

Photoinduced and dark complexation of unsaturated viologen analogues containing two ammonium tails with cucurbit[8]uril†

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Complex formation between cucurbit[8]uril (CB[8]) and unsaturated viologen analogues **1a,b** bearing two ammoniopropyl substituents was studied using ¹H NMR spectroscopy and X-ray diffraction. The complex stability constants were measured by ¹H NMR titration. CB[8] was found to encapsulate 1,2-di(4-pyridyl)ethylene derivative (*E*)-**1a** in water/acetonitrile solution to form only inclusion complex of 1 : 1 composition. The high stability of CB[8]·**1a** (lg $K_{1:1} \geq 5$) is apparently due to the possibility of hydrogen bond formation between two NH₃⁺ groups of **1a** and the O=C fragments of both portals of CB[8]. Contrarily, the derivative of 1,2-di(4-quinolyl)ethylene (*E*)-**1b** gave three types of inclusion complexes upon mixing with CB[8]. The stability of the 1 : 1 complex (lg $K_{1:1} = 4.6$) is decreased compared to (*E*)-**1a**, suggesting a poorer fit with respect to the bulky (*E*)-**1b** in the cavity of CB[8] for the simultaneous hydrogen bonding of the both ammonium groups. This is the driving force for the formation of an unusual 2 : 1 complex, {CB[8]}₂·(*E*)-**1b**. The expanded π -system of (*E*)-**1b** allows also two tetracationic molecules of the acceptor to form a 1 : 2 complex owing to stacking interactions. Crystallization of a **1b**/CB[8] mixture under irradiation resulted in an inclusion complex of the *Z*-isomer of **1b**. The supramolecular complex is formed because the shape of (*Z*)-**1b** fits well to the host cavity and the ammonium groups form a system of hydrogen bonds with oxygen atoms of both portals of CB[8]. The features of crystalline complexes CB[8]·(*Z*)-**1b** and CB[8]·HClO₄ are discussed.

Introduction

The complexing properties of a relatively new class of cavitand molecules, cucurbit[*n*]urils (CB[*n*]) that have a hydrophobic electron-donating cavity have been intensively studied in recent years.^{1–7} Of special interest is the ability of CB[*n*] to form strong complexes with positively charged organic molecules in an aqueous medium; thus, they represent a promising alternative to known macrocyclic hosts, cyclodextrins.

It is known that CB[6], having a relatively small cavity, is able to form strong complexes with ammonium salts of the alkane series in which an important role is played by the formation of hydrogen bonds between the guest ammonium

groups and the oxygen atoms of the CB[6] portals.^{4,8–12} On the other hand, CB[7] and CB[8], containing larger cavities, can encapsulate one or two planar guest molecules.^{5–7} The interaction between the host and the guest involving hydrogen bonds has been little studied for cucurbit[*n*]urils (*n* = 7, 8).^{13,14} The study of guest molecules capable of changing the spatial arrangement of groups involved in hydrogen bonding on exposure to light is of special interest due to the possibility of controlling the stability of their complexes with cucurbiturils. Such photoswitchable systems could be used for the development of molecular motors and devices.^{15–17}

Recently,^{18–20} we have synthesized a series of new π -acceptor molecules, analogues of viologen **1** with two *N*-alkylammonium substituents and studied their complexation with bis(18-crown-6)-containing stilbene. It was found that the acceptor **1** forms strong complexes with the donor bis-crown stilbene in which effective charge transfer in the ground state takes place owing to pre-organization of the acceptor and donor regions. The main contribution to the stability of these supramolecular complexes is made by the host–guest type interaction between the two terminal NH₃⁺ groups of the acceptor and the two bis-18-crown-6-stilbene fragments. The relatively good solubility in water and clear-cut acceptor properties make viologen analogues **1** promising objects for studying the complexation with CB[*n*]. Another attractive feature is the possibility of relatively easy *N*-functionalization of the ammonium groups in the complexes with CB[*n*], as this

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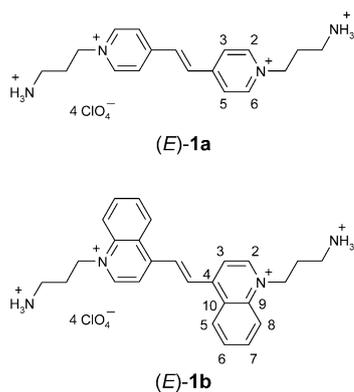
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Scheme 1 Structure of acceptors **1a** and **1b**.

was done for the diammonium compounds of a simpler structure.²¹ The presence of the C=C double bond capable of reversible photoinduced transformations (*E*-*Z*-isomerization and [2 + 2]-cycloaddition) in the molecule of acceptor **1** offers the opportunity of constructing light-controlled rotaxane- and pseudorotaxane-type molecular machines from these molecules.

Therefore, we studied the ability of acceptors **1a,b** (Scheme 1) to form complexes with cucurbit[8]uril, the influence of the terminal ammonium groups in the acceptor and the structure of the central fragment on the stability of these complexes using ¹H NMR spectroscopy and X-ray diffraction.

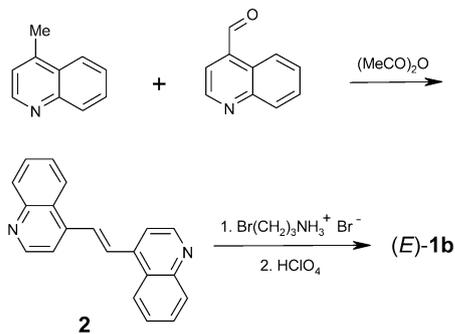
Results and discussion

A. Synthesis

Synthesis of acceptor salt **1a** was described recently.^{18,20} Salt (*E*)-**1b** was prepared in two steps (Scheme 2). The condensation of lepidine and 4-formylquinoline in acetic anhydride gave (*E*)-1,2-di(4-quinolyl)ethylene (**2**). Quaternization of **2** with 3-bromopropylamine hydrobromide followed by treatment with concentrated perchloric acid yielded the target compound (*E*)-**1b** in a total yield of 21%. Compounds **2** and (*E*)-**1b** were characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis.

B. NMR studies

The complexation of CB[8] with viologen analogues **1a** and **1b** that contain two ammoniopropyl substituents was studied by



Scheme 2 Synthesis of acceptor **1b**.

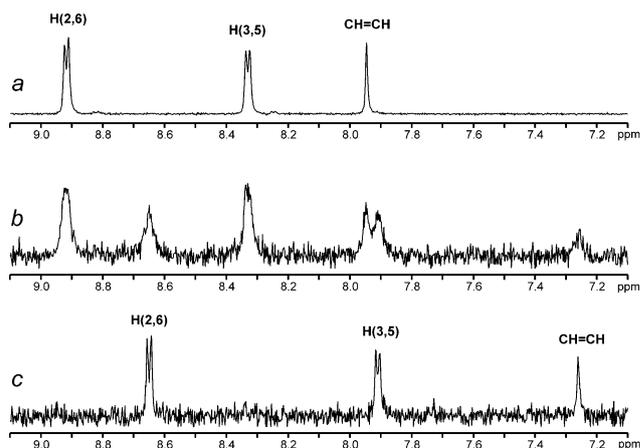
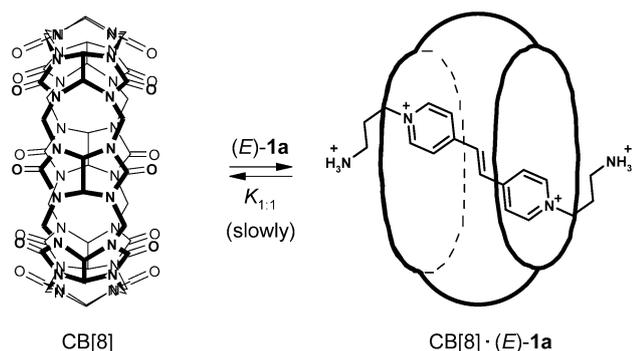


Fig. 1 ¹H NMR spectra (aromatic proton region, D₂O/CD₃CN (10 : 1), 30 °C) of free (*E*)-**1a** (a), and mixtures of (*E*)-**1a** and CB[8] 3 : 1 (b) and 1.2 : 1 (c).

¹H NMR spectroscopy in a D₂O/CD₃CN mixture (10 : 1). The task was complicated by the poor solubility of CB[8] in this solvent system, $c_{\text{CB}[8]} = 1.30 \times 10^{-4}$ M, calculated based on ¹H NMR data for CB[7], which is readily soluble in this system. The addition of an equimolar amount of (*E*)-**1a** to a saturated solution of CB[8] resulted in a set of narrow signals (Fig. 1c), which were markedly shifted upfield relative to the signals of pure (*E*)-**1a** (Fig. 1a). The maximum shift, $\Delta\delta = 0.7$ ppm, was found for the signals of the CH=CH ethylene protons. This implies the formation of a strong supramolecular complex between CB[8] and (*E*)-**1a**, in which the electron-withdrawing tetracation of the viologen analogue resides inside the electron-donating cavity of CB[8], which has a shielding effect on the protons of the guest molecule. The results are in good agreement with the known data on complexation of cucurbit[*n*]urils ($n = 7, 8$) with viologens and pyridinium salts.^{21–25}

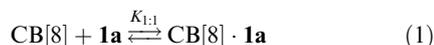
An increase in the content of **1a** in the mixture brought about two sets of broadened signals in the aromatic region (Fig. 1b) due to the protons of free and complexed (*E*)-**1a**. This implies an exchange of the guest molecule, slow on the ¹H NMR time scale, which is also in good agreement with published data for cucurbit[*n*]uril complexes. It should be noted that the signals of the CB[8] protons were somewhat broadened but not split to form two sets corresponding to free CB[8] and its complex with **1a**. This situation is also typical of cucurbit[*n*]urils, although it has not been commented in the literature. Apparently, the exchange mechanism is fairly complex and differs for the host and guest molecules. It was also found that at relatively high concentrations of **1a** ($c_{\text{1a}} > 4 \times 10^{-4}$ M), salting-out of CB[8] takes place, resulting in a substantial decrease in the concentration of its saturated solution (Fig. 1S in the electronic supplementary information (ESI) to this article).

In order to estimate the stoichiometry and stability of the complex, we carried out ¹H NMR titration of the CB[8]/(*E*)-**1a** system, while varying the concentration of the acceptor **1a**. Due to the slow exchange, the concentration range $c_{\text{1a}} = (3.5–10) \times 10^{-4}$ M covering both sets of rather intensive signals of protons of **1a** was chosen for calculations. The



Scheme 3 Complex formation between CB[8] and acceptor **1a**.

averaged chemical shift of the H(2,6) signals, which are the only signals not overlapped with other ^1H NMR signals, was calculated taking into account the integral intensities of the signals of free and complexed **1a**. The dependence of the positions of low-field signals of the methylene group protons of CB[8] that are most sensitive to complexation, on the concentration of **1a** in the mixture was also used in the calculations. Despite the relatively large error in the calculation of the real concentration of CB[8], substantial broadening of spectral lines and the low signal/noise ratio, the model found for cucurbit[8]uril complexation with the acceptor (*E*)-**1a** corresponded to a 1 : 1 stoichiometry (eqn (1)):



where $K_{1:1} = [\text{CB[8]} \cdot \mathbf{1a}] / ([\text{CB[8]}] \cdot [\mathbf{1a}])$ (M^{-1}) is the formation constant for the 1 : 1 complex. The calculation of the stability constant using the HYPNMR software²⁶ has shown that the

value of the constant exceeds the upper limit of applicability of ^1H NMR titration ($\lg K_{1:1} \geq 5$). The result obtained for complex $\text{CB[8]} \cdot (\text{E})\text{-1a}$ is consistent with published data on the stoichiometry and stability constants for $\text{CB}[n]$ ($n = 7, 8$) with viologens in aqueous solutions.^{21,22,24,25,27,28} The formation of only one type of complex (1 : 1) reflects apparently the ability of the relatively small tetracation (*E*)-**1a** to be loosely accommodated inside the CB[8] cavity (Scheme 3). The ammonium groups of the acceptor can apparently participate in the formation of hydrogen bonds with the oxygen atoms of both host portals, which should increase theoretically the stability of this inclusion complex.

A different spectral pattern was observed in the study of the complexation between CB[8] and di(4-quinoly)ethylene derivative (*E*)-**1b**. Mixing of the components resulted in a pronounced broadening of the spectral lines of the host molecule over the whole concentration range, thus precluding the assignment (Fig. 2c). The obvious upfield shift of the broadened lines (*E*)-**1b** compared to the free acceptor (Fig. 2a) by 0.2–0.9 ppm, as in the case of (*E*)-**1a**, attests to the formation of a 1 : 1 inclusion complex with CB[8].

Due to the substantial steric interaction of the H(5) protons and the CH=CH group, molecule (*E*)-**1b** can probably acquire only the conformation in which the ethylene group points away from the annelated benzene ring (see Scheme 1 for atom numbering). This conclusion is supported by our X-ray diffraction study²⁹ of the model bis-quaternary salt **3** (Fig. 3). This conformation does not allow molecule (*E*)-**1b** to be accommodated in the cavity of CB[8] in such a way that the terminal ammonium groups are able to form relatively strong hydrogen bonds with the oxygen atoms of both portals of the host molecule (Scheme 4). This suggests a lower stability of the

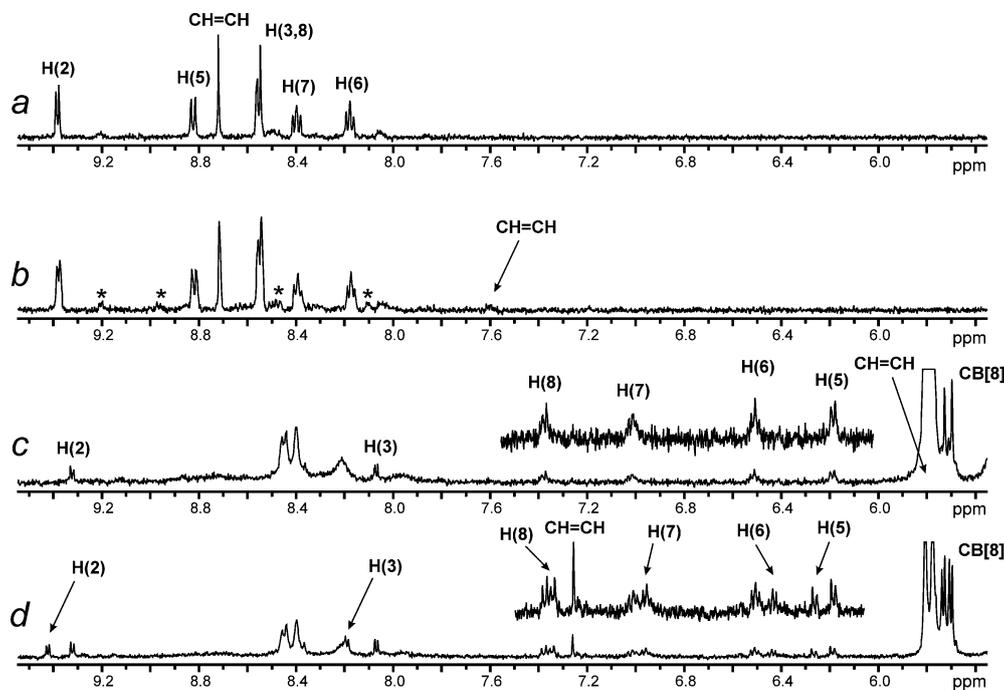


Fig. 2 ^1H NMR spectra ($\text{D}_2\text{O}/\text{CD}_3\text{CN}$ (10 : 1), 30 °C) of (*E*)-**1b** (a, b) and 1 : 1 mixture of (*E*)-**1b** and CB[8] (c, d) before (a, c) and after (b, d) irradiation with a visible light. Assignments were made for the proton signals of (*E*)-**1b** (a), (*Z*)-**1b** (b), $\text{CB[8]} \cdot \{(\text{E})\text{-1b}\}_2$ (c), and $\text{CB[8]} \cdot (\text{Z})\text{-1b}$ (d). Probable signals of free (*Z*)-**1b** are marked by asterisks in spectrum (b).

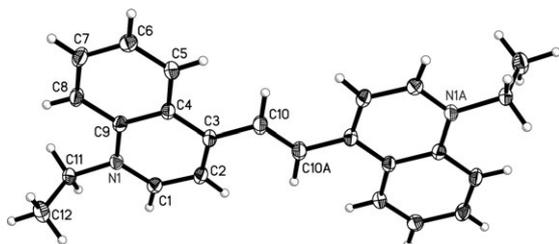


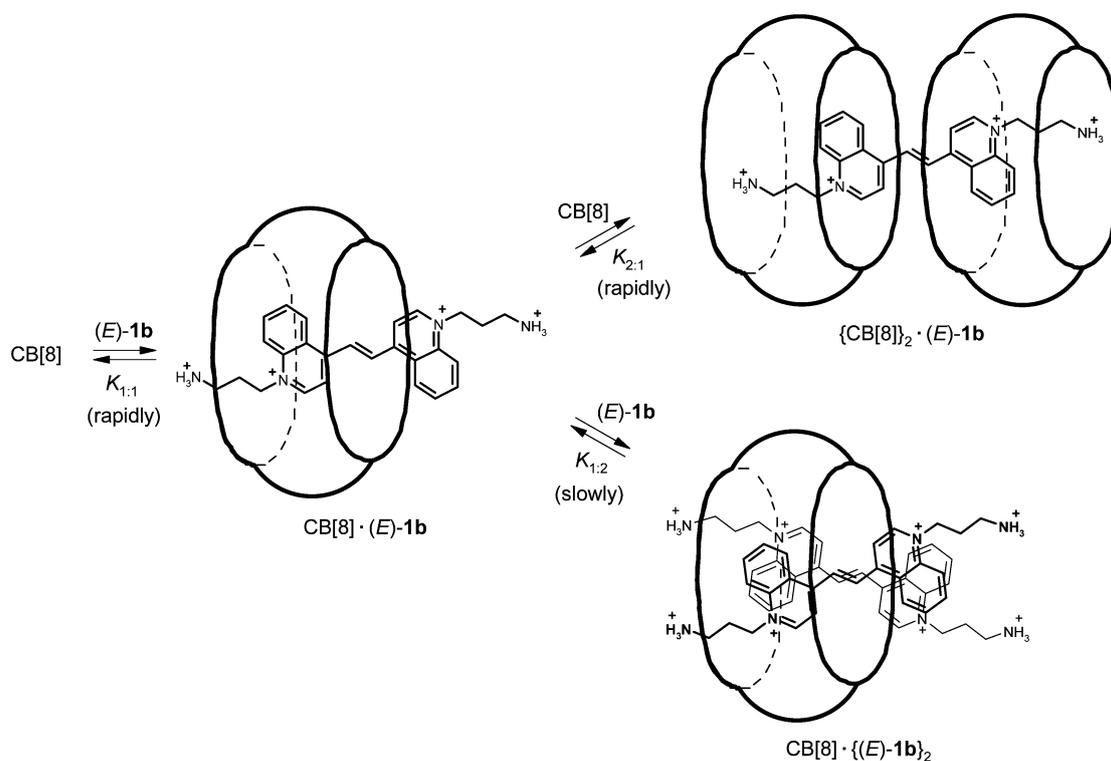
Fig. 3 Dication of *N,N'*-diethyl (*E*)-1,2-di(4-quinoliniumyl)ethylene diperchlorate (**3**) is drawn with anisotropic displacement parameters at the 50% probability level.

complex $\text{CB}[8] \cdot (E)\text{-1b}$ with respect to the 1 : 1 complex formed by (*E*)-**1a**.

In addition to the set of broadened lines, the spectrum of a mixture of $\text{CB}[8]$ and (*E*)-**1b** contains one more set of relatively narrow low-intensity lines due to the guest molecule located in another complex with a slow, on the ^1H NMR time scale, exchange of **1b**. The signal assignment for this complex is shown in Fig. 2c. The unusually great upfield shifts of the H(5)–H(8) and $\text{CH}=\text{CH}$ proton signals in (*E*)-**1b** (1.2–2.9 ppm) attest to substantial shielding of these protons. This type shielding is expected for the formation of 1 : 2 complexes in which two acceptor molecules are arranged one above another in the $\text{CB}[8]$ cavity. The most probable mutual arrangement of (*E*)-**1b** in the complex $\text{CB}[8] \cdot \{(E)\text{-1b}\}_2$ is shown in Scheme 4. The acceptor guests form a sandwich structure owing to the secondary orbital p_z interactions in which the tetracations overlap through their benzene and ethylene fragments, which

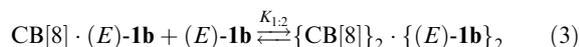
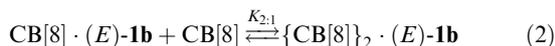
minimizes the Coulomb repulsion. All signals of $\text{CB}[8]$ in the ^1H NMR spectrum of the 1 : 2 complex are also manifested separately and at a higher field than the main signals of the host (for instance, Fig. 2c), their relative intensity increasing with an increase in the $c_{1b}/c_{\text{CB}[8]}$ ratio. Our conclusion concerning the formation of complex $\text{CB}[8] \cdot \{(E)\text{-1b}\}_2$ is confirmed by published data. It is known that $\text{CB}[8]$ can incorporate two guest molecules of stilbene,¹³ bis(imidazolyl)naphthalene,³⁰ substituted cinnamic acid,³¹ viologen or tetrathiafulvalene radical ion,^{27,32} or two different molecules forming a charge transfer complex.^{23,33,34}

Due to the substantial broadening of the spectral lines of (*E*)-**1b** on complexation with $\text{CB}[8]$, the signals of the acceptor could not be used to determine the stoichiometry and the stability of the resulting complexes. However, the variation of the positions of the low-field signals of the CH_2 group protons of $\text{CB}[8]$ during ^1H NMR titration in the $\text{CB}[8]/(E)\text{-1b}$ system (Fig. 2S, ESI) allowed us to obtain the desired characteristics. Due to the slow exchange between the complex $\text{CB}[8] \cdot \{(E)\text{-1b}\}_2$ and other states of $\text{CB}[8]$, the averaged chemical shift of the signals of these protons was calculated taking into account the integral intensities of two signals from these protons at 5.7–5.9 ppm. Variation of the content of the acceptor **1b** in a saturated solution of $\text{CB}[8]$ has shown that, unlike the $\text{CB}[8]/(E)\text{-1a}$ system, an increase in the concentration of (*E*)-**1b** leads to a substantial increase in the solubility of $\text{CB}[8]$ (Fig. 1S, ESI). Taking into account the change in the real concentration of a saturated solution of $\text{CB}[8]$ during the titration, the proposed model of $\text{CB}[8]$ complexation with (*E*)-**1b** was in good agreement with the formation of three types of



Scheme 4 Complex formation between $\text{CB}[8]$ and acceptor (*E*)-**1b**.

complexes, 1 : 1 (see eqn (1)), 2 : 1 and 1 : 2 (eqns (2) and (3)):

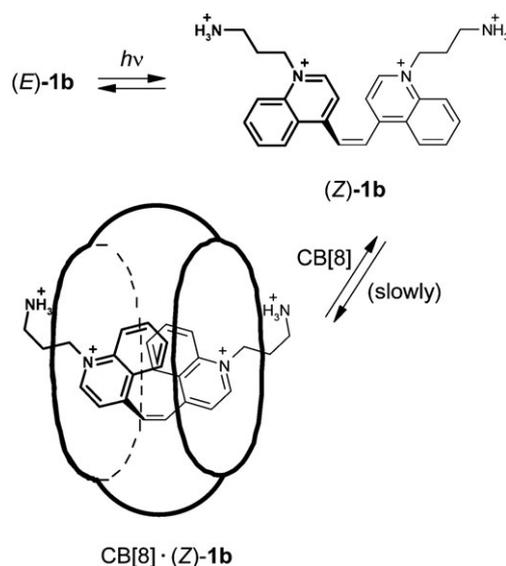


where $K_{2,1} = [\{\text{CB}[8]\}_2 \cdot (E)\text{-1b}] / [\text{CB}[8] \cdot (E)\text{-1b} \cdot \text{CB}[8]]$ (M^{-1}) and $K_{1,2} = [\text{CB}[8] \cdot \{(E)\text{-1b}\}_2] / [\text{CB}[8] \cdot (E)\text{-1b} \cdot (E)\text{-1b}]$ (M^{-1}) are the formation constants for 2 : 1 and 1 : 2 complexes, respectively.

Using the HYPNMR software,²⁶ we obtained the following values for the stability constants of CB[8] complexes with (*E*)-**1b**: $\lg K_{1,1} = 4.6 \pm 0.1$, $\lg K_{2,1} = 3.2 \pm 0.3$, and $\lg K_{1,2} = 3.0 \pm 0.1$. Thus, the complex $\text{CB}[8] \cdot (E)\text{-1b}$ proved, as expected, less stable than a similar complex formed by (*E*)-**1a**, which reflects the failure of the ammonium groups of acceptor (*E*)-**1b** to form simultaneously hydrogen bonds with both portals of CB[8]. Apparently, this results in the formation of the less stable $\{\text{CB}[8]\}_2 \cdot (E)\text{-1b}$ complex in which the central part of the acceptor (*E*)-**1b** is located outside the host cavity but its ammonium groups can interact with the carbonyl groups of two molecules CB[8] (Scheme 4). It should be noted that this complex is apparently a first example of 2 : 1 complex for cucurbit[8]uril with simple guest molecules. The study of complexes of this structure is evidently hampered by the relatively fast exchange with 1 : 1 complexes whose stability is usually too high for precise measurements ($\lg K_{1,1} \geq 5$).

The long-term irradiation of a solution of free (*E*)-**1b** in the NMR tube using visible light directly gave rise to a set of low-intensity ¹H NMR signals, which were attributed to the *Z*-isomer of the acceptor (Fig. 2b). The ratio of the *E* and *Z*-isomers calculated from the integral intensities of the proton signals in the aromatic region was about 92 : 8; on keeping the sample in the dark it changed towards the *E*-isomer due to thermal *Z* → *E* isomerization. Most of the signals of the aromatic protons of the *Z*-isomer are shifted upfield relative to analogous signals in (*E*)-**1b**; the greatest shift is found for the ethylene proton signals (1.1 ppm). This reflects the substantial decrease in the electron-withdrawing influence of the heteroaromatic residues on the CH=CH protons caused by the essential decrease in the conjugation in the Het-CH=CH-Het chain of unsaturated bonds (*Z*)-**1b**, which is related to the twisting caused by the substantial steric interaction of the bulky substituents at the double bond of the *Z*-isomer (Scheme 5).

The irradiation of a 1 : 1 mixture of CB[8] and (*E*)-**1b** with visible light under the same conditions gave rise to a new set of signals in the ¹H NMR spectrum (Fig. 2d); the intensity of these signals did not change on storage of the sample in the dark for a long time (more than 2 weeks). The positions of the new proton signals for both CB[8] and the acceptor resemble that of complex $\text{CB}[8] \cdot \{(E)\text{-1b}\}_2$, except for the proton signal of the CH=CH group, which is located in a lower field. Evidently, the new set of signals refers to complex $\text{CB}[8] \cdot (Z)\text{-1b}$ in which the mutual arrangement of two quolinium residues at CH=CH in (*Z*)-**1b** (Scheme 5) brings about shielding effects similar to these effects in the sandwich structure $\text{CB}[8] \cdot \{(E)\text{-1b}\}_2$. The signals of the (*Z*)-CH=CH group protons in $\text{CB}[8] \cdot (Z)\text{-1b}$ are shielded only by the walls of CB[8], which accounts for their lower-field position (by ~1.5



Scheme 5 Photoisomerization of **1b** and complex formation between CB[8] and (*Z*)-**1b**.

ppm) compared to those in the sandwich complex (*E*)-**1b**. The stability of *Z*-isomer of the acceptor against the dark *Z* → *E* isomerization is apparently explained by good compliance between its shape and the size of the cavity of CB[8] and the possibility of simultaneous binding of ammonium groups with the O=C groups of both host portals (see also X-ray section). It should be noted that the calculated content of (*Z*)-**1b** in photostationary mixtures in the presence and in the absence of CB[8] is approximately the same (~6–8%), and, hence, it is determined by the ratio of the quantum yields of the forward and back photoisomerization reactions of free **1b**.

C. X-ray diffraction

We attempted to obtain single crystals of complexes formed by **1a,b** with CB[8]. To this end, the solutions of complexes in aqueous acetonitrile were slowly evaporated at room temperature until yellowish crystals were formed. From a $\text{CB}[8]/(E)\text{-1a}$ mixture, fine crystals of **4a** were grown, whose X-ray diffraction analysis showed the absence of the guest molecule in the CB[8] cavity. It was found that the perchlorate anion is their structural unit. Coarser crystals **4b** were obtained from the $\text{CB}[8]/\text{1b}$ mixture, as well as crystals **4a**; these consisted of a free molecule of CB[8] and the $\text{CB}[8] \cdot (Z)\text{-1b}$ complex. Apparently, growing of the crystalline complexes in the light resulted in *E* → *Z* isomerization of acceptor **1b** and only the structure of $\text{CB}[8] \cdot (Z)\text{-1b}$ allowed construction of a single crystal with close packing.

The structure of $\text{CB}[8] \cdot \text{HClO}_4$ (**4a**) is shown in Fig. 4 in different projections. It consists of the main element, the CB[8] molecule, and includes perchlorate anion and several small molecules, which, apparently, represent water and oxonium cation. The perchlorate anion and small molecules are situated outside the hydrophobic CB[8] cavity.

The CB[8] molecule and perchlorate anion are situated at different special position having *mm* symmetry. The shape of both symmetrically equivalent portals is slightly oblate, with

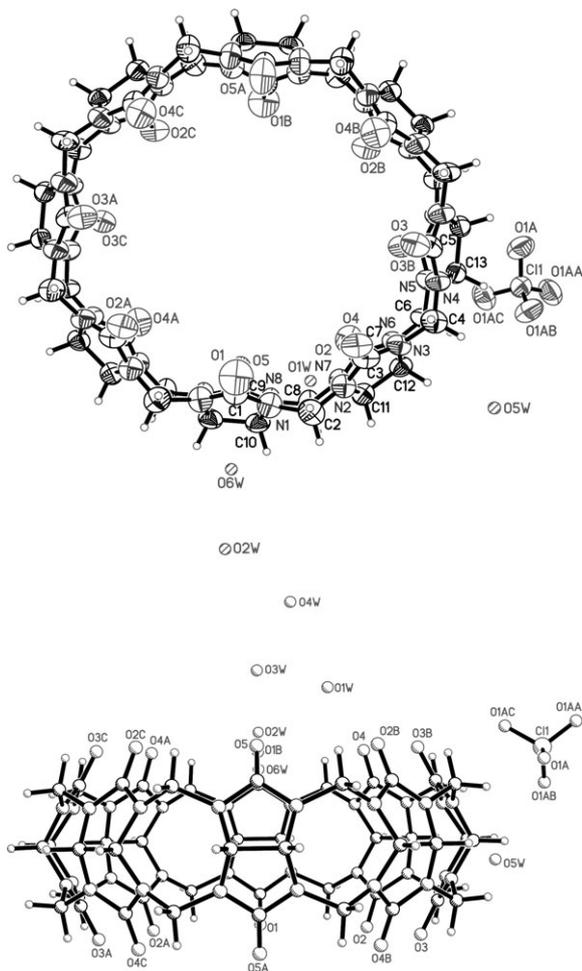


Fig. 4 Structural elements of **4a** in different projections. In the top the CB[8] molecule and perchlorate anion are drawn with anisotropic displacement parameters at the 50% probability level.

maximum and minimum O··O distances between opposite atoms equal to 10.241 and 9.569 Å. Apparently, the sizes of the CB[8] cavity and portals are too large to encapsulate tightly a molecule of viologen analogue **1a**.

The Cambridge Structural Database³⁵ includes data on only seven CB[8] and two CB[7] molecules, although CB[6] molecules are much more abundant (~80 entries). All these structures contain different additional elements. The CB[8] structures represent various clathrates^{30,36,37} or complexes with metal aqua ions.³⁸ Only structure LIRTOV³⁰ does not contain a guest molecule in the cavity of CB[8]. In the structure IMOBUH,³⁸ a water molecule and one nitrate anion are located in the hydrophobic cavity of CB[8]. In the other aforementioned structures, the CB[8] cavity is occupied by a big hydrophobic guest molecule. In structure OBIPUK³⁶ the cavity houses two different molecules forming a charge-transfer complex. According to *ab initio* calculations, 4,4'-diammonium stilbene having lateral size comparable to that of **1a** may be captured by the CB[7] cavity in both *cis* and *trans* forms unlike the CB[8].¹⁴ It is of interest that cation of *para*-xylylene diammonium, comparable in lateral size with (*E*)-**1a**, is encapsulated by CB[6] cavity.³⁹ These data show that smaller

cavities in CB molecules are more suitable for capturing molecules with lateral size similar to **1a**.

The crystal lattice **4a** includes only perchlorate anions, water molecules and probably oxonium cations as stabilizing elements. Fig. 3S in the ESI shows two different projections of the crystal packing of **4a**. The small molecules are involved in a system of hydrogen bonds with the carbonyl oxygens of CB[8].

Although perchlorate anions commonly tend to form hydrogen bonds, in this structure, it does not participate in the system of hydrogen bonds with water or oxonium molecules, because they are widely separated. Apparently, perchlorate anions fit exactly to the shape and size of the lattice voids in which they are located, thus making crystal packing less loose.

The structure of **4b** contains two different CB[8] molecules one of which captures a molecule of **1b**. The structure of this host-guest system is shown in Fig. 5.

The free CB[8] molecule is situated at a symmetry center. The free and occupied CB[8] molecules in **4b** have a somewhat different shape (Fig. 6). One of them is markedly oblate, whereas the other one is more symmetrical. The maximum and minimum O··O distances in both portals of the occupied molecule are 10.988 and 8.786 Å. Similar geometric parameters for the free molecule are 10.317 and 9.826 Å. The more distorted CB[8] molecule captures molecule of **1b**. These

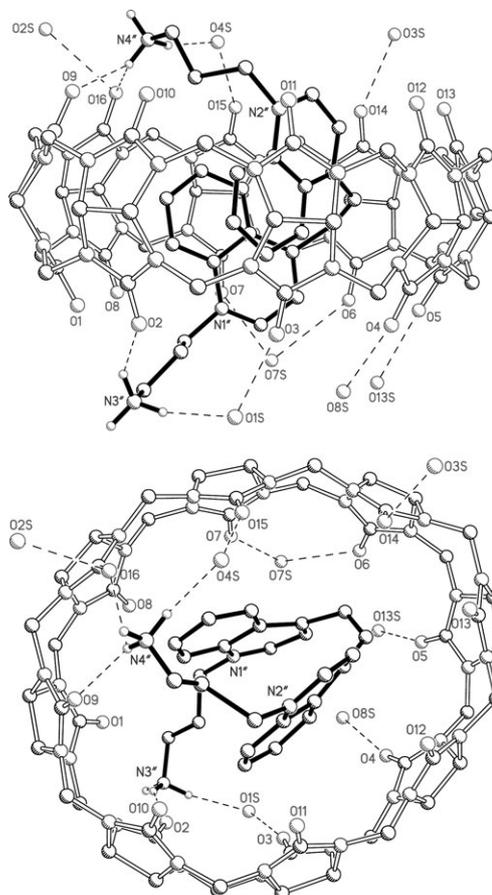


Fig. 5 Structure of the host-guest component of the unit cell of **4b** in different projections.

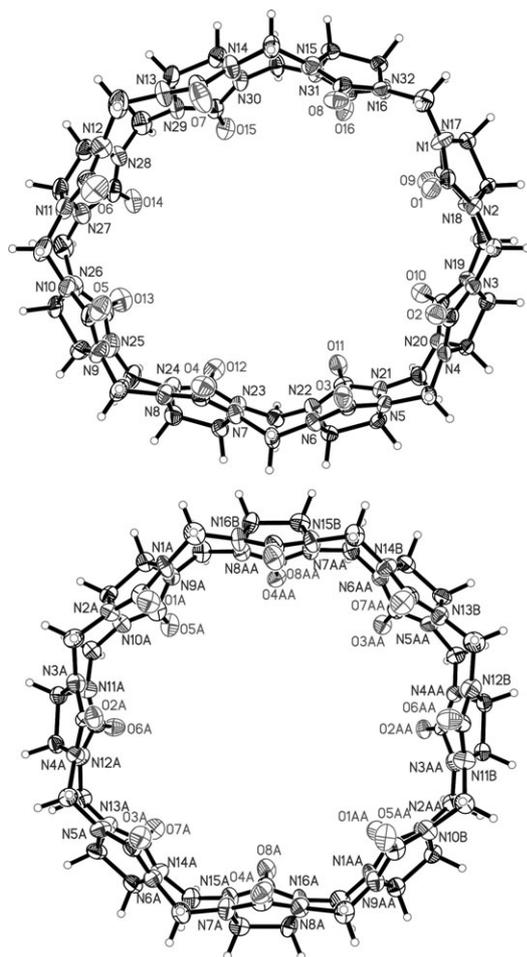


Fig. 6 Structure of two independent CB[8] molecules in **4b**. The molecules are drawn with anisotropic displacement parameters at the 50% probability level.

results mean that the skeleton of CB[8] is not too rigid; encapsulating a big molecule in its cavity results in a rather significant deformation of the CB[8] cage.

It is important that the guest molecule **1b** adopts a *Z*-conformation in **4b** (Fig. 7). The torsion angle C(3'')–C(20'')

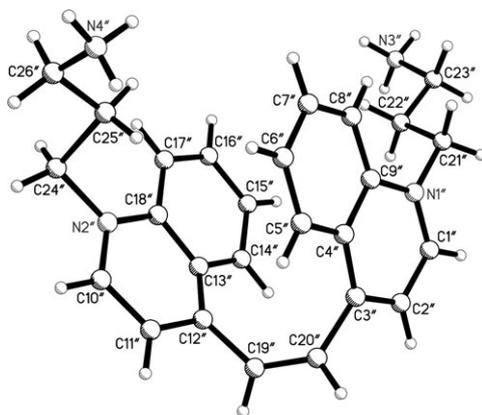


Fig. 7 Structure of guest molecule (*Z*)-**1b** encapsulated by a CB[8] molecule in **4b**.

–C(19'')–C(12'') about the ethylene bond is equal to 36.6(3)°. The dihedral angle between the quinoline systems of the molecule is 27.4(3)°.

As stated in the NMR section, reversible *E*–*Z* isomerization of **1b** occurs in solution when exposed to visible light. However, the *Z*-isomer is thermodynamically less favorable than the *E*-isomer. Apparently, the spatial structure of (*Z*)-**1b** fits well into the cavity of CB[8]. An additional stabilization of the host–guest system is provided by hydrogen bonds (NH₃⁺...O=C) formed by the ammonium tails of **1b** with carbonyl oxygens of CB[8].

The guest molecule forms hydrogen bonds of the NH₃⁺...O=C type with the both portals of the CB[8] molecule. It also forms hydrogen bonds of NH₃⁺...H₂O and NH₃⁺...Br[–] types. One ammonium group forms two hydrogen bond of the first type and one hydrogen bond with water molecule. The distances N(3'')...O(5A) and H(3''A)...O(5A) are 2.813 and 2.05 Å; N(3'')...O(1S) and H(3''C)...O(1S), 2.894 and 2.01 Å; N(3'')...O(2) and H(3''B)...O(2) 2.700 and 1.91 Å, respectively. The second ammonium group forms one hydrogen bond with the portal carbonyl group, one with halogen anion, and one with water molecule. The distances N(4'')...Cl(3) and N(4'')...Br(3) are 3.00(1) Å and 3.26(1) Å, with the corresponding distances H...halogen, 2.10 and 2.42 Å, respectively. The N(4'')...O(9) and H(4''B)...O(9) distances are 2.88 and 2.10 Å, N(4'')...O(4S) and H(4''C)...O(4S) are 2.88 and 2.00 Å, respectively.

Commonly, *Z*-isomers of bisquaternary salts of 1,2-di(4-pyridyl)ethylene and 1,2-di(4-quinolyl)ethylene are unstable because the barrier to the back *Z* → *E* isomerization is low, which shifts the equilibrium to the more stable *E*-isomers. Capturing the *Z*-isomer of **1b** into the cavity of the CB[8] structure provides its stabilization. Interestingly, the *E*-isomer of acceptor **1b**, existing in solution in equilibrium with its *Z*-isomer, does not form a crystal complex. Apparently, the size of this isomer is too small for the cavity of CB[8] to allow a stable inclusion complex to form in the solid state.

Conclusions

Thus, the structure of the viologen analogue has a substantial influence on the stoichiometry and stability of its inclusion complexes with CB[8]. The NH₃⁺ groups of the acceptor are involved in hydrogen bonds with carbonyl groups of the two portals of CB[8], which markedly enhanced the stability of the complexes. Three types of pseudorotaxane type inclusion complexes of unsaturated viologen analogue and CB[8] were found. The importance of a good fit of the acceptor-guest molecule to the cavity of the host molecule in order to form stable complex in the crystal is obviously demonstrated in the case of the *Z*-isomer of the di(4-quinolyl)ethylene derivative. This complex is the first example of a complex formed by the *Z*-isomer of 1,2-dihetaryl-substituted ethylene with CB[*n*] in the crystalline state. The data obtained demonstrate the possibility of constructing light-controlled shuttle molecular machines based on unsaturated viologen analogues and cucurbiturils.

Experimental

General methods

The melting points are measured with a MEL-Temp II apparatus. The ^1H and ^{13}C NMR spectra were recorded on Bruker DRX500 instrument using the solvent as internal reference. ^1H – ^1H and ^1H – ^{13}C COSY spectra (HSQC, HMBC) were used to assign the proton and carbon signals. IR spectrum was recorded on a Bruker IFS-113V spectrophotometer in Nujol between KBr plates. Elemental analysis was performed at the microanalytical laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds of the RAS in Moscow, Russian Federation.

Preparations

Synthesis of 1-(3-ammoniopropyl)-4-(*E*)-2-[1-(3-ammoniopropyl)-4-pyridiniumyl]-1-ethenylpyridinium tetraperchlorate (**1a**) has been described elsewhere.^{18,20}

4-[(*E*)-2-(4-Quinoly)-1-ethenyl]quinoline (2). A solution of lepidine (0.50 mL, 3.82 mmol) and 4-formylquinoline (0.50 g, 3.19 mmol) in acetic anhydride (10 mL) was heated at 140 °C for 30 h. The solution was cooled to –10 °C, and the crystalline precipitate was filtered, washed with hexane and dried in air to give crude product (0.74 g), which was purified by column chromatography on silica gel (Kieselgel 60, 0.063–0.200 mm, Merck) using a gradient mixture of benzene and EtOAc up to 50% of the latter. (*E*)-**2** (0.68 g, 76%) was obtained as a yellow solid, mp 200–206 °C (lit. data⁴⁰ 205 °C). ^1H NMR (DMSO-*d*₆, 30 °C) δ : 7.70 (m, 2H, 2 H(6)), 7.83 (m, 2H, 2 H(7)), 8.09 (d, J = 7.9 Hz, 2H, 2 H(8)), 8.17 (d, J = 4.3 Hz, 2H, 2 H(3)), 8.41 (s, 2H, CH=CH), 8.58 (d, J = 8.5 Hz, 2H, 2 H(5)), 8.99 (d, J = 4.3 Hz, 2H, 2 H(2)). ^{13}C NMR (DMSO-*d*₆, 30 °C) δ : 117.80 (2 C(3)), 124.02 (2 C(5)), 125.66 (2 C(10)), 126.74 (2 C(6)), 128.99 (CH=CH), 129.42 (2 C(7)), 129.47 (2 C(8)), 141.24 (2 C(4)), 148.20 (2 C(9)), 150.19 (2 C(2)).

1-(3-Ammoniopropyl)-4-(*E*)-2-[1-(3-ammoniopropyl)-4-quinoliniumyl]-1-ethenylquinolinium tetraperchlorate semihydrobromide (1b). A finely ground mixture of (*E*)-**2** (50 mg, 0.18 mmol) and 3-bromopropylamine hydrobromide (230 mg, 1.06 mmol) was heated at 140 °C for 4 h and then at 190 °C for 2 h. After cooling to rt, the mass obtained was treated with anhydrous EtOH (10 mL), and the insoluble substance was filtered, washed with anhydrous EtOH (4 \times 5 mL) and then with chloroform (2 \times 10 mL), and dried *in vacuo* to yield the corresponding tetrabromide salt (53 mg) as a yellowish-green solid. The tetrabromide salt was dissolved in a mixture of EtOH (10 mL) and the minimum quantity of water with heating, and 70% aq. HClO₄ (51 μL , 0.59 mmol) was added to the hot solution. After cooling to –10 °C, the precipitate formed was filtered, washed with anhydrous EtOH (5 mL), and dried *in vacuo* to give the corresponding tetraperchlorate salt **1b** (41 mg, a complex with HBr) as a yellowish-green solid in 27% overall yield; mp 306–308 °C (decomp.). IR ν/cm^{-1} : 3410 (br., OH, HBr, NH). ^1H NMR (DMSO-*d*₆, 30 °C) δ : 2.33 (m, 4H, 2 CH₂CH₂NH₃⁺), 3.06 (m, 4H, 2 CH₂NH₃⁺), 5.18 (t, J = 7.4 Hz, 4H, 2 CH₂N⁺), 7.82 (br.s, 6H, 2 NH₃⁺), 8.19 (m,

2H, 2 H(6)), 8.40 (m, 2H, 2 H(7)), 8.72 (d, J = 9.2 Hz, 2H, 2 H(8)), 8.99 (s, 2H, CH=CH), 9.02 (d, J = 6.5 Hz, 2H, 2 H(3)), 9.15 (d, J = 8.8 Hz, 2H, 2 H(5)), 9.68 (d, J = 6.5 Hz, 2H, 2 H(2)). ^{13}C NMR (DMSO-*d*₆, 30 °C) δ : 27.31 (2 CH₂CH₂NH₃⁺), 35.99 (2 CH₂NH₃⁺), 54.42 (2 CH₂N⁺), 119.28 (2 C(8)), 119.63 (2 C(3)), 126.93 (2 C(5)), 127.48 (2 C(10)), 129.92 (2 C(6)), 132.98 (CH=CH), 135.46 (2 C(7)), 137.91 (2 C(9)), 148.54 (2 C(2)), 150.50 (2 C(4)). Anal. calcd for C₂₆H₃₂Cl₄N₄O₁₆ \times 0.5HBr \times H₂O: C, 36.45; H, 4.06; N, 6.54%; found: C, 36.24; H, 3.81; N, 6.27%.

^1H NMR titrations

The titration experiments were performed in D₂O/CD₃CN (10 : 1) solutions at 30 \pm 1 °C. The concentration of CB[8] in saturated solutions, containing finely dispersed solid CB[8] (total amount \sim 6 \times 10^{–4} M), was changed gradually with increasing of the added **1a,b**, starting from 1.30 \times 10^{–4} M (Fig. 1S, ESI). The real concentrations of CB[8] were calculated from integral intensities of signals of CHD₂CN and methylene protons of CB[8], proceeding from the data on CB[7] in this system of solvents. The concentration of **1a,b** in the solution was gradually increased starting from zero. The highest **1a,b**/CB[8] real concentration ratios were \sim 50 for **1a**, and \sim 3 for **1b**. The proton chemical shifts were measured as a function of the **1a,b**/CB[8] ratio. In the case of slow exchange on the ^1H NMR time scale, the average chemical shifts were calculated taking into account the integral intensities of corresponding signals, and the complex formation constants were then calculated using the HYPNMR program.²⁶

X-Ray crystallography

Single crystals of **4a** and **4b** were grown by slow evaporation from water–acetonitrile solutions containing CB[8] and **1a** or **1b**, respectively, under day light conditions. The crystal of **4b** had an irregular shape, eroded surface, and was of a rather bad quality. However, it gave X-ray reflection and the orientation matrices were determined in both cases. Experimental data were collected for **4a** and **4b** on a Bruker SMART CCD diffractometer [graphite monochromatized MoK α -radiation, ω scan mode, 10 s frame^{–1}].

Structure **4a** was solved in *P*₄/*ncm* tetragonal space group and refined anisotropically. Almost all hydrogen atoms were located from the difference electron density map. However, their coordinates were calculated and further refined using the riding model. The strongest peaks in the residual electron density map were assigned with partial site occupation factors. The difference Fourier map contained many electron density peaks at distances from other atoms corresponding to van der Waals contacts. However, structure refinement with additional oxygen atoms attributed to these peaks did not result in any improvement of the refinement parameters and gave unacceptable values for their thermal parameters. An attempt to refine the structure in the monoclinic space group *P*₂₁/*c* did not allow us to achieve better refinement parameters and we failed to identify the residual peaks of electron density as definite small molecules or atoms. For this reason we accepted as a final the tetragonal space group.

Crystal data for **4a**: $C_{48}H_{52.26}ClN_{32}O_{21.63}$, $M = 1459.01$, tetragonal, $a = 26.2548(8)$, $b = 26.2548(8)$, $c = 12.7555(5)$ Å, $V = 8792.6(5)$ Å³, $T = 120.0(2)$ K, space group $P4_2/nm$ (no. 138), $Z = 4$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.121$ mm⁻¹, 60288 reflections measured, 4966 unique ($R_{\text{int}} = 0.0964$) which were used in all calculations. The final R_1 and wR_2 were 0.1903 and 0.4958 for $I > 2\sigma(I)$, 0.2546 and 0.5266 for all data.

Structure **4b** was solved and refined in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were fixed at calculated positions and refined using the riding model. In the structure, one anionic position was occupied with bromide. Two other anionic positions were simultaneously occupied with ClO_4^- and Br^- with different occupations. The fourth anion is a perchlorate disordered over at least two positions with rotational disorder in each of the two positions. Because of the rotational disorder we failed to find oxygen atoms for most of the perchlorate groups. It should be noted that an occurrence of Br^- anions partly replacing perchlorate anions does not contradict the conditions of synthesis.

Crystal data for **4b**: $C_{98}H_{123}Br_{1.53}Cl_{2.47}N_{52}O_{43.38}$, $M = 2933.39$, monoclinic, $a = 15.5210(7)$, $b = 25.5665(11)$, $c = 32.4483(14)$ Å, $\beta = 101.039(2)^\circ$, $V = 12637.8(10)$ Å³, $T = 120.0(2)$ K, space group $P2_1/n$ (no. 14), $Z = 4$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.658$ mm⁻¹, 150412 reflections measured, 30519 unique ($R_{\text{int}} = 0.2618$) which were used in all calculations. The final R_1 and wR_2 were 0.1253 and 0.3255 for $I > 2\sigma(I)$, 0.3045 and 0.3702 for all data.

Crystallographic parameters, data collection, structure solution and refinement parameters for **4a** and **4b** are given also in Table 1S (ESI).

All the calculations were performed using SHELXTL-Plus software.⁴¹ CCDC reference numbers 288096 and 288097. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511456j

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