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Femtosecond absorption spectroscopy of bis-aza-18-crown-6-containing dibenzylidenecyclobutanone complexes with alkali and alkaline-earth metal cations

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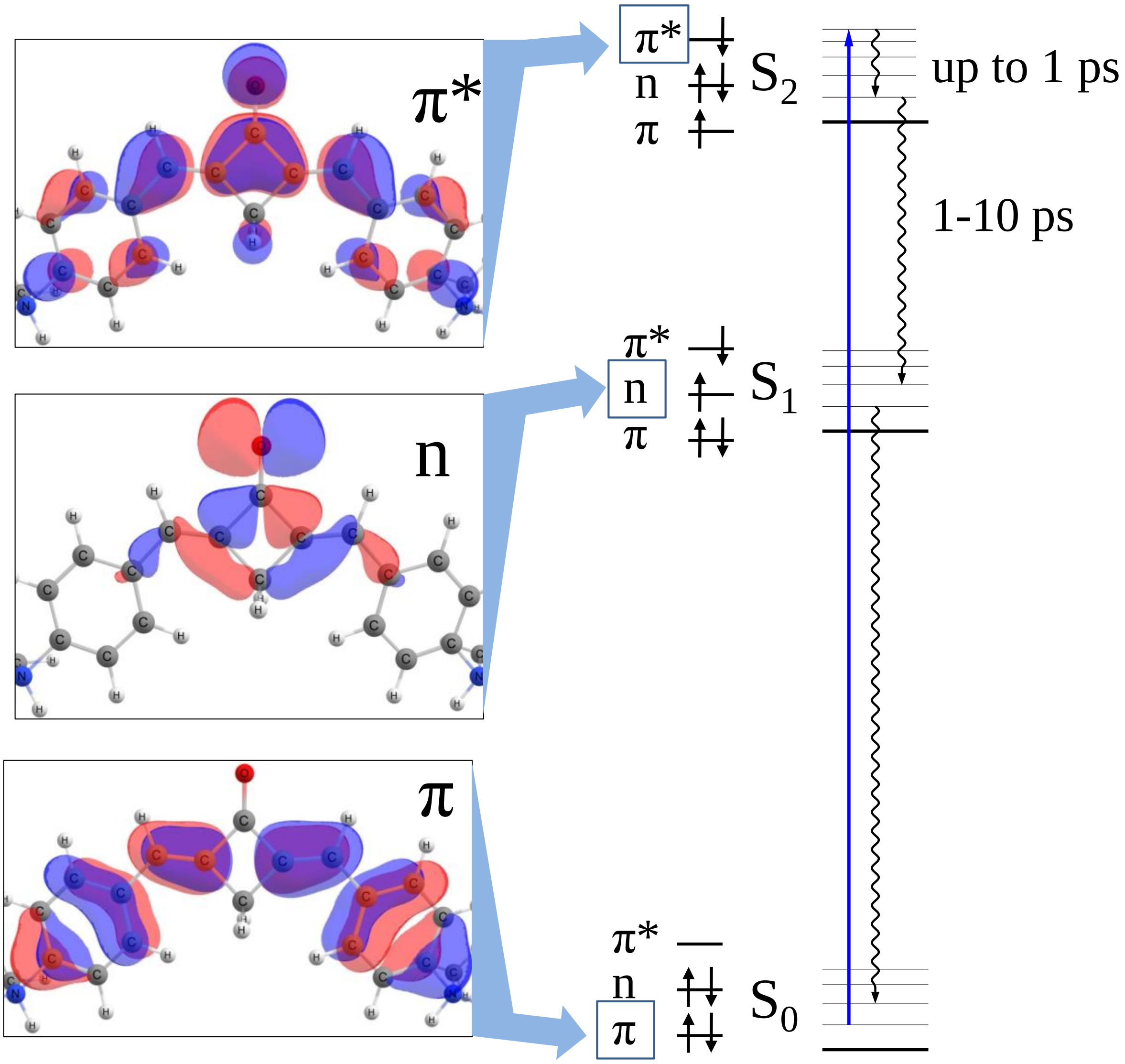

Figure S1 Relaxation path of excitation energy for the complex **1**·(H$^+$)$_2$

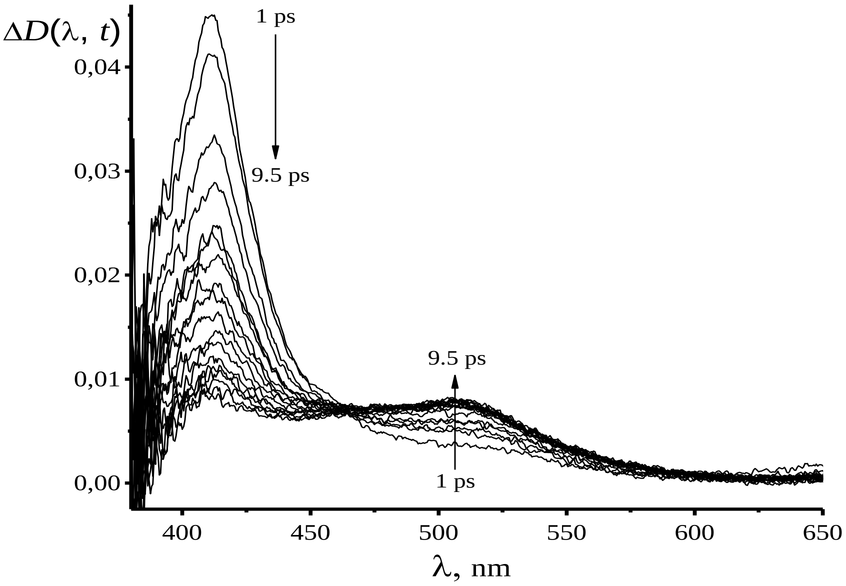

Figure S2 Time-resolved spectra of $S_2 \rightarrow S_m$ (left) and $S_1 \rightarrow S_n$ (right) absorption of the complex **1**$\cdot(H^+)_2$ in MeCN in a range of 1–9.5 ps, increment – 0.5 ps. Excitation at 350 nm, halfwidth of excitation pulse – 30 fs. Concentration of CF_3COOH – 0.05 M.

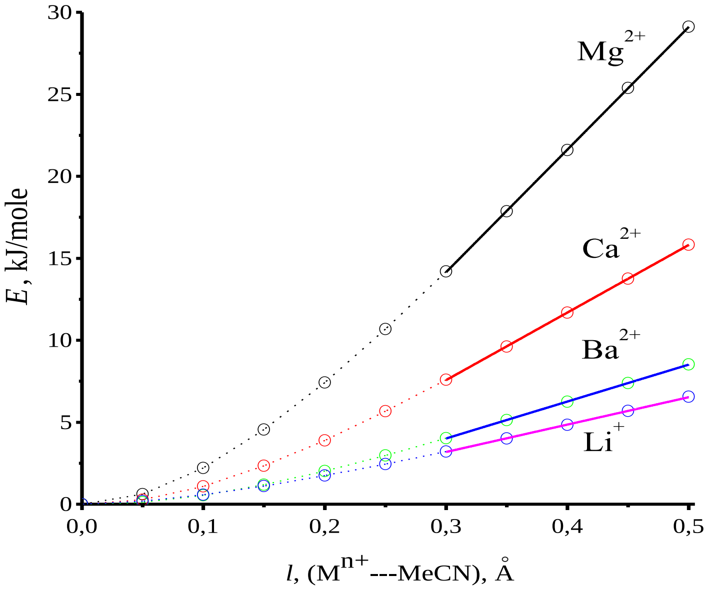

Figure S3 Energy of complex **1**$\cdot(M^{n+}\cdot mMeCN)_2$ as a function of length: M^{n+}---MeCN.

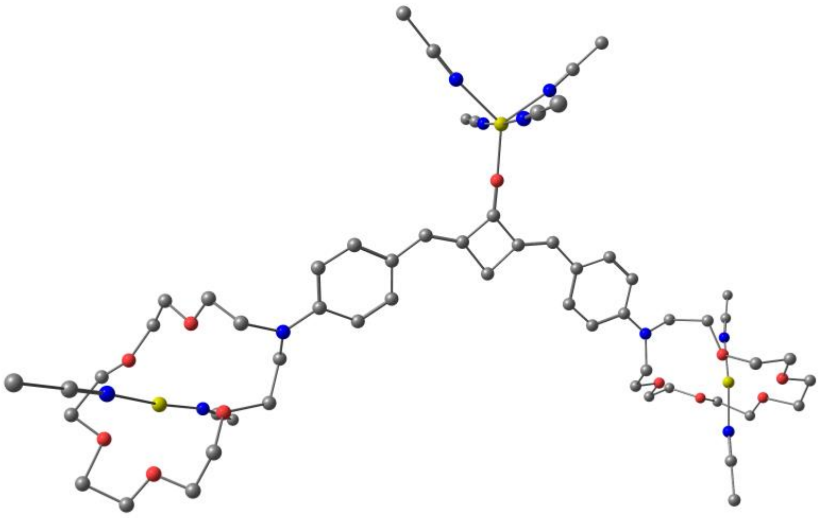

Figure S4 Molecular structure of the Mg^{2+}·**1**·$(Mg^{2+})_2$ complex (solvated by MeCN) in the ground state.

Table S1 Calculated parameters for dye **1** and metal complexes: *d* is the maximum interatomic distance the in molecule (without its solvent shell), k_d is the estimated size of the molecule (*d*/*d*(complex with Mg^{2+})), *V*′ is the volume of the cavity occupied by the molecule, V_s' is the volume of the sphere with a square surface identical to that of the cavity, V_{ss}' is the volume of the nearest solvent shell (for the complexes with Li^+ and Mg^{2+} the volumes of the solvent shell of the crowned cation and the metal cation coordinated with the carbonyl group are shown separately)

Species[a]	*d*, Å	k_d	*V*′, Å^3	V_{ss}', Å^3	V_s', Å^3
1	22	0.738	870	–	2300
1·$(Ba^{2+}\cdot 4MeCN)_2$	27	0.906	1260	1880	4210
1·$(Ca^{2+}\cdot 3MeCN)_2$	29.8	1	1100	1230	3420
$(Li^+ \cdot 3MeCN)$·**1**·$(Li^+\cdot 2MeCN)_2$	27.6	0.926	1210	830+760	3740
$(Mg^{2+}\cdot 5MeCN)$·**1**·$(Mg^{2+}\cdot 2MeCN)_2$	29.8	1	1270	830+1280	4240

[a]The total energy of the complex *vs* M^{n+}---MeCN distance plot is shown in Figure S3.

Experimental details

(2E,4E)-2,4-Bis[4-(1,4,7,10,13-penthaoxa-16-azacyclooctadecane-16-yl)benzylidene]-cyclobutanone **1**. A solution of cyclobutanone (3.5 mg, 0.05 mmol) of in ethanol (0.2 ml) was added to 4'-formylphenylaza-18-crown-6-ether **2** (38.5 mg, 0.11 mmol). Then, 3% NaOH in an ethanol–water mixture (4:1, 50 μl) was added dropwise at constant stirring. The reaction mixture was kept at room temperature for 96 h (TLC control), acidified with a 0.5 M solution of hydrochloric acid to pH = 6–7, diluted with water (5 ml), and extracted with chloroform (5 × 4 ml). The resulting extracts were evaporated *in vacuo*; the residue was purified by column chromatography on aluminum dioxide (Type T, Basisch, 63-200 μL, Merck), eluting with benzene as well as various mixtures: benzene–MeCN (100 : 1), benzene–MeCN (8 : 1), benzene–MeCN (1 : 1). The product (19 mg, 50%) was obtained as a brown-red oil. R_f 0.63 (EtOH–EtOAc, 1:10, DC-Alufolien Aluminiumoxid 60 F_{254} neutral, Merck). ^{1}H NMR spectrum (Bruker DRX500, MeCN-d_3, 27°C) δ: 3.58 (m, 32H, $16CH_2O$); 3.66 (m, 16H, $4CH_2CH_2N$); 3.74 (m, 2H, $CH_2(3)$); 6.78 (d, 4H, 2H(3’), 2H(5’), *J* 8.8 Hz); 7.01 (s, 2H, 2H(α)); 7.49 (d, 4H, 2H(2’), 2H(6’), *J* 8.8 Hz). ^{13}C NMR spectrum (Bruker DRX500, MeCN-d_3, 27 °C) δ: 34.35 (C(3)); 50.37 ($4CH_2N$); 67.58 ($4CH_2CH_2N$); 69.66, 69.71, 69.81, 69.86 ($16CH_2O$); 111.23 (2C(3’), 2C(5’)); 121.83 (2C(α)); 125.17 (2C(1’)H); 131.06 (C(2’), C(6’)); 141.12 (C(2), C(4)); 148.92 (2C(4’)); 188.95 (C=O). IR spectrum (Bruker IFS-113V, KBr, ν: 1702 cm^{-1} (ν C=O). UV-VIS (MeCN, λ_a^{max}: 280 nm (ε = 219000 $M^{-1}\cdot cm^{-1}$), 420, shoulder (ε = 30800 $M^{-1}\cdot cm^{-1}$), 477 (ε = 57600 $M^{-1}\cdot cm^{-1}$). Fluorescence (MeCN), λ_{exc}: 470 nm, λ_f^{max}, 577 nm. Mass. spectrum (m/z): 769.43 $[M + H]^+$, 791.41 $[M + Na]^+$. Experimental (%): C, 65.75; H, 7.79; N, 3.72. $C_{42}H_{60}N_2O_{11}$ (768.93268). Calculated (%): C, 65.60; H, 7.86; N, 3.64.

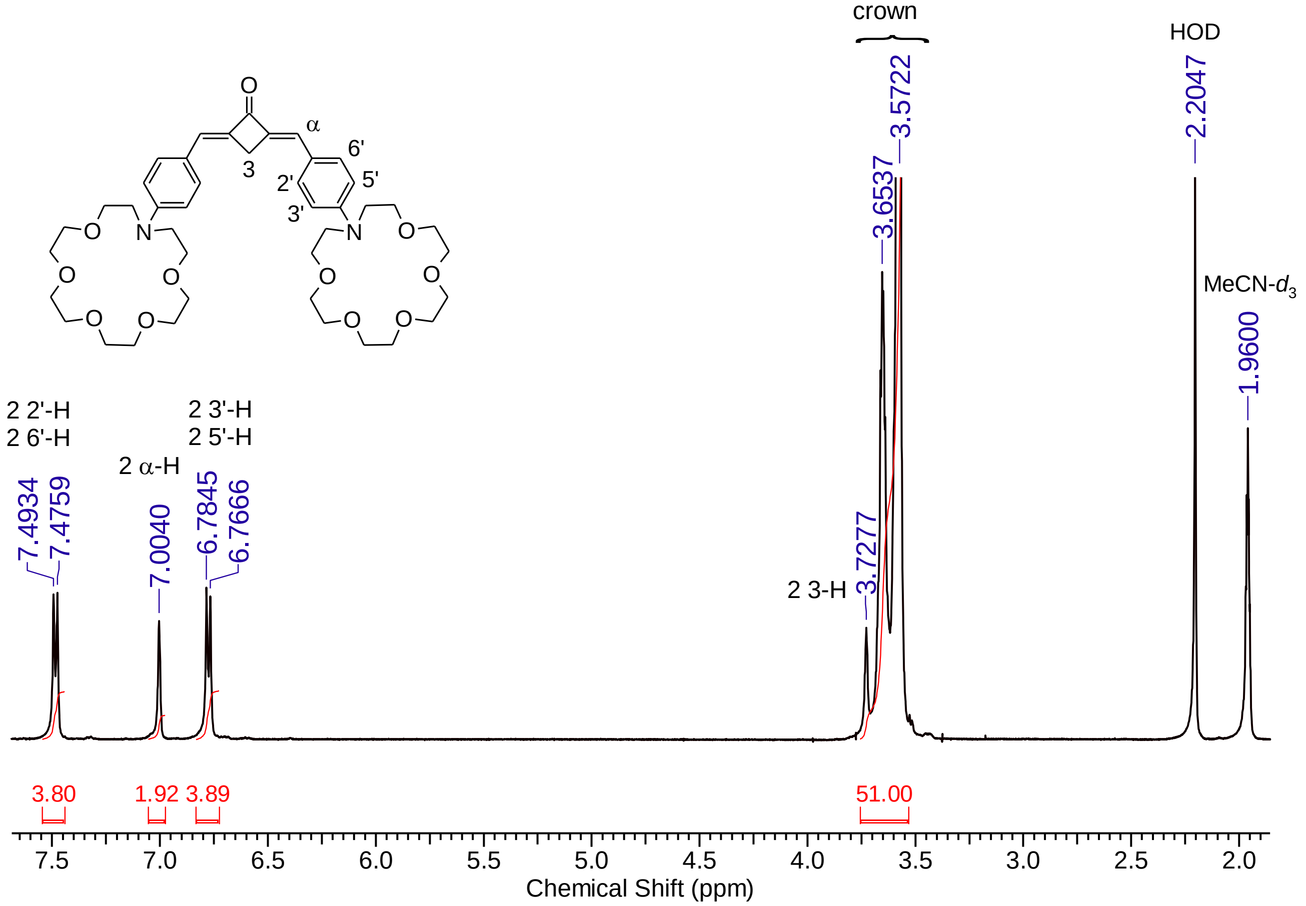

Figure S5 ^{1}H NMR spectrum of compound **1** in MeCN-d_3.

For the measurement of transient absorption spectra, freshly prepared solutions of the fluorophores in MeCN ("Fisher", HPLC gradient grade, water content 0.0021 mass %) were used. The details of time-resolved measurements were reported earlier.[S1] For complexation, the spectrally pure dry perchlorates of Li, Na, K, Mg, Ca, and Ba (Merck) were used. Dehydration was performed *via* calcination of the salts in a "VacuCell" vacuum drying oven (0.01 mm Torr) at 200° C for 5 hours. The protonated forms of dye **1** were produced with 100% trifluoroacetic acid. Steady-state absorption spectra, registered after time-resolved measurements, showed a minimal decomposition of the samples. The stability constants of the complexes were calculated using the "Equilibrium" program based on a multivariable nonlinear least squares method.[S2]

Quantum chemical calculations were performed using Firefly 8.2[S3] and Orca 5.0[S4] program packages. For conformation plots, the geometries of the compounds in their ground states were optimized at fixed M^{n+}---N distances by means of DFT; the excited state geometry was optimized by means of TDDFT (BHHLYP functional) within the 6-31G(d,p) basis for all atoms excluding barium. For the barium atom, def2-SVP and def2-ECP bases were used. The optimized geometric parameters for the compounds in their ground and excited states were calculated by DFT and TDDFT methods

(BHHLYP functional) in the same basis, accounting for solvation with the SMD model, relying upon electron density.[S5] The ground and excited state energies of the compounds were calculated by the same approaches (DFT+SMD and TDDFT+SMD) using the B3LYP functional with the same basis, amended with the addition of diffuse functions for the nitrogen and oxygen atoms.

References

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