

Uranyl ion coordination polymers with the dibenzobarrelene-based *rac*- and (*R,R*)-*trans*-9,10-dihydro-9,10-ethanoanthracene-11,12- dicarboxylate ligands

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Supporting Information

Synthesis of the ligands

Racemic 11*R,12*R**-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (*rac*-**deadcH₂**).**¹ A mixture of anthracene (12.48 g, 70.0 mmol) and fumaric acid (2.71 g, 23.3 mmol) in dry 1,4-dioxane (100 mL) was refluxed for 72 h under a nitrogen atmosphere. After cooling the reaction mixture down to ambient temperature, the solvent was evaporated off under reduced pressure. Saturated aqueous NaHCO₃ solution (50 mL) was added to the residue and the mixture stirred overnight. Unreacted anthracene was removed by extraction with ethyl acetate, the aqueous phase then acidified with 2.0 M HCl (to pH = 1) and the white solid deposited was filtered off, washed with water and dried at 70 °C (6.4 g, 93%). (Note that this procedure is derived from the supplementary information of ref. 1).

(11*R*,12*R*)-(+)-9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (*R,R*-deadcH₂**) and its enantiomer (*S,S*-**deadcH₂**).**² 11*R**,12*R**-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (6.4 g, 21.75 mmol) and *L*-proline (2.6 g, 22.58 mmol) were dissolved in methanol (70 mL) at 50 °C and stirred for 4 h at ambient temperature. The reaction mixture was left to cool overnight,

giving a precipitate of needle-like crystals, which were collected by filtration, and the filtrate was stored separately for use in the subsequent step. The first-deposited crystals were washed with cold methanol and recrystallized 3 times from hot methanol to give pure diastereomer, which was added to a mixture of water (50 mL) and diethyl ether (50 mL). The mixture was stirred for 2 h at ambient temperature, the phases separated and the aqueous layer further extracted with diethyl ether (30 mL \times 3). The combined ethereal layer was washed with brine (20 mL) before drying over MgSO₄. The solvent was evaporated under reduced pressure and the residue dried under vacuum to give optically pure (11*S*,12*S*)-(–)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid as a white powder (1.4 g, 22%). The filtrate stored in the previous step was slowly evaporated at ambient temperature to produce block-like crystals, which were filtered off and washed with cold methanol before their dissolution in a mixture of water (50 mL) and diethyl ether (50 mL). The mixture was stirred for 2 hours, the phases separated and the aqueous layer further extracted with diethyl ether (30 mL \times 3). The combined ethereal extracts were washed with brine (20 mL) then dried over MgSO₄. The solvent was evaporated under reduced pressure and the residue dried under vacuum to give (11*R*,12*R*)-(+)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (1.7 g, 27%).

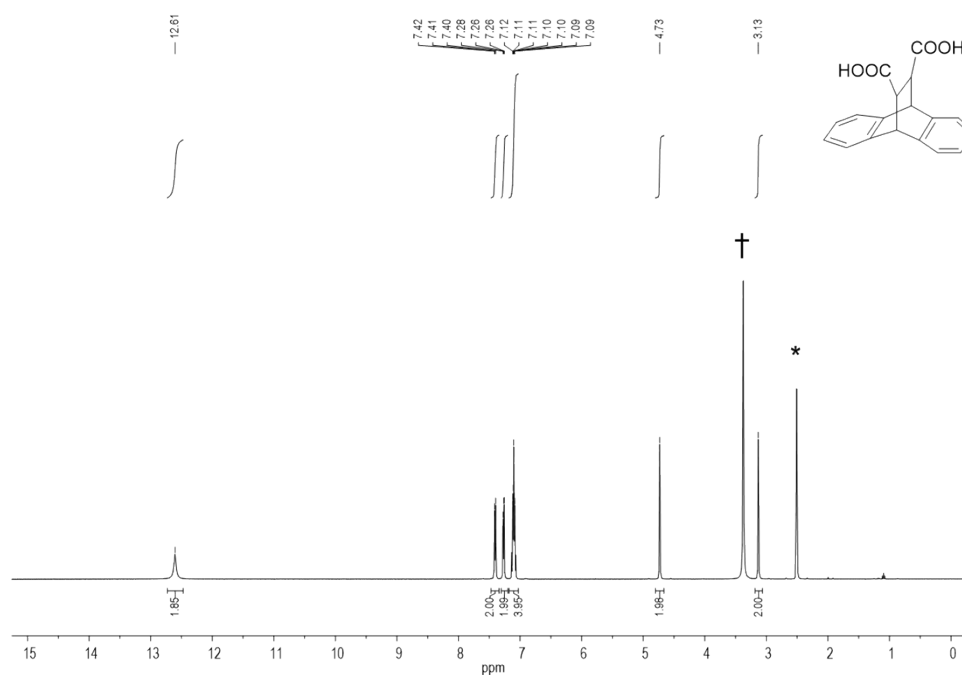


Fig. S1 ¹H NMR spectrum of 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid in DMSO-d₆ (* from CD₃SOCD₂H and † from water).

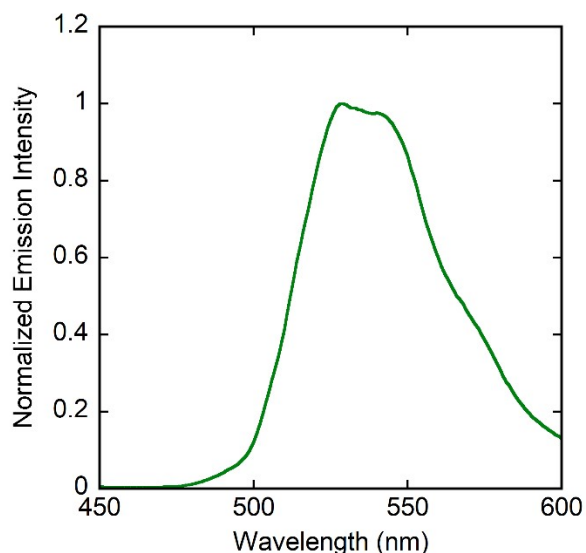


Fig. S2 Emission spectrum of complex **3** in the crystalline state upon excitation at 420 nm.

Table S1 Selected dihedral angles in the dicarboxylate motif ($^{\circ}$) and intercarboxylic/ate C \cdots C separation (\AA) in complexes **1–8** and in various deadCH $_n$ species.

	C–C–C–C	H–C–C–H	(O ₂)C–C–C–C(O ₂)	O ₂ C \cdots CO ₂
1	4.4	133.4	99.8	3.445(6)
2	2.5	134.2/126.5	100.9/117.6	3.468(3)/ 3.713(4)
3	4.0/7.1	134.4/134.9	99.2/100.0	3.46(2)
4	7.0	128.8/131.9	110.8/105.9	3.673(7)/3.468(7)
5	3.6	132.9	101.1	3.456(9)
6	5.5	137.7	127.0	3.694(3)
7	3.2/5.9	120.3/129.6	120.8/111.2	3.672(5)/3.575(7)
8	9.0/6.2	137.7/132.3	97.8/109.0	3.478(3)/3.618(4)
Model Chem3D	3.3	129.4	106.2	3.523
Complexes from the CSD ^a	0.1–13.7	117.8–144.2	88.3–117.8	3.340–3.623

^a Cambridge Structural Database, ver. 5.44. CCDC numbers 908951, 908955, 1168948, 1887850, 1880177, 1253506–1253508, 1261319, 2077286, 2150101–2150279, and 2210049–2211198.

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