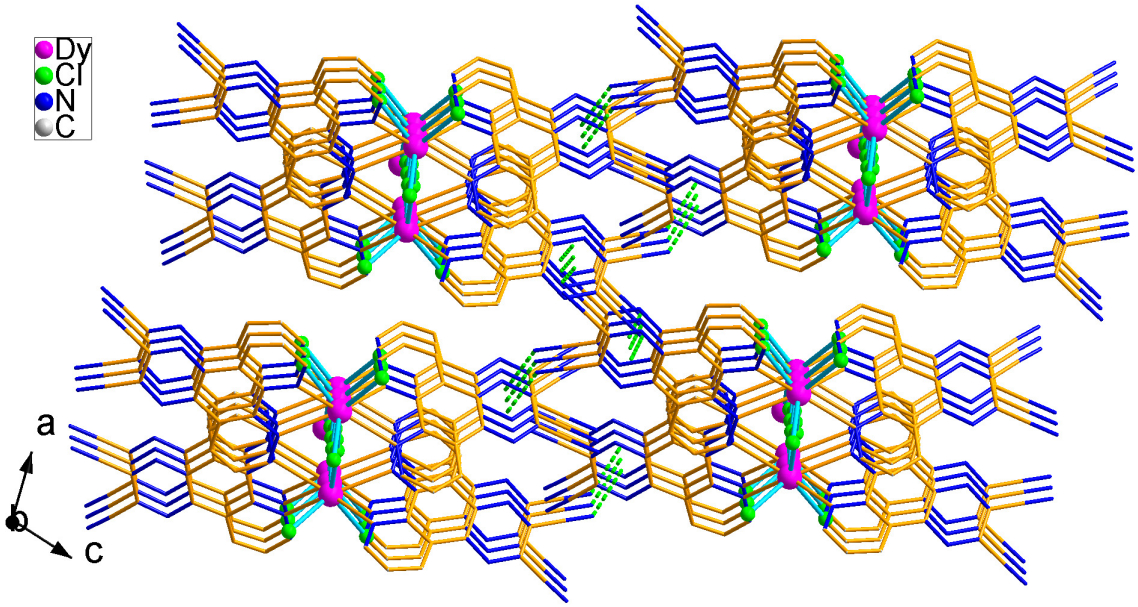


Figure S4. The 3-D supramolecular network of **1** with C≡N···π close contacts being shown as green dashed lines.

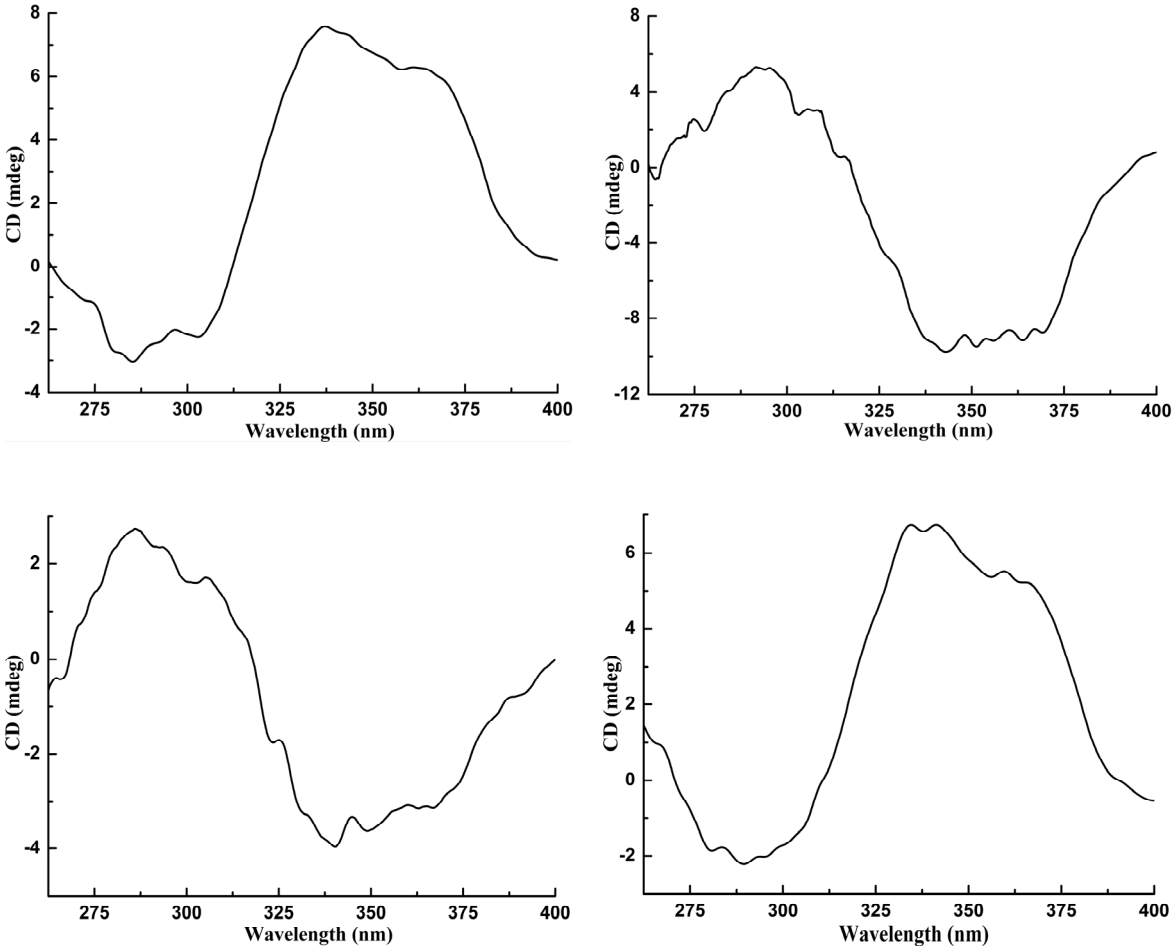
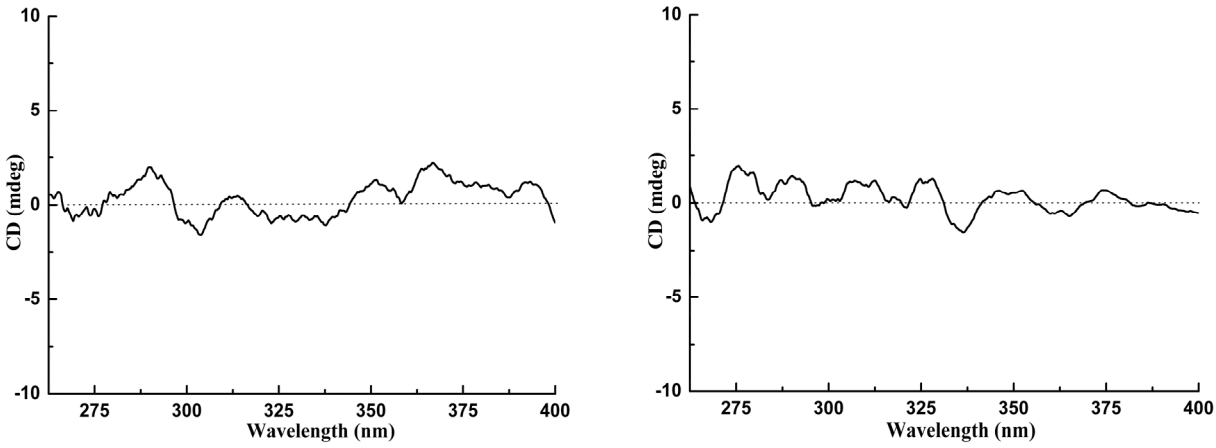


Figure S5. Solid state CD spectra of four bunches of crystals chosen randomly from four crystallizations showing that every bunch is CD-active. For each CD measurement *ca.* 0.3 mg crystalline sample was taken to be mixed with 40 mg KCl powder.



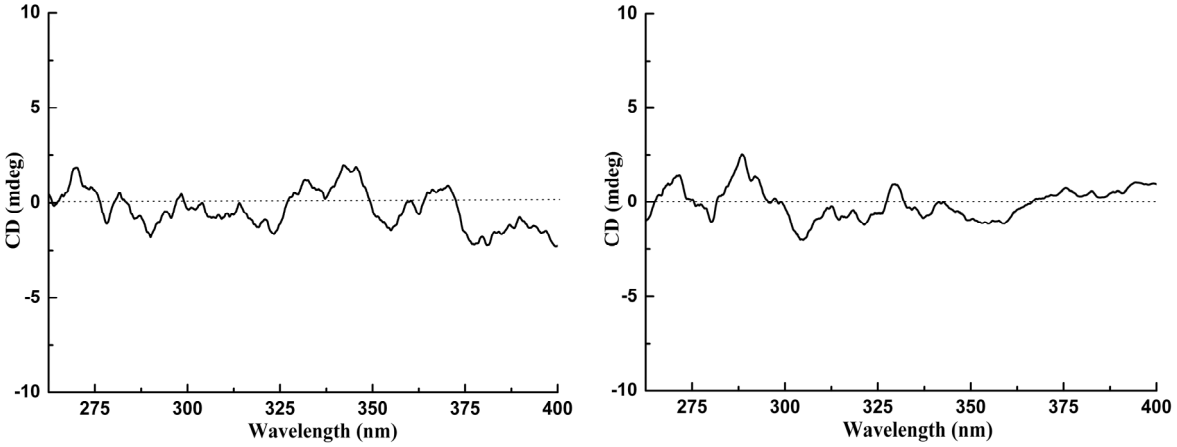


Figure S6. Solid state CD spectra of four powered samples chosen randomly from the total product of 50 crystallizations showing no CD signal. All crystals were well ground, and then *ca.* 0.3 mg powder sample was taken to mix with 40 mg KCl powder for each measurement.