Facile access to a series of large polycondensed pyridazines and their utility for the supramolecular synthesis of coordination polymers†

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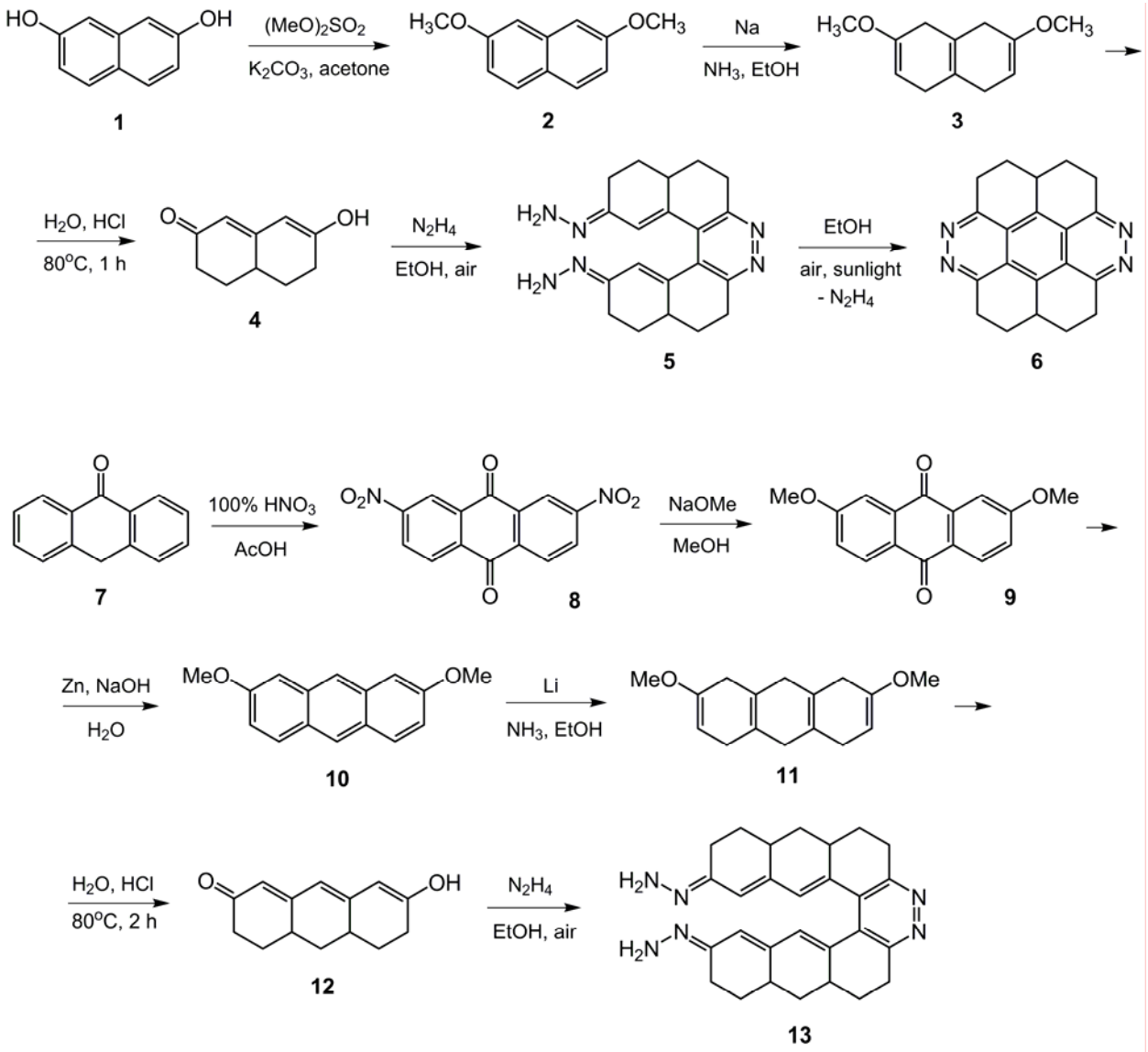
Contents:

1. Organic Syntheses:



Bi- and tricyclic ketoenols (**4** and **12**) were prepared by multi-stage syntheses starting with commercially available 2,7-dihydroxynaphthalene and anthrone, respectively. This strategy was based upon a literature synthetic scheme (U. Lawrentz, W. Grahn, K. Lukaszuk, C. Klein, R. Wortmann, A. Feldner and D. Scherer, *Chem. Eur. J.* 2002, **8**, 1573), with the appropriate preparative modifications.

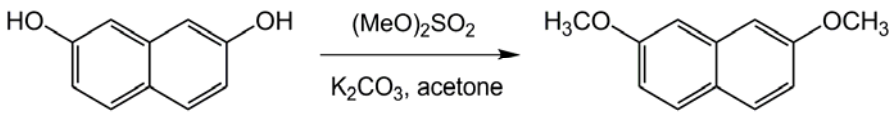
In both the cases, the key stage was Birch reduction of dimethoxyaromatic species in liquid ammonia/ ethanol media (THF as a suitable co-solvent). 2,7-Dimethoxynaphthalene undergo the reduction very smoothly and cleanly, under standard conditions with using of sodium metal. For 2,7-dimethoxyanthracene, this method was insufficient and led to a mixture of hexahydroanthracene **11** and partially reduced products. In this case the reduction was successful

with utilization of lithium metal. Acid hydrolysis of the reduced species **3** and **11** is accompanied with migration of double bonds yielding conjugated ketoenols.

Preparation of 2,7-dimethoxyanthracene was based upon dinitration of anthrone (yielding corresponding dinitroanthraquinone) followed by nucleophilic substitution by methoxide. Clemmensen reduction of 2,7-dimethoxyanthraquinone proceeds very smoothly (Martin modification, with addition of toluene).

Full preparative details are presented below.

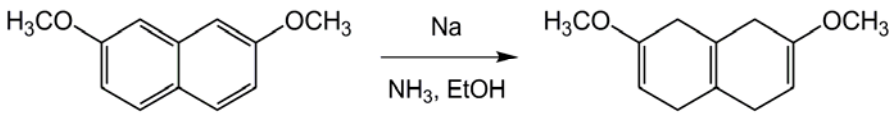
1.1. Preparation of 2,7-dimethoxynaphthalene.



25.00 g (0.156 mol) of 2,7-dihydroxonaphthalene was dissolved in 500 mL acetone. Then 87 g (0.63 mol) of powdered K_2CO_3 and 37.5 mL (50.0 g, 0.397 mol) of dimethylsulfate were added and the mixture was stirred under reflux for 10 h. It was cooled to r.t., 600 mL of water was added with stirring and, after dissolution of inorganic salts, the colorless deposit was filtered. It was washed with 3 × 100 mL of water and dried in air. Yield: 28.88 g (98.3%).

Pure material was obtained after recrystallization from methanol. *Anal.* for $C_{12}H_{12}O_2$. Calc. (%): C, 76.57; H, 6.43. Found: C, 76.66; H, 6.34%.

1.2. Preparation of 2,7-dimethoxy-1,4,5,8-tetrahydronaphthalene.



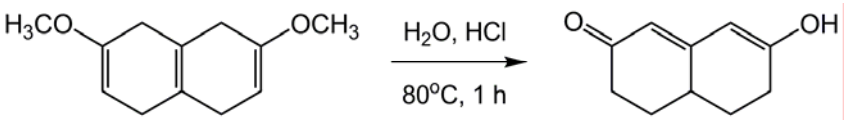
The syntheses 1.2 and 1.3 were based upon method of P. Radlick (*J. Org. Chem.*, 1965, **30**, 3208), with certain modifications.

The 2 L three-necked round-bottom flask, equipped with adapter for condensation of liquid ammonia, low-temperature termometer, gas introduction inlet and powerfull teflon-covered magnetic stirring bar, was cooled to -60°C in a acetone/liquid nitrogen bath. After 800-850 mL of dry liquid ammonia was condensed into the flask, a solution of 22.5 g (0.12 mol) 2,7-dimethoxynaphthalene in 150 mL of dry THF was added dropwise followed by addition of 90 mL dry of ethanol. The mixture was cooled to -65±5°C and 15.0 g (0.65 mol) of Na metal was

added in small portions for a period of 3 h, with efficient stirring. After dissapearance of a blue color, the cooling bath was removed and liquid ammonia was allowed to evaporate for several hours. The residue was diluted with 1.5 L of water. The crystalline deposit was filtered, dried in air and recrystallized from 120 mL of methanol yielding 16.9 g (74%) of pure product (colorless needles, m.p. = 67-68°C).

Anal. for $C_{12}H_{16}O_2$. Calc. (%): C, 74.97; H, 8.39. Found: C, 75.16; H, 8.44%.

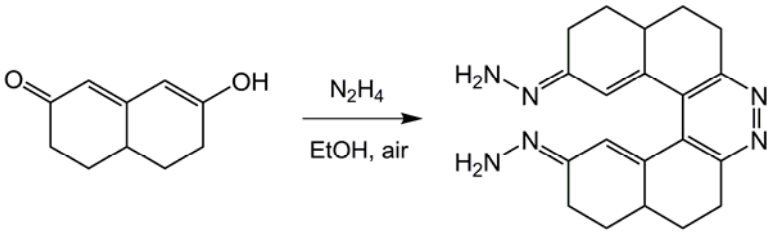
1.3. Preparation of $\Delta^{9,10}$-octaline-2,7-dione.



2.98 g (15.5 mmol) of 2,7-dimethoxy-1,4,5,8-tetrahydronaphthalene was added to dilute HCl solution (4.5 mL of concentrated HCl and 40 mL of water) and the mixture was heated with stirring at 80-85°C for 1 h. Clear yellow solution was cooled to r.t. and pale-yellow crystalline deposit of the product was filtered, washed with three 10 mL portions of water and dried in air. Yield: 2.23 g (87%).

Anal. for $C_{10}H_{12}O_2$. Calc. (%): C, 73.14; H, 7.37. Found: C, 73.01; H, 7.50%.

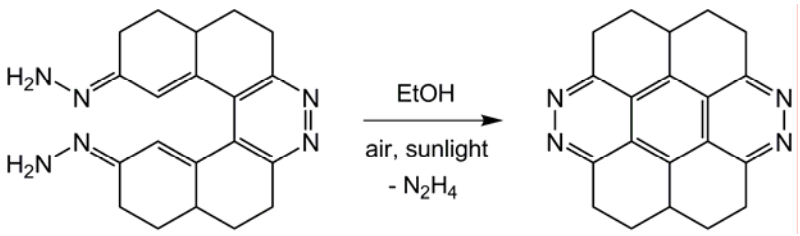
1.4. Preparation of 1,2,6,6a,7,8,14,14a-octahydrobenzo[*f*]naphtho[2,1-*c*]cinnoline-9,12(5*H*,13*H*)-dihydrazone.



Solution of $\Delta^{9,10}$-octaline-2,7-dione (2.20 g, 13.4 mmol) in 80 mL of dry ethanol was added dropwise within 1 h to 4.0 mL of 100% $N_2H_4 \cdot H_2O$ (82 mmol) in 20 mL of dry ethanol with stirring and cooling to 0°C. Deep-red color of the mixture was developed immediately. The mixture was stored overnight at 0°C, after which the solution was evaporated under reduced pressure to a volume of 30 mL. The resulting deep-red solution was left for 20-25 d at r.t. in a open 100 mL flask granting free contact with air. The product (solvate with 0.5 ethanol and 0.5 water) crystallizes as large deep-red blocks in a 1.79 g (70%) yield.

Anal. for $C_{42}H_{56}N_{12}O_2$. Calc. (%): C, 66.28; H, 7.42; N, 22.09. Found: C, 66.42; H, 7.29; N, 22.24%.

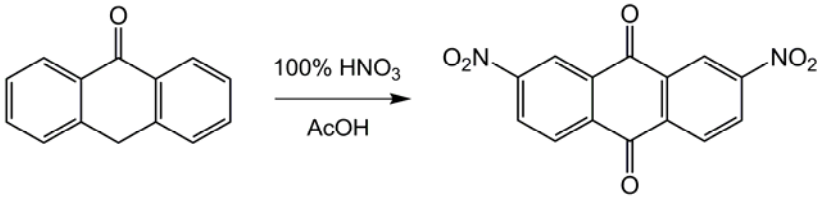
1.5. Preparation of 3,4,4a,5,6,9,10,10a,11,12-decahydroanthra[1,9,8-*cdef*:5,10,4-*c'd'e'f'*]dicinnoline.



The above dihydrazone (1.32 g, 3.5 mmol; solvate with 0.5 water and 0.5 ethanol) was stirred in 40 mL of 95% ethanol in a open 100 mL Pyrex flask when being exposed to a direct sunlight until a total dissolution was observed within a period of 3-4 d. The clear, almost colorless, solution was slowly evaporated at r.t. to a volume of 6-7 mL and the pale-yellow needles of *N*$_4$*cor*·2H$_2$O were filtered, washed with ether and dried (1.13 g, 93%).

Anal. for $C_{20}H_{22}N_4O_2$. Calc. (%): C, 68.55; H, 6.33; N, 15.99. Found: C, 68.37; H, 6.49; N, 15.82%.

1.6. Preparation of 2,7-dinitroanthraquinone.



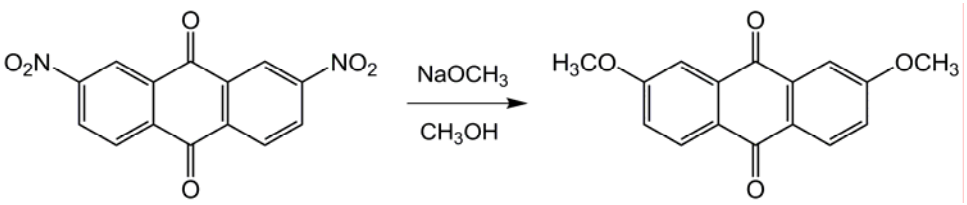
The synthesis was based upon the literature method (P. J. Perry, A. P. Reszka, A. A. Wood, M. A. Read, S. M. Gowan, H. S. Dosanjh, J. O. Trent, T. C. Jenkins, L. R. Kelland and S. Neidle, *J. Med. Chem.*, 1998**, 41**, 4873).

Anthrone (23.0 g, 0.118 mol) was added in small portions within 1.5 h to 150 mL of 100% HNO_3 (obtained by a slow Vigreux destillation of a mixture of 350 mL 85% HNO_3 and 700 mL concentrated H_2SO_4; b.p. = 83-85^{o}C) under stirring and efficient ice/NaCl cooling (internal temperature 0-3^{o}C). The cooling bath was removed and the mixture was allowed to warm slowly to r.t., after which it was poured into 450 mL of glacial AcOH.

This mixture was stored in a flask granting free gas outlet for 15 d and then the light-yellow deposit was filtered, washed with glacial acetic acid and hexane and dried. It was dissolved in 1.0 L of boiling AcOH and refluxed for 3 h, until evolution of nitrogen dioxide ceased. When cooled, the filtered solution deposites pure light-yellow crystalline 2,7-dinitroanthraquinone. The yield was 20.9 g (59%).

Anal. for $C_{14}H_6N_2O_6$. Calc. (%): C, 56.38; H, 2.03; N, 9.40. Found: C, 56.33; H, 1.87; N, 9.23%.

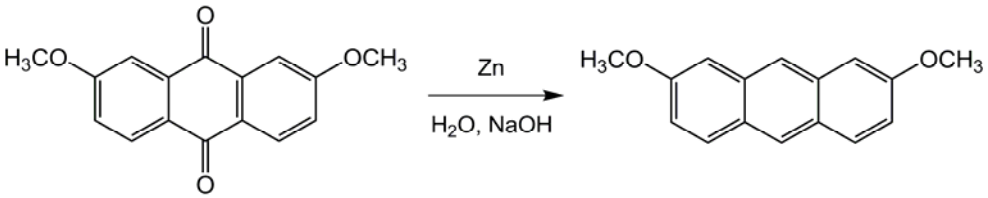
1.7. Preparation of 2,7-dimethoxyanthraquinone.



10.1 g (0.44 mol) of Na metal was dissolved in 700 mL of dry methanol and this solution was added dropwise within 1 h at a reflux temperature to a well-stirred suspension of 30.0 g (0.10 mol) 2,7-dinitroanthraquinone in 1.2 L of dry methanol. The mixture was stirred and vigorously refluxed for 3 h, after which it was left overnight. Yellow solid was filtered, washed with methanol and hexane and air-dried giving 24.4 g (91%) of crude 2,7-dimethoxyanthraquinone. Pure product (bright-yellow crystalls) was obtained after recrystallization from 400 mL toluene (15.0 g, 56%). M.p. = 212-213°C.

Anal. for $C_{16}H_{12}O_4$. Calc. (%): C, 71.63; H, 4.51. Found: C, 71.49; H, 4.37%.

1.8. Preparation of 2,7-dimethoxyanthracene.



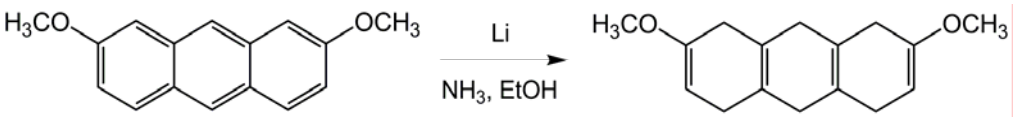
90.0 g (1.37 mol) of Zn powder was added to a solution of 0.12 g $CuSO_4 \cdot 5H_2O$ in 100 mL water and stirred for 20 min. Then a solution of 38.4 g NaOH in 500 mL water was added followed by addition of 12.0 g (0.045 mol) of 2,7-dimethoxyanthraquinone and 200 mL toluene. The mixture was heated in an oil-bath under a gentle reflux and efficient stirring, in a slow stream of argon, for 60 h. The cherry-red color of the mixture (developed after first 3-4 h of the reaction) turns to orange within 20-24 h and then to light-yellow after 50-55 h.

The toluene layer was separated while hot and the remainder was 5 times extracted with 200 mL portions of warm benzene. The combined organic extracts were evaporated under reduced pressure giving a yellow-brown residue. This material was triturated with 50 mL of hot

acetonitrile, filtered and carefully washed with 3 × 20 mL acetonitrile and dried in air to yield 7.8 g (73%) of pale-yellow fluorescent crystals of 2,7-dimethoxyanthracene.

Anal. for $C_{16}H_{14}O_2$. Calc. (%): C, 80.65; H, 5.92. Found: C, 80.26; H, 5.86%.

1.9. Preparation of 2,7-dimethoxy-1,4,5,8,9,1-hexahydroanthracene.



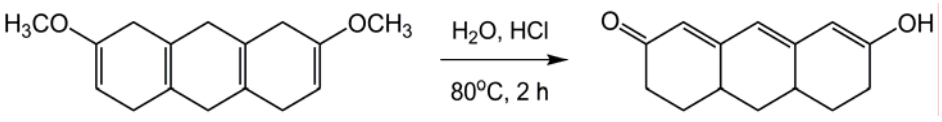
For preparation of the following compounds (syntheses 1.9 and 1.10), we have developed compilation of two literature procedures (G. Heilig und W. Lüttke, *Chem. Ber.*, 1987, **120**, 1863; Yu. L. Slominskii, A. L. Skulbidenko and A. I. Tolmachev, *Zhurn. Org. Khimii* (*Russ. J. Org. Chem.*), 1975, **11**, 392).

1 L flask was cooled to -40°C in a acetone/liquid nitrogen bath and 200 mL of dry ammonia (dried by passing NH_3 gas through 1 m column charged with granulated KOH) was condensed using standard adapter charged with acetone/liquid nitrogen mixture. 0.95 g (137 mmol) of Li metal was added in small pieces with stirring and, after dissolution of lithium, 4.00 g (16.8 mmol) of 2,7-dimethoxyanthracene in 170 mL of dry THF was added dropwise within 1 h and the mixture was stirred for one more hour at -40°C. Then it was cooled to -60°C, 20 mL of dry ethanol was added dropwise followed by addition of 0.96 g (138 mmol) Li metal in small pieces within next 2 h. Efficient stirring of the mixture (at -60°C) was continued until dissappearance of blue color, then 14.0 g (262 mmol) of solid NH_4Cl was added, cooling bath removed and ammonia allowed to evaporate for several hours.

The residue was diluted with 700 mL ice-cold water, stirred for 1 h and the crude product (3.98 g, 97%) was filtered, washed with water and air-dried. It was purified by recrystallization from 60 mL of heptane (partial evaporation of the filtrate is required) giving 3.27 g (80%) of colorless crystalline material.

Anal. for $C_{16}H_{20}O_2$. Calc. (%): C, 78.65; H, 8.25. Found: C, 78.37; H, 8.22%.

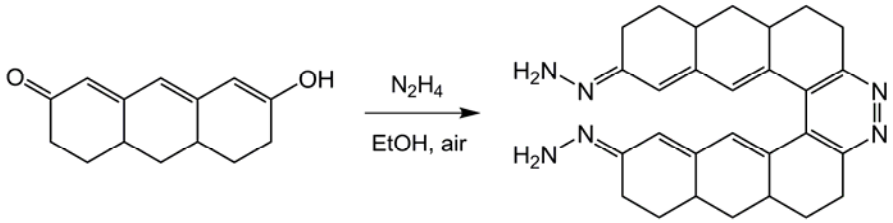
1.10. Preparation of 7-hydroxy-4,4a,5,6,10,10a-hexahydroanthracene-2(3*H*)-one.



A mixture of 5.0 mL concentrated HCl and 40 mL of water was heated in a oil-bath to 80-85°C and 3.27 g of the above solid dimethoxy substrate was added in small portions within 1 h under vigorous stirring. The stirring was continued for 2 h at 80°C and then the mixture was cooled and filtered. The product (yellow powder) was washed with 2 × 10 mL of water, 10 mL of ethanol and dried in air. The yield is quantitative: 2.89 g.

Anal. for $C_{14}H_{16}O_2$. Calc. (%): C, 77.75; H, 7.46. Found: C, 77.89; H, 7.51%.

1.11. Preparation of 1,2,6,6a,7,7a,8,9,17,17a,18,18a-dodecahydroanthra[2,1-*c*]naphtho[2,3-*f*]cinnoline-10,15(5*H*,16*H*)-dihydrazone.



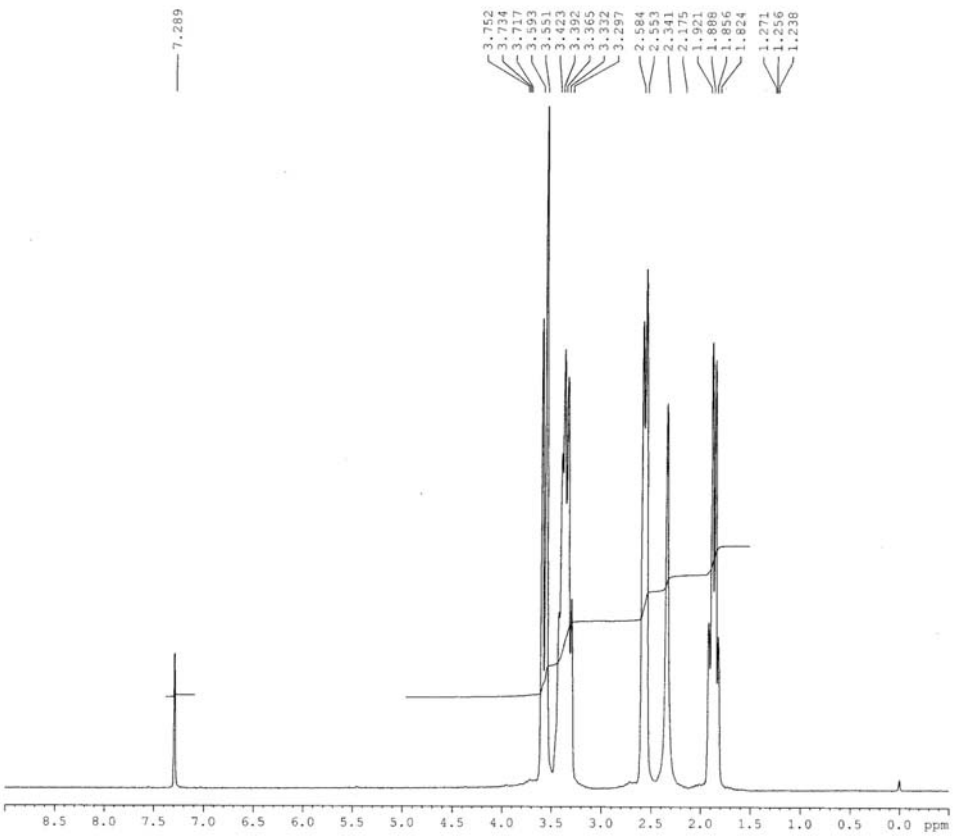
Suspension of 2.86 g (13.2 mmol) of the above ketoenol in 500 mL of dry ethanol (about half of the compound dissolves in this amount of the solvent) was added in small portions within 2 h to a solution of 7.4 mL (7.55 g, 236 mmol) of dry hydrazine in 20 mL of dry ethanol, under efficient stirring and cooling to 0-5°C. Deep-red color of the mixture, with strong green fluorescence, was developed immediately. The fluorescence dissapears after 2 h of stirring. The mixture was left overnight at 0°C and then it was evaporated under reduced pressure to a volume of 70-80 mL. The resulting deep-red solution was left for 20-25 d at r.t. in a open 100 mL flask granting free contact with air, after which red-black crystalline product was filtered, repeatedly washed with ethanol and for short time dried in air (readily loses solvate ethanol molecule within 1-2 h; the crystals then became opaque). The yield was 1.55 g (47%).

Anal. for $C_{30}H_{38}N_6O$. Calc. (%): C, 72.25; H, 7.68; N, 16.86. Found: C, 72.44; H, 7.89; N, 16.61%.

Microanalysis data for coordination compounds:

Anal. for $[Cu_2I_2(N_4cor)]\cdot CH_3CN\cdot CHCl_3$ (**4**), $C_{23}H_{22}Cl_3Cu_2I_2N_5$. Calc. (%): C, 32.28; H, 2.59; N, 8.19. Found: C, 32.16; H, 2.71; N, 7.95%.

Anal. for $[Cu_2Cl_2(N_4cor)]\cdot 4CH_3CN$ (**5**), $C_{28}H_{30}Cl_2Cu_2N_8$. Calc. (%): C, 49.70; H, 4.47; N, 16.57. Found: C, 49.36; H, 4.38; N, 16.21%.

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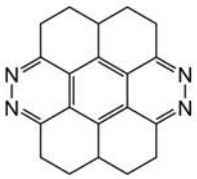

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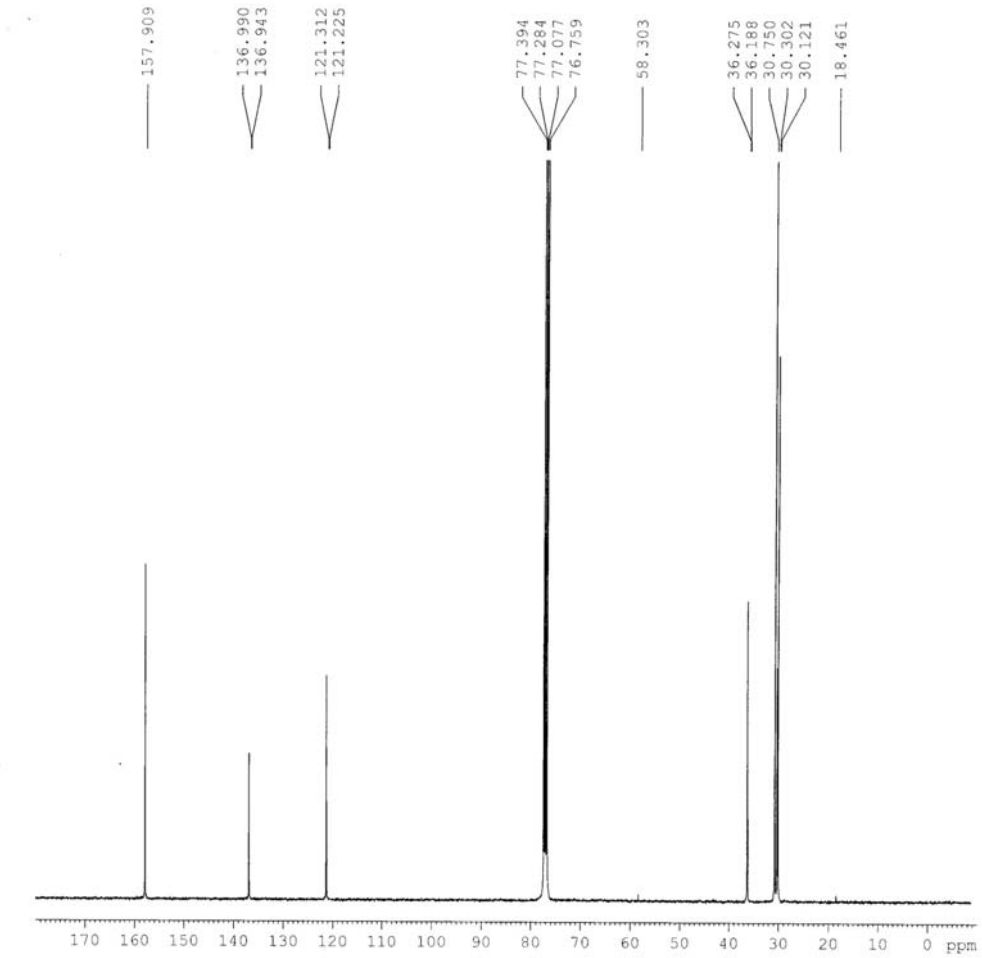
Solv = $CDCl_3$

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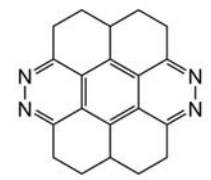
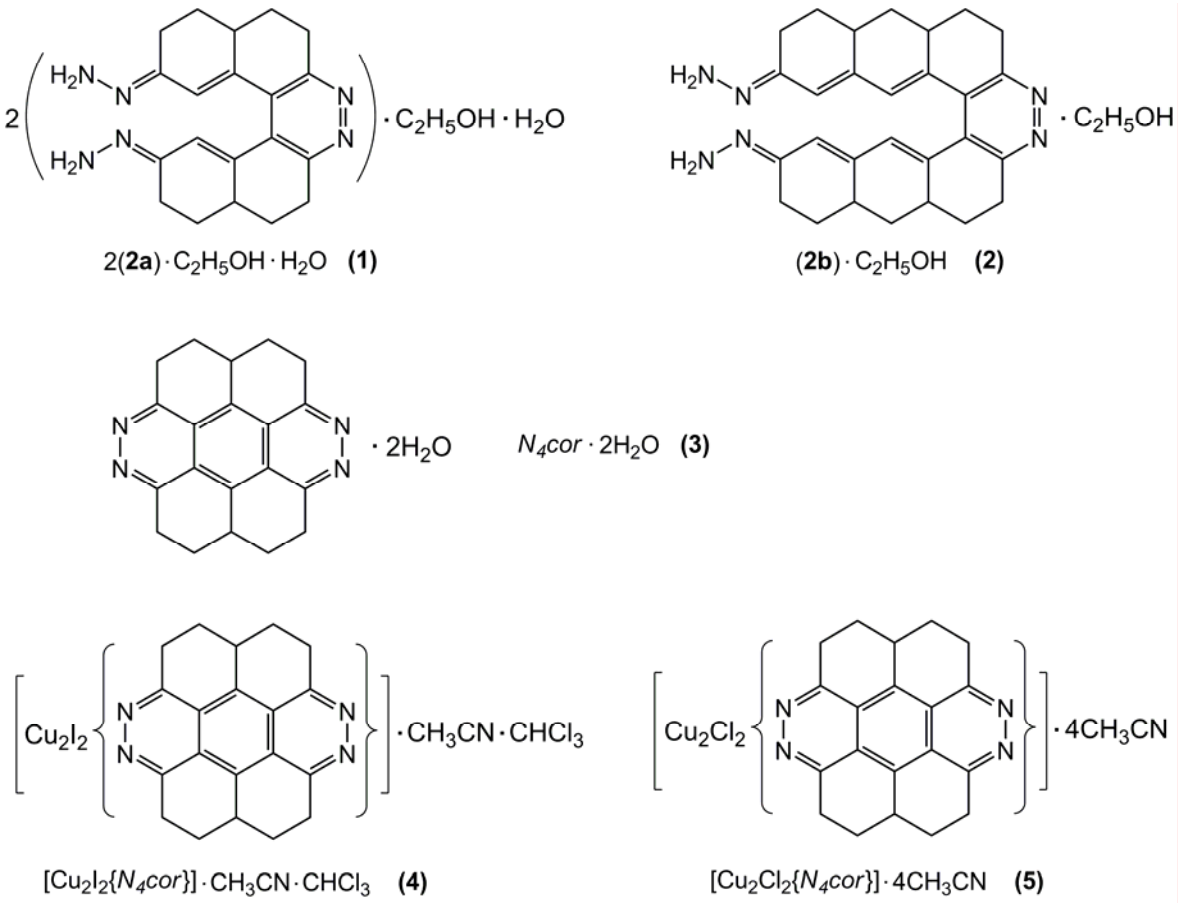


NMR ^{13}C
Solv = $CDCl_3$

NMR spectra of the final coronene-like polycyclic product.

2. Details for the crystal structure refinements



2.1. Data collection.

Crystallographic measurements were made at 213 K using a *Stoe Image Plate Diffraction System* (for **1**, **3** and **5**, numerical absorption correction using X-RED and X-SHAPE) (Stoe & Cie. *X-SHAPE*. Revision 1.06. Stoe & Cie GmbH, Darmstadt, Germany, 1999; Stoe & Cie. *X-RED*. Version 1.22. Stoe & Cie GmbH, Darmstadt, Germany, 2001) and at 100 K using a *Bruker APEXII* CCD area-detector diffractometer for **2** and **4** (φ scans) with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz-polarization effects and for the effects of absorption (multi-scans method).

2.2. Calculations

The structures were solved by direct methods and refined in anisotropic approximation using SHELXS-97 and SHELXL-97 (G. M. Sheldrick, SHELX97, A system of computer

programs for X-ray structure determination, University of Göttingen, Göttingen, Germany, 1997; G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467).

Graphical visualization of the structures was made using the program Diamond 2.1e (K. Brandenburg, *Diamond 2.1e*, Crystal Impact GbR, Bonn, 1999).

The topological analysis of the framework structures **4** and **5** was performed using TOPOS 4.0 (V. A. Blatov, TOPOS, *IUCr CompComm Newsletter*, 2006, **7**, 4; V. A. Blatov, A. P. Shevchenko and V. N. Serezhkin, *J. Appl. Crystallogr*., 2000, **33**, 1193).

2.3. Refinement of 2(2a)·EtOH·H_2O (1).

Crystals of the compound exhibit pseudo-merohedral twinning emulating monoclinic *C* lattice with the unit cell dimensions: a = 20.489, b = 10.711, c = 18.616 Å; β = 105.2°. It was possible to solve the structure in space group *C*2/*c*. However, the subsequent refinement led to a poor convergence at *R*1=0.13 level, with systematically $F_o^2 \rangle\rangle F_c^2$ and with unresoluble disorder of methylene linkage and with total disorder in the region of solvate molecules. No improved refinement model was found for space groups *C*2 and *Cc*. The structure was successfully solved and refined in triclinic space group $P\ \bar{1}$ (of twice lower unit cell volume) and refined as twin with contributions of the twin components 0.73 and 0.27. The twin law is {1 0 0 1 $\bar{1}$ 0 0 0 $\bar{1}$}.

Both unique molecules in the structure display disorder of the alicyclic linkage, for one of two present octaline fragments (See Fig. S1). The refined partial occupancy factors were 0.65/0.35 and 0.60/0.40. The disordered atoms were freely refined anisotropically and the hydrogen atoms were added to both components and considering the present disordering scheme.

The solvate ethanol molecule is unequally disordered by two overlapping positions. Partial occupancies of 0.75 and 0.25 were suggested by refinement of isotropic thermal parameters. The disorder was resolved with the restrained geometry (±0.01 Å). Atoms of the major contribution were refined anisotropically and the H-atoms were constrained. Atoms of the minor component were left isotropic and refined with equal thermal parameter (EADP); hydrogen atoms were not added in this case. NH_2 and OH hydrogen atoms were located and then constrained with U_{iso} parameter at 1.5 of U_{eq} parameter for the carrier N(O) atom.

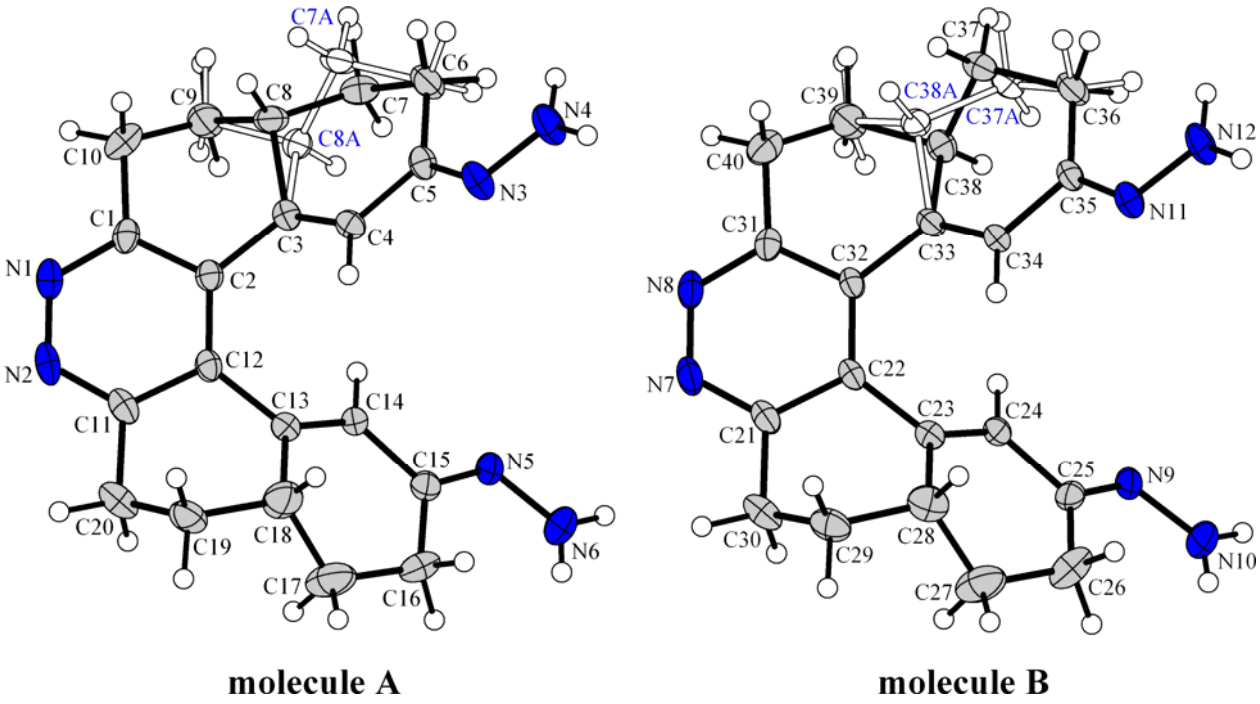


Figure S1. Two independent molecules in the structure of **2(2a)·EtOH·H_2O**, showing the atom labeling and the refined disordering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

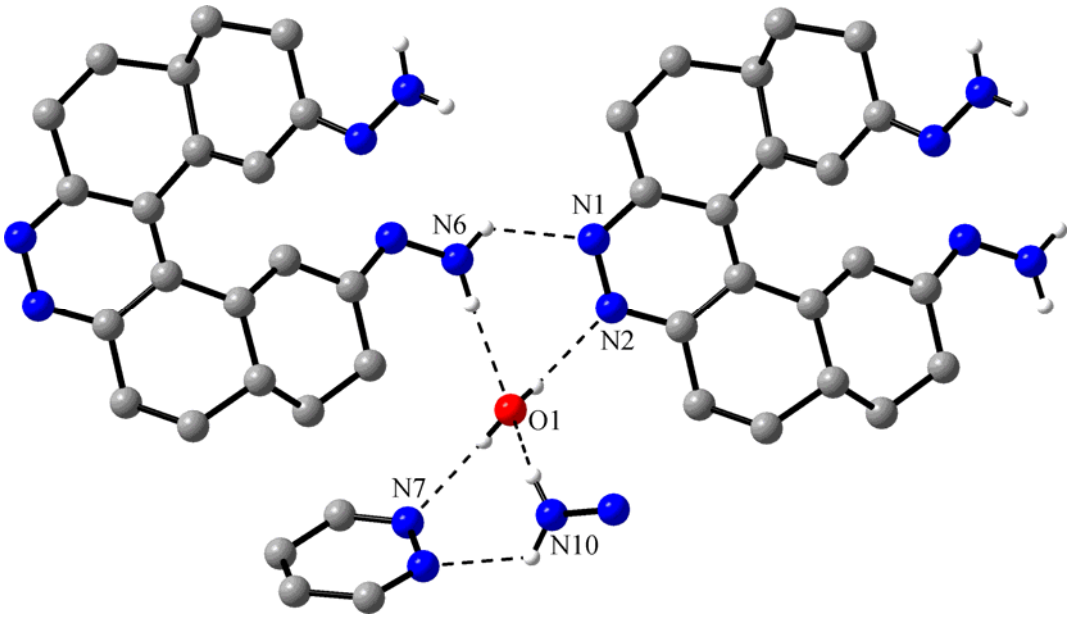


Figure S2. Role of solvate water molecule in the structure of **2(2a)·EtOH·H_2O**. For details of hydrogen bonding parameters see Table S1.

Table S1. Hydrogen bonding scheme for the structure **2(2a)·EtOH·H_2O.**

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O1	H1W	N2 (1-*x*, 2-*y*, 1-*z*)	0.86	2.07	2.843(3)	149.6
O1	H2W	N7 (2-*x*, -*y*, 1-*z*)	0.86	2.05	2.820(3)	149.3
O2	H3W	N11	0.89	1.98	2.871(6)	174.0
N4	H1N	N5 (1-*x*, 1-*y*, 1-*z*)	0.87	2.45	3.249(4)	152.9
N4	H2N	N1 (*x*, -1+*y*, *z*)	0.87	2.67	3.409(4)	143.9
N6	H3N	O1 (2-*x*, 1-*y*, 1-*z*)	0.87	2.34	3.110(5)	147.7
N6	H4N	N1 (1+*x*, -1+*y*, *z*)	0.87	2.39	3.055(4)	133.2
N10	H5N	O1 (2-*x*, 1-*y*, 1-*z*)	0.87	2.41	3.165(5)	145.7
N10	H6N	N8 (*x*, 1+*y*, *z*)	0.87	2.56	3.074(3)	118.9
N12	H7N	N9 (1-*x*, 1-*y*, -*z*)	0.87	2.44	3.247(4)	153.6
N12	H8N	N8 (-1+*x*, 1+*y*, *z*)	0.87	2.60	3.341(4)	143.4

2.4. Refinement of (2b)·EtOH

For one of two present alicyclic fragments, the side -CH_2-CH- linkage is unequally disordered, as was indicated by very high anisotropy for the thermal motion. The disorder was resolved without any restraints in geometry and refined anisotropically with partial occupancy factors of 0.62 and 0.38 (suggested by refinement of the isotropic thermal parameters). The CH-hydrogen atoms were constrained; they were added to both components of the disorder with the corresponding partial occupancies. NH_2 and OH hydrogen atoms were located and then constrained with U_{iso} parameter at 1.5 of U_{eq} parameter for the carrier N(O) atom.

O-atom of the solvate ethanol molecule is unequally (0.85/0.15) disordered over two positions. It was possible to refine this solvent molecule anisotropically (minor component of O-atom was left isotropic) and the hydrogen atoms were constrained.

Table S2. Hydrogen bonding scheme for the structure **(2b)·EtOH.**

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O1	H1W	N5 (1-*x*, 1-*y*, -*z*)	0.87	2.05	2.912(5)	177.7
N4	H4A	N1 (*x*, 1.5-*y*, -0.5+*z*)	0.87	2.59	3.274(4)	136.0
N4	H4B	N2 (*x*, 2.5-*y*, -0.5+*z*)	0.87	2.36	3.204(3)	162.3
N6	H6B	O1	0.87	2.07	2.930(6)	168.5

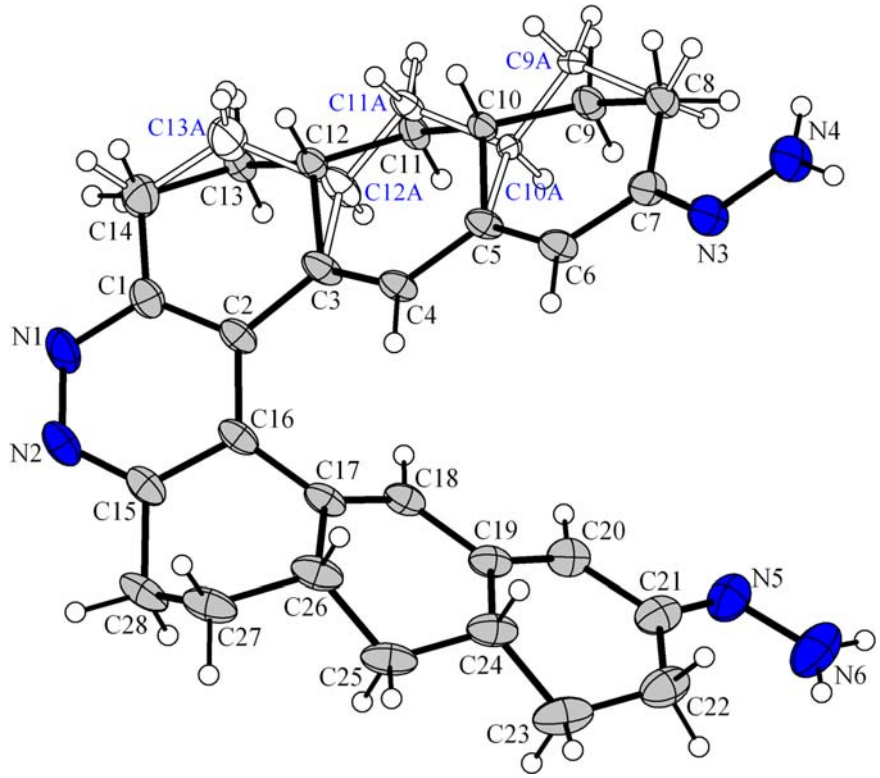


Figure S3. The structure of **(2b)·EtOH** (solvate ethanol molecule omitted), showing the atom labeling and the refined disordering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

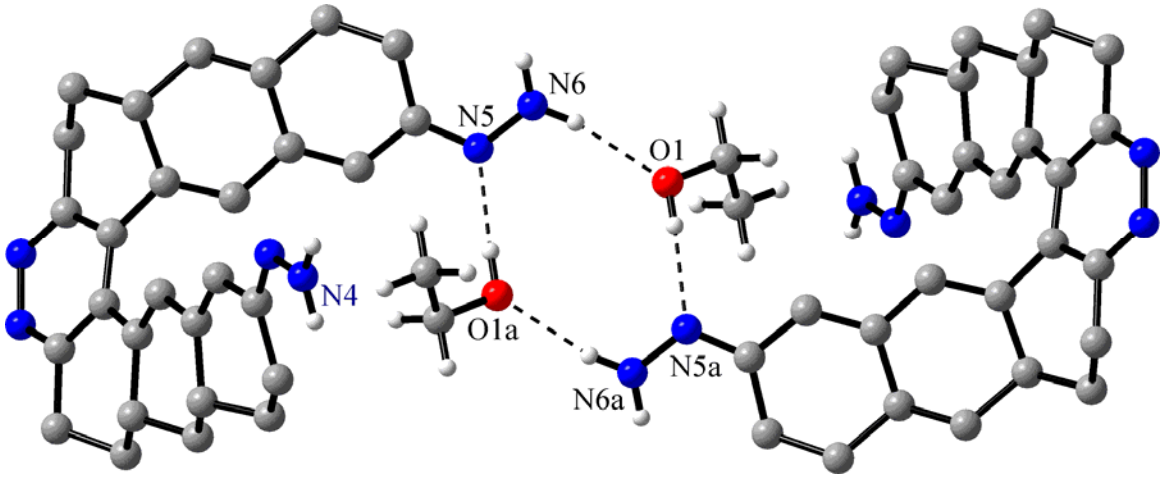


Figure S4. Mode of hydrazone/ethanol hydrogen bonding in the structre of **(2b)·EtOH** leading to a cyclic pattern. CH-hydrogen atoms are omitted for clarity.

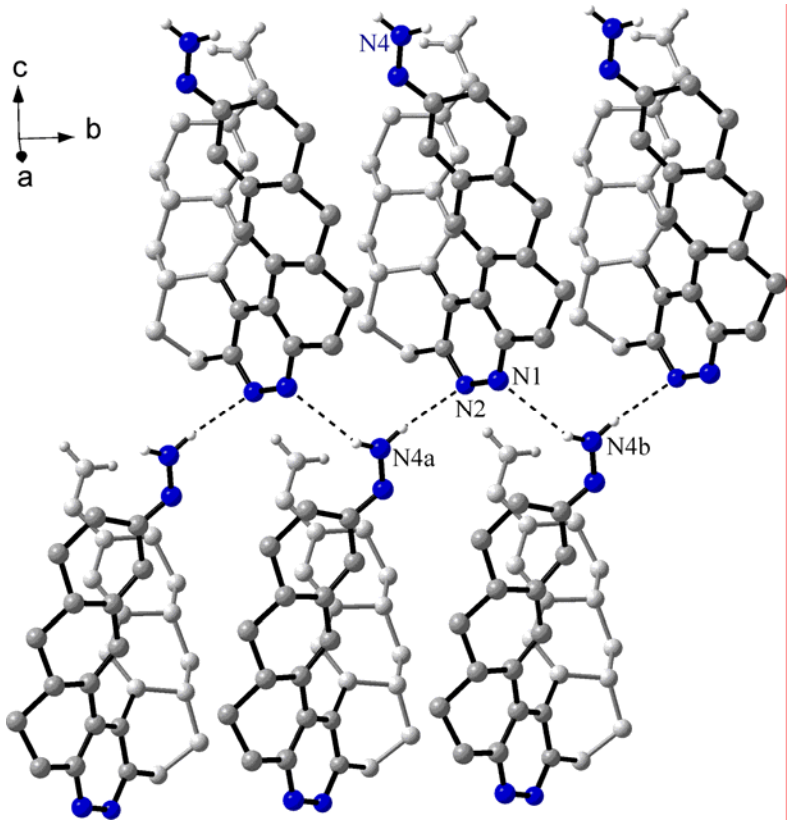


Figure S5. Weak hydrazone/pyridazine N-H···N hydrogen bonding, which is responsinble for interconnection of bulk organic molecules into the layers parallel to the *bc* plane. For details of H-bond interactions see Table S2.

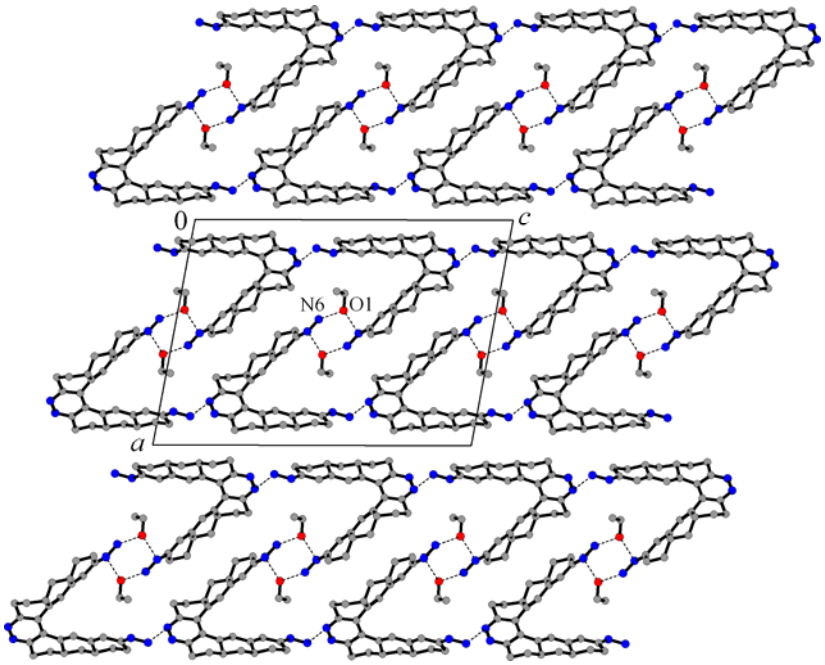


Figure S6. The structure of **(2b)·EtOH**, viewed as a projection of the *ac* plane. Note the formation of "double layers", which originate in the connection of H-bonded organic layers through hydrazone/ethanol "dimers".

2.5. Refinement of *N₄cor*·2H₂O (3)

The organic molecule is situated across a center of inversion. The alicyclic fragments possess the conformation, which is typical for the six-membered ring with three sp^2-atoms. Thus five carbon atoms are coplanar and only the side CH_2 group deviates from this plane. Accordingly, both these CH_2 groups are disordered at two axial sides of the molecule. The disorder was resolved without restraints in geometry and refined anitropically with partial contributions 0.80 and 0.20. The hydrogen atoms were added to both components of the disorder. For the solvate water molecule, the hydrogen atoms were located and then fixed with U_{iso} = 1.5U_{eq}(O) and O-H distance 0.85 Å. One of the water H-atoms is equally disordered by symmetry and adopt two positions, which were refined with partial occupancy 0.5.

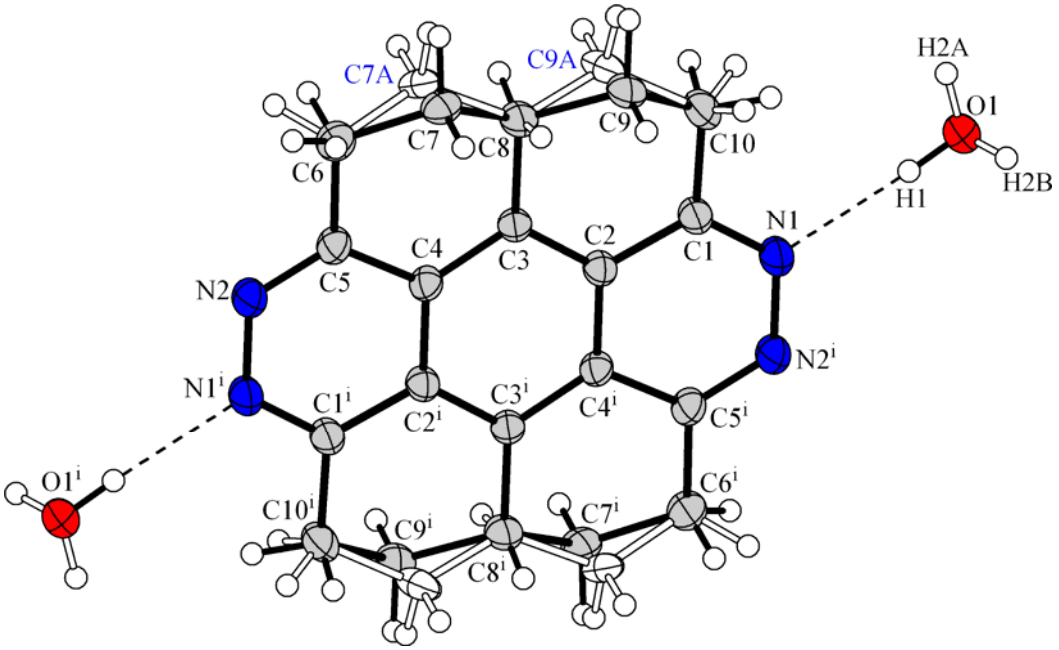


Figure S7. The structure of ***N₄cor*·2H₂O (3)**, showing the atom labeling and the refined disordering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Note disorder by symmetry of the O-H hydrogen atom by two positions (H2A and H2B). The organic molecule is situated across a center of inversion [Symmetry code: (i) –*x*, 1-*y*, 1-*z*].

Table S3. Hydrogen bonding scheme for the structure ***N*$_4$*cor*·2H$_2$O (3).**

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O1	H1	N1	0.85	2.07	2.9183(17)	177.4
O1	H2A	O1 (-*x*, -*y*, 1-*z*)	0.85	2.05	2.821(3)	150.8
O1	H2B	O1 (1-*x*, -*y*, 1-*z*)	0.85	1.97	2.821(3)	176.7

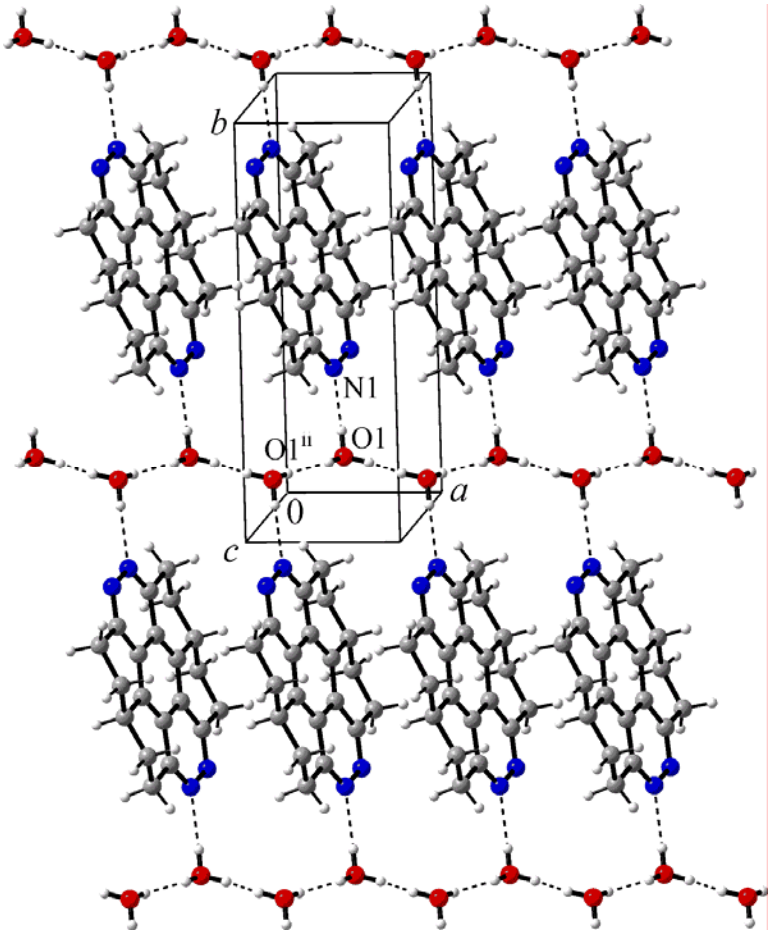


Figure S8. Fragment of the structure of ***N*$_4$*cor*·2H$_2$O (3),** showing principal hydrogen bonding leading to the interconnection of the organic and water molecules into flat layers. Note the formation of 1D hydrate chains. The adjacent water molecules are related by inversion symmetry, which explains the nature of H-atom disorder.

2.6. Refinement of [Cu$_2$I$_2$(*N*$_4$*cor*)]·CH$_3$CN·CHCl$_3$ (4)

The methylene groups are disordered at two axial sides of the ligand, as was indicated by very high anisotropy for thermal motion. The disorder was resolved with partial occupancy factors 0.65 and 0.35 and with a set of restraints: the corresponding C-C bonds were restrained at

1.50±0.01 Å as well as SIMU restraint was applied for thermal parameters of disordered atoms C5 and C5A (anisotropic refinetement). The hydrogen atoms were added to both components of the disorder, considering the above partial occupancies.

The solvate $CHCl_3$ molecule is disordered by overlapping positions, with Cl1 atom common for two different orientations. Considering the nature of the disorder, the atoms were refined with partial occupancy factors 0.25 and left isotropic (U_{iso} = 0.17-0.36 Å^2). To improve the refinement stability, the C-Cl bond lengths were restrained at 1.74±0.01 Å and intramolecular contacts Cl···Cl at 2.90±0.01 Å. The CH_3CN guest molecule is unresoluble disordered over multiple ovelapping positions. We were not successful to find the appropriate disordering model. In this view, the corresponding electron density was modelled using SQUEEZE routine implemented in PLATON.

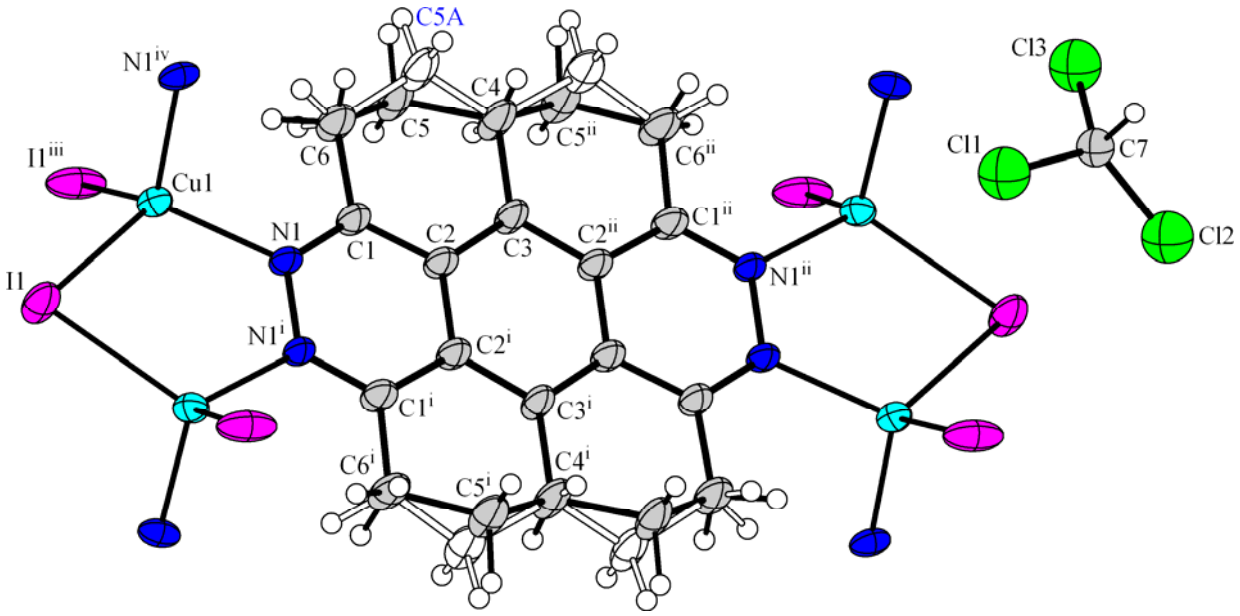


Figure S9. The structure of **[Cu_2I_2(*N_4cor*)]·CH_3CN·$CHCl_3$ (4)**, showing the atom labeling and the refined disordering scheme (two components are marked by solid and open bonds). Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms of the solvate chloroform molecule are isotropic. Symmetry codes: (i) *x*, 1-*y*, -*z*; (ii) 1-*x*, *y*, *z*; (iii) -0.25+*y*, 0.75-*x*, 0.25+*z*; (iv) 0.75-*y*, 0.75-*x*, 0.25-*z*.

2.7. Refinement of [Cu_2Cl_2(*N_4cor*)]·4CH_3CN (5)

Similarly to the above cases, the side CH_2 groups are disordered from two axial sides of the ligand. The refined contributions of the disorder were 0.77 and 0.23 (Figure S10, A). This

disorder was resolved with soft geometry restraints for the corresponding C-C bonds (±0.01 Å) and SIMU restraints for the thermal parameters of the disordered atoms. All the atoms were refined anisotropically and the H-atoms were added geometrically, taking into account two components of the disorder and the corresponding partial occupancy factors.

One solvate CH_3CN molecule was located and refined considering equal disorder over two closely separated positions (Figure S10, B). For both the components, the atoms were left isotropic and the molecular geometries (±0.01 Å) and isotropic thermal parameters (SIMU) were restrained, while the hydrogen atoms were added geometrically. Second independent solvate CH_3CN is badly disordered over multiple ovelapping positions and it was not possible to find a stable disordering scheme. Therefore, this electron density was modelled using SQUEEZE routine implemented in PLATON.

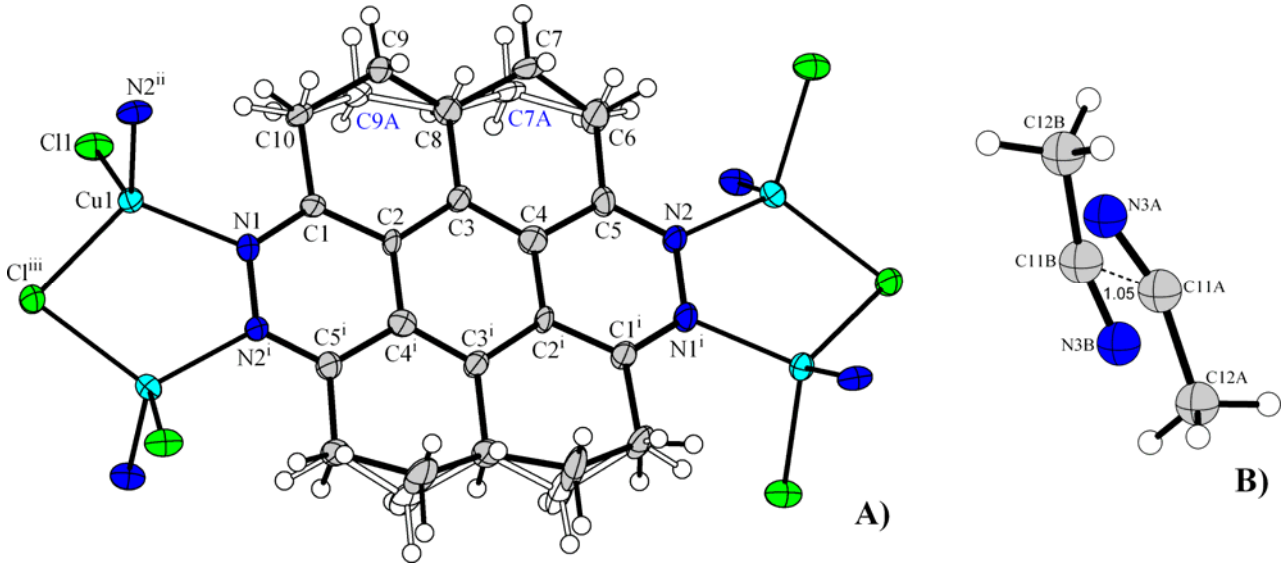
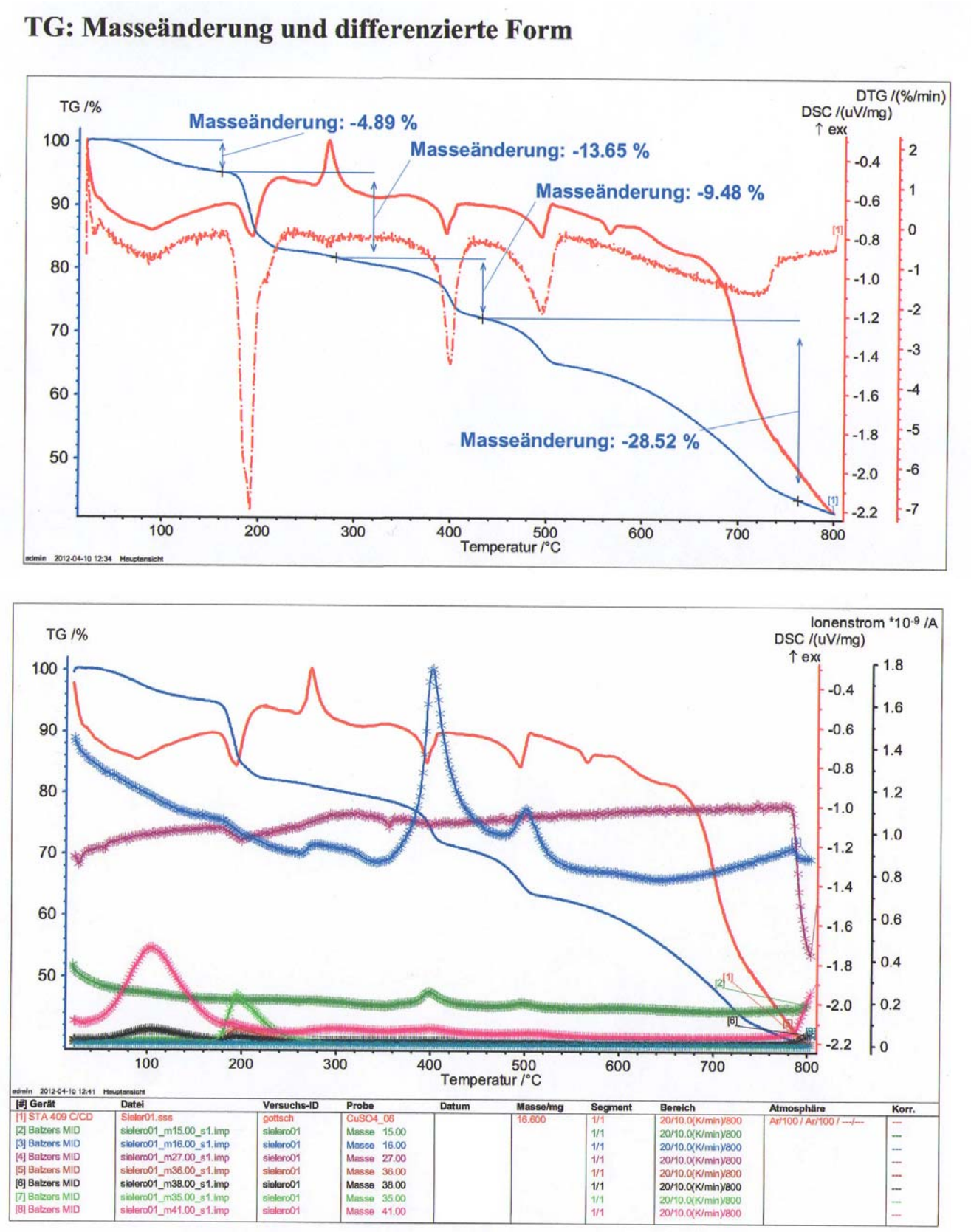
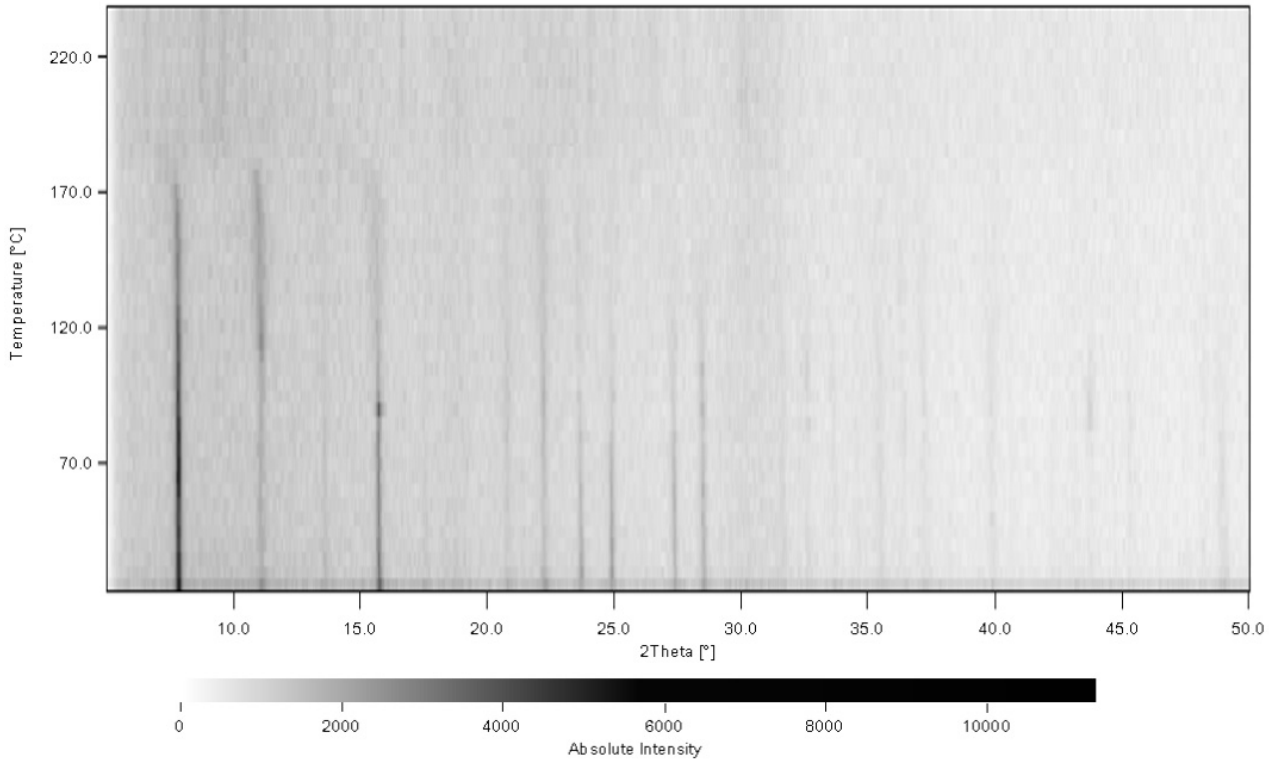


Figure S10. A) The structure of **[Cu_2Cl_2(*N_4cor*)]·4CH_3CN (5)**, showing the atom labeling and the refined disordering scheme (two components are marked by solid and open bonds). Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. B) Refined disordering scheme for the solvate CH_3CN molecules (the carbon and nitrogen atoms of both components are isotropic). Symmetry codes: (i) *y*, *x*, 1-*z*; (ii) 0.5-*x*, -0.5+*y*, 0.75-*z*; (iii) 0.5+*y*, 0.5-*x*, 0.25+*z*.

3. Complex $[Cu_2I_2(N_4cor)]\cdot CH_3CN\cdot CHCl_3$ (4): thermoanalytical studies



The TG analyses were carried out on a Netzsch STA 449 F1 Jupiter device connected to an QMS 403C Aeolos mass spectrometer.



Thermo-XRPD pattern (2θ = 0-50°C) for $[Cu_2I_2(N_4cor)]\cdot CH_3CN\cdot CHCl_3$ **(4):** the framework structure remains intact up to 180°C. Second stage of the thermal desolvatation is accompanied by loss of the crystallinity of the sample.

The temperature dependent X-ray measurements were carried out on a Stoe STADI P using Cu-Ka radiation and with an high temperature attachment and image plate detector system.