Highly ordered luminescent calix[4]azacrown films showing an emission response selective to volatile tetrahydrofuran

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Single Crystal Growth and X-ray Diffraction

Slow diffusion of methanol into an acetonitrile solution of **2** previously heated to reflux produces crystals **2a** (**2**•CH_3CN•CH_3OH). Colorless plate crystals were selected for X-ray analysis. Data collection was carried out in a Bruker-Nonius Kappa APEX II diffractometer equipped with a CCD area-detector,[1] using a suitable single crystal glued on top of a glass fiber. A fine-focus sealed X-ray tube followed by a graphite monochromator were used to provide incident radiation of mean wavelenght 0.71070 Angstrom (Mo Kalpha). Starting unit cell and orientation matrix were determined prior to data collection. Final cell refinements were performed using SAINT or Denzo and Scalepak (HKL2000 package).[2, 3] Absorption correction was carried out with the multi-scan algorithm.[4] SHELXS97 and SHELXL97[5] were used to solve and refine the structures, respectively. SHELXL97 and PLATON[6] were also useful in the preparation of material for publication. CCDC 1003653 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

A summary of further crystallographic and structure refinement information is given in table S1.

Table S1 Crystal data and structure refinement for **2a**.

Compound	**2a**
Empirical formula	$C_{59}H_{79}N_3O_{11}$
Molecular weight	1001.93
Crystal size	0.3 x 0.3 x 0.1 mm
a (Å)	11.1992(4)
b (Å)	12.9239(5)
c (Å)	21.1547(7)
α (deg.)	91.865(2)
β (deg.)	103.252(2)
γ (deg.)	114.341(2)
Unit cell volume	2687.4(2)
F000	1079
Data collection temperature	100(2)
Theta max	27.5
Total reflections	41232
Unique reflections	9798
Reflections I>2sigma	6122
R_{int}	0.073
GooF	1.079
R1	0.0822
wR2	0.2279
Refined parameters	717
Restraints	6

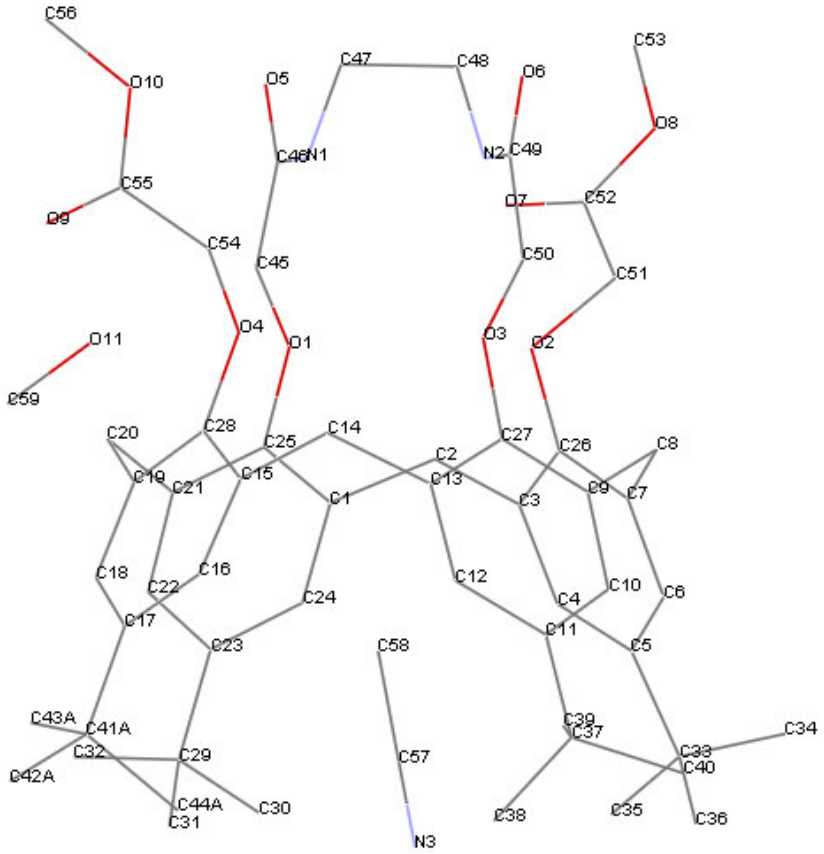

Figure S1. Crystal structure of **2a** with atom numbering.

Parameters of the Conformation of 2 and the geometry of the azacrown bridge in Crystal 2a

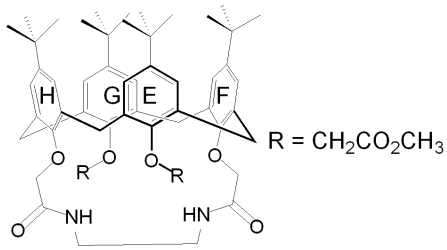

Table S2 Parameters of the conformation of **2**.

φ_{EM}[a]	φ_{FM}	φ_{GM}	φ_{HM}	φ_{EG}	φ_{FH}	O•••O distance[b]	N•••N distance[b]
64.66	64.96	66.70	63.58	48.88	50.97	O1•••O3 4.49(4) O2•••O4 4.51(4)	2.86(5)

[a] dihedral angle (º) between the planes E and M (mean plane defined by the methylene carbon atoms)
[b] distance (Å)

The torsion angles which characterize the geometry of –NH–$(CH_2)_2$–NH– bridge are, respectively, -106.3 (4)º, -54.8(5)º, and -108.9(4)º.

The torsion angles which characterize the geometry of the pendant arms –O–CH_2–CO–OCH_3 are, respectively, 168.1(3)º and -144.9(3)º.

Intermolecular interactions stabilizing the crystal lattice in 2a

The overall J-dimer units framework is sustained by strong O–H•••O hydrogen bond [C(46) – O(5)•••H(11) – O(11) 1.93 Å] and weak C–H•••O hydrogen bond network involving oxygen amide and ester [C(54) – H(54B)•••O(11) – C(59) 2.36 Å, , C(56) – H(56B)•••O(5) – C(46) 2.70 Å, C(18) – H(18)•••O(9) – C(55) 2.69 Å, C(14) – H(14B)•••O(7) – C(52) 2.65 Å, and C(32) – H(32A)•••O(10) – C(55) 2.69 Å]. Additionally, H•••H dihydrogen bonds [C(53) – H(53B)•••H(35C) – C(35) 2.32 Å, C(40) – H(40C)•••H(35A) – C(35) 2.34 Å, and C(56) – H(56C)•••H(31B) – C(31) 2.22 Å].

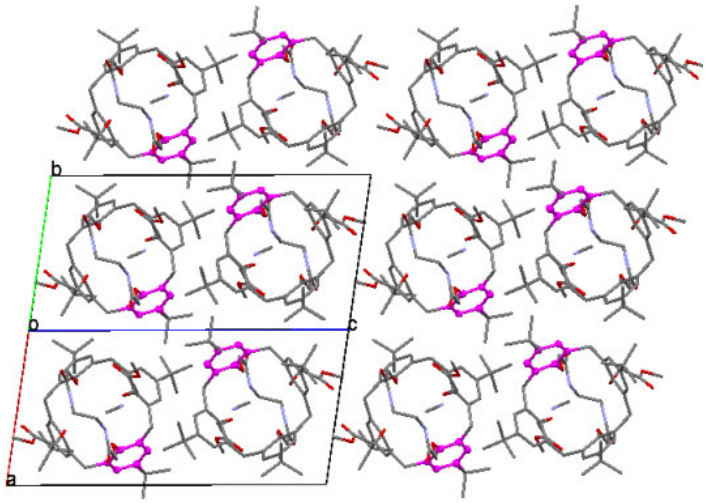

Figure S2. Crystal packing showing the network of dimer units in **2a**.

References

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4. G. M. Sheldrick, Bruker AXS Inc., Madison, Wisconsin, USA, SADABS 2.10 edn., 2003.

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6. A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148-155.