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Molecular fan based on photoinduced recoordination in bis(aza-18-crown-6) cyclohexanone $EtNH_3^+$ complexes: mechanism and its unusual aspects

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Details of time-resolved absorption spectroscopy

Freshly produced MeCN ("Panreac", HPLC grade, water content 0.02% w/w) solutions of the dye and corresponding complexes were used in time-resolved spectroscopic experiments. Time-resolved $S_1 \rightarrow S_n$ TA spectra were detected with an fs-resolution pulse differential absorption spectrometer at N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences. The exact details of time-resolved spectroscopy measurements are given in [S1,S2]. For excitation, Gaussian pulses with ~60 GHz PRF, ~40 fs duration and ~350 mJ energy were used (radiation maxima at 325, 340, 370, 417, 430 nm). Pump and probe pulse polarizations were oriented at a "magic angle" (54.7°) against each other. The measured $\Delta D(\lambda,t)$ differential spectra were corrected accounting for continuum group velocity dispersion, following the procedure described in [S3]. The experiments were carried out at 21°C in a 0.5 mm optical cell. Further details are provided in the manuscript.

Details of quantum-chemical calculations

Quantum-chemical calculations were carried out in Firefly 8.2 and Orca 5.0 packages [S4,S5]. For potential energy profiles, the geometries of **CD6** and its complexes with M^{n+} were optimized in the ground electron state with a fixed N---M^{n+} distance *via* DFT (BHHLYP, 6-31G(d,p)) for all atoms except barium where the def2-SVP and def2-ECP levels were used. The optimized geometric parameters for the ground and excited states of **CD6** and its complexes were calculated *via* DFT and TD DFT with the BHHLYP functional and the same basis. Solvation was accounted for with the SMD model [S6]. The energies of ground and excited states were also determined *via* DFT+SMD and TDDFT+SMD with the B3LYP functional and the same basis amended with diffuse functions for the nitrogen and oxygen atoms.

Fluorescence spectra of CD6·$(H^+)_2$ in MeCN.

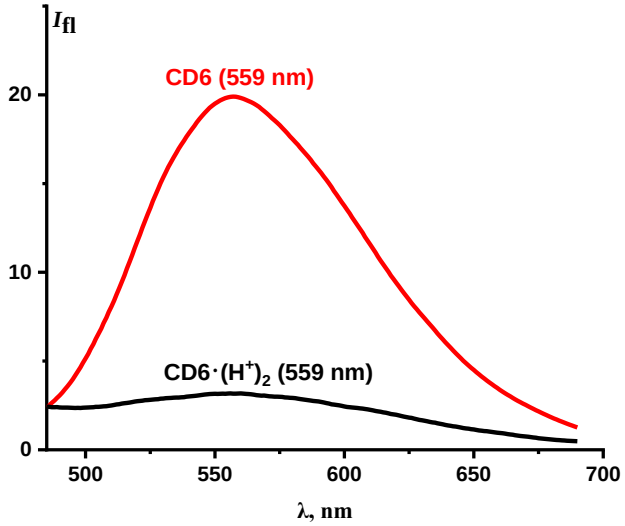

Figure S1. Fluorescence spectra of CD6 (red line) and CD6·$(H^+)_2$ in MeCN ($C(H^+) = 10^{-4}$ M) (black line), λ_{exc} = 380 nm.

Femtosecond-scale TA spectra of CD6·$(H^+)_2$ in MeCN.

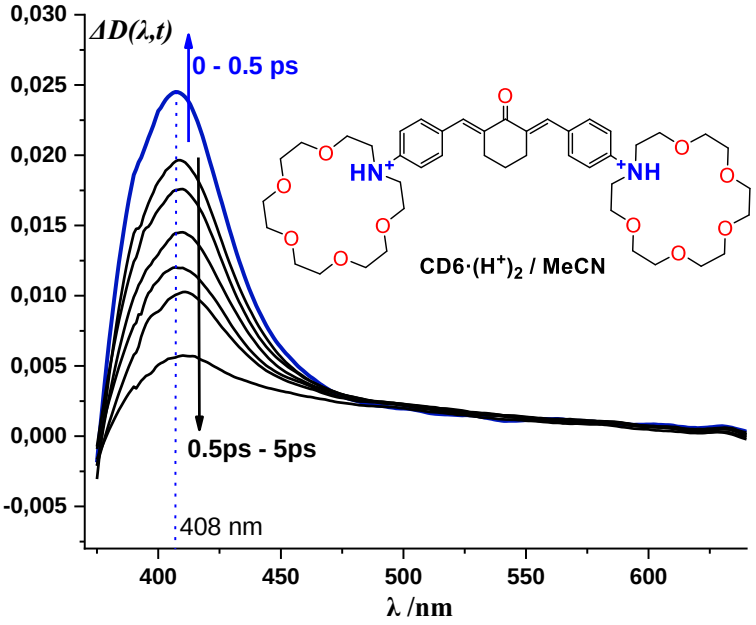

Figure S2. TA spectra for CD6·$(H^+)_2$ in MeCN (0—5 ps), λ_{exc} = 325 nm. Insert: CD6·$(H^+)_2$ structure in MeCN.

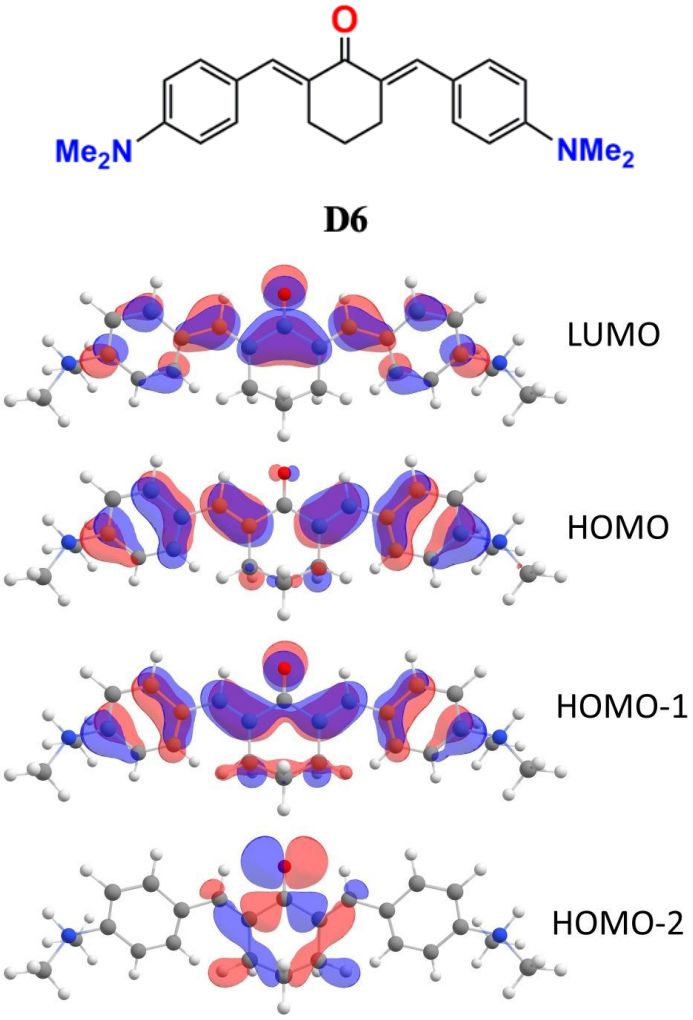

Figure S3. Molecular orbitals involved in the formation of the three lowest electronically excited states of **D6**·$(H^+)_2$: S_1 (HOMO−2 → LUMO), S_2 (HOMO → LUMO), S_3 (HOMO−1 → LUMO).

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