Supplementary Information

Chiral Crystals from Porphyrinoids Possessing a Very Low Racemization Barrier

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Instrumentation:

NMR experiments:

¹H, ¹³C CP MAS and ¹H–¹³C, ¹H–¹H correlation experiments were carried on a Bruker Avance III 600 spectrometer equipped with 1.3mm ¹H/BB (³¹P–¹⁵N) CP MAS probe-head with the ¹H, ¹³C resonance frequencies of 600.13 and 150.90 MHz, respectively. In all experiments sample was spun at 42 kHz. At this spinning speed and when probe was cooled down to 253K, the average sample temperature was 302K (checked by Pb(NO₃)₂ NMR thermometers). CP based experiment was carried out with ZQ-1 Hartman–Hahn matching condition with ramp from 90 to 100% on ¹H channel. For setup we used ¹³C, ¹⁵N uniformly labeled histidine hydrochloride or target sample. ¹H–X inverse detected HETCOR experiment was carried out employing sequence described by Pruski and coworkers.¹ In this case carefully optimization (initial parameters were get from ¹H–X CP MAS experiment) of ¹H RF during first and second CP transfer was done using target sample.

Circular dichroism (CD) spectroscopy:

The solid-state ECD spectrum was obtained using the Diffused Transmission Circular Dichroism (DTCD) mode placed into a Jasco J-815 spectrometer. Freshly prepared pellet (0.61 mg per 100 mg KCl) has been measured according measurements procedure described before² using the following parameters: 200-800 nm measurement range, 50 nm min⁻¹ scanning speed, a step size of 0.5 nm, a bandwidth of 2 nm, a response time of 1 s, and an accumulation of 15 scans. The resulting spectrum was background corrected. Linear dichroism (LD) was also measured and the order in considered measurement range was in the range of $\pm 2.1 \times 10^{-3}$ OD indicating its small impact on measured ECD spectrum.

The solid-state absorption spectrum was collected using a Jasco V-670 UV-Vis-NIR spectrometer equipped with the integrating sphere (Model ISN-723). Diffuse transmission UV spectra were obtained using the following parameters: 200-800 nm measurement range, 50 nm min⁻¹ scanning speed, a step size of 0.5 nm, a bandwidth of 5 nm, a fast response time, and an accumulation of 3 scans.

X-ray:

The diffraction data of form **1** were recorded on Oxford SuperNova single-crystal diffractometer with micro source Cu K α radiation ($\lambda = 1.5418$ Å) with a Titan detector. The crystal diffraction data of form **2** were recorded on Oxford Xcalibur Onyx Nova single-crystal diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). Diffraction data collection, cell refinement and data reduction were performed using the *CrysAlis PRO* program (Oxford Diffraction). The structure was solved by direct methods (*OLEX2* (Dolomanov *et al.*, 2009)) and refined using full-matrix least-squares methods *SHELX97*. The hydrogen atoms ware set geometrically with exception of thus connected to the nitrogens which ware localized on difference Fourier map and then refined as reading.

Experimental section:

Materials:

The corrole was prepared using chemicals which were purchased from Sigma Aldrich and used without further purification. Reagent grade solvents were purchased from Polish Chemicals Reagents and were distilled prior to use. Silica gel columns for chromatography were prepared with silica (Kieselgel 60, 200-400 mesh).

Synthesis and characterization of 5,10,15-tris(pentafluorophenyl)corrole:



Fig. 1. The synthetic route of 5,10,15-tris(pentafluorophenyl)corrole

5,10,15-tris(pentafluorophenyl)corrole was prepared according to the literature methods³ (Fig. 1).

A pre-prepared solution TFA in CH₂Cl₂ (1: 10; 21 μ L) was added to a round bottomed flask containing 2,3,4,5,6-pentafluorobenzaldehyde (185 μ L, 1.5 mmol). Then, a solution of pyrrole (210 μ L, 3.0 mmol) was added to the mixture and vigorously stirred at room temperature for 10 min. The reaction flask was stoppered. The reaction mixture was dissolved in 120 mL CH₂Cl₂ and a solution of DDQ (551.5 mg, 2.4 mmol) in toluene (3 mL) was added to the reaction mixture and energetically stirred. The reaction was protected from light and stirred at room temperature for further 5 min. Subsequently, the solution was passed over a chromatography column (silica, hexane: methylene chloride, 3:2) and further purified by column chromatography (silica, hexane: methylene chloride, 4:1). Solvent evaporation and afforded pure corrole which was recrystallized from mixture of methylene chloride; pentane to give a dark purple crystals (81 mg, 15%). The full structural study of this compound was published.⁴

Crystallization and X-ray structure determination of 5,10,15-tris(pentafluorophenyl) corrole in chiral 1 and achiral 2 crystal forms

The studied compound crystallized in two polymorphic crystal forms. Sample of chiral crystals **1** ($P2_12_12_1$ space group 19) was obtained by very slow isothermic evaporation of deuterated methylene chloride (CD_2Cl_2) at room temperature. Sample **2** ($P2_1/c$ space group 14) was crystallized from a mixture of deuterated methylene chloride (CD_2Cl_2) with pentane (vol:vol 1:1). The morphology of crystal **1** was better and choice of the species for data collection was easy. Form **2** created clusters of thin plate prisms and required separation to obtain a single monocrystal.

Crystallographic data for **1** and **2** have been deposited in the Cambridge Structural Database under accession number CCDC1439086 and CCDC1439085, respectively. The corresponding CIF files are included in the supplementary materials. In both crystal forms the asymmetric unit contains one molecule of 5,10,15-tris(pentafluorophenyl)corrole and two molecules of methylene chloride, and the unit cells are filled with four such assemblies. The carbon hydrogens were set geometrically and refined as riding, the hydrogen atoms connected with nitrogens were found on the difference Fourier map and refined with geometrical restrains. The anisotropic thermal parameters were applied for all nonhydrogen atoms and isotropic for hydrogens, equal to 1.2 of the thermal parameter of their parental atoms. The absolute configuration of **1** was assigned based on the Flack parameter equal to 0.007(7). The chirality was checked for 8 crystals for which the diffraction data was collected in low (100 K) and room temperature; all of them showed the same chirality.

Form **1** crystallizes in one of the most popular group for chiral compounds - $P2_12_12_1and 2$ in the most common centrosymmetric space group - $P2_1/c$. The unit cell dimensions for both crystal forms is determined by crystal packing. In **1** the guest solvent molecules located tightly between parallelly arranged corrole molecules are fully ordered, but in **2** the perpendicular oriented host corrole molecule creates cages where the two guest CD_2Cl_2 molecules have a higher level of freedom. Both molecules show some disorder, although the dominating position and orientation can still be clearly determined. The density of crystal form **1** is slightly higher what may suggest that molecules adopt the required conformation first and then take part in the crystallization process in a chiral lattice arrangement, which is more densely packed.

The observed and calculated structure factors, atoms coordinates and refinement statistics are deposited in Crystallographic Data Center with the deposition number CCDC1439086 and CCDC1439085 for **1** and **2** respectively. A copy of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1233-336033 or e-mail: deposit@ccdc.cam.ac.uk].

NMR spectra:



Fig. 2. ¹H NMR spectrum of a) amorphous sample b) sample **1** and b) sample **2** recorded at spinning speed equal to 42 kHz using 1.3 mm probe.



Fig. 3. ¹³C CP MAS NMR spectrum of a) sample **1** and b) sample **2** recorded at spinning speed equal to 42 kHz using 1.3mm probe.

Reference:

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- 4 W. Bocian, P. Paluch, A. Nowak-Król, D. T. Gryko, M. J. Potrzebowski, J. Śniechowska, J. Sitkowski, E. Bednarek and L. Kozerski, *Magn. Reson. Chem.* 2015, **53**, 167-171.