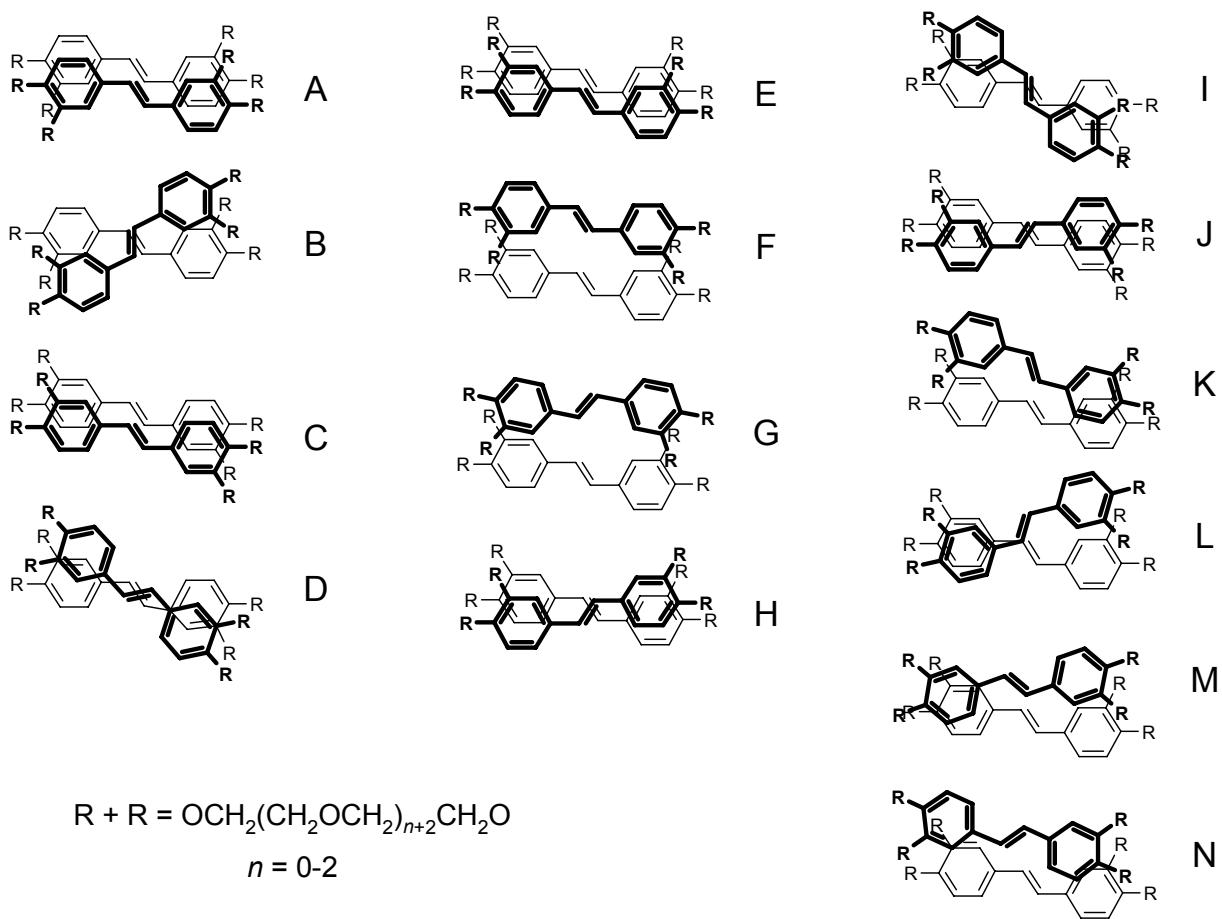


Electronic Supplementary Information

for the article “Controlled self-assembly of bis(crown)stilbenes into unusual bis-sandwich complexes:
structure and stereoselective [2+2] photocycloaddition”

by Sergey P. Gromov,* Artem I. Vedernikov, Natalia A. Lobova, Lyudmila G. Kuz'mina, Stepan S. Basok, Yuri A.
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Scheme S1 Combination of conformers of stilbenes (*E*)-**1a-c** within bis-sandwich complexes.

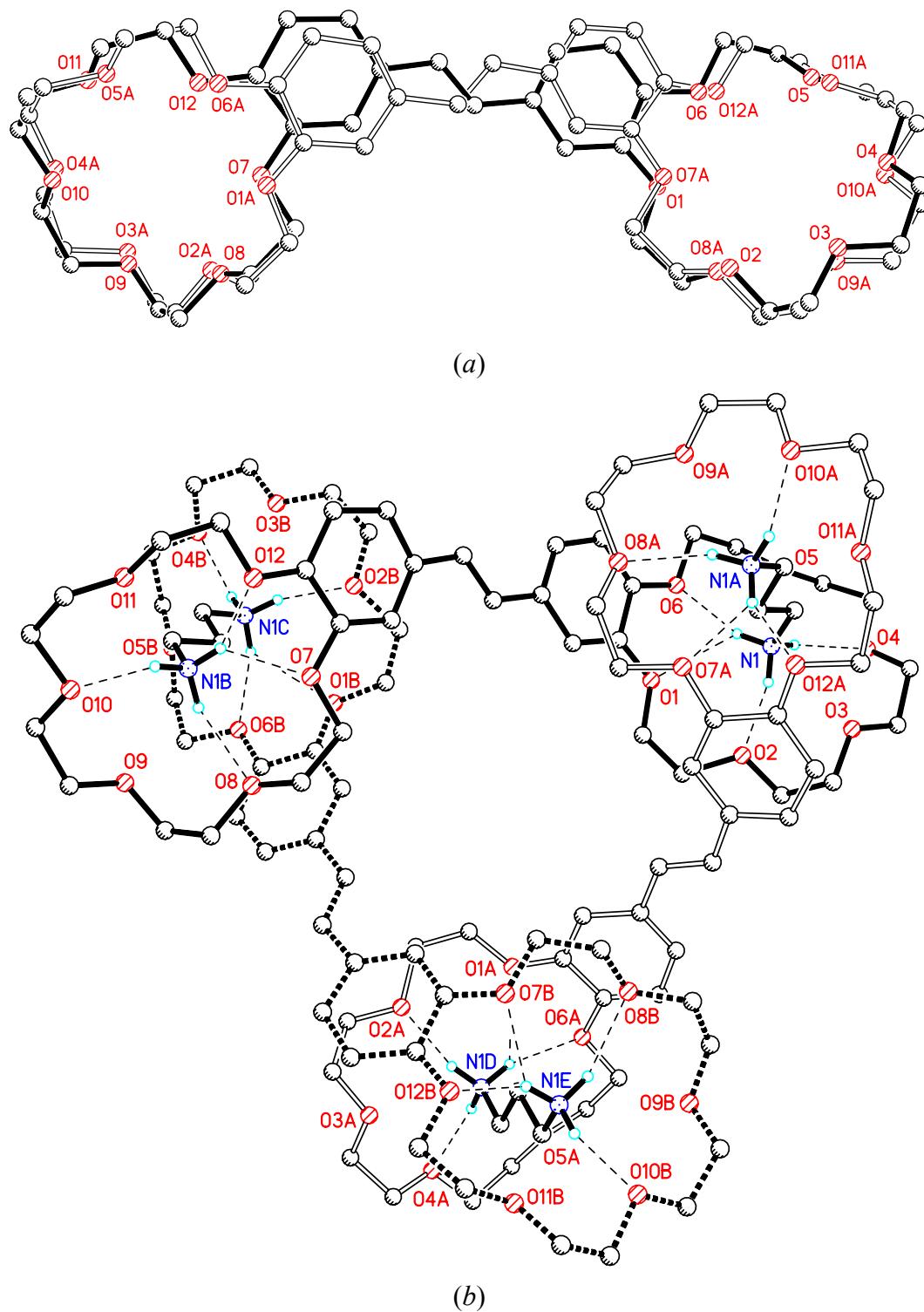


Fig. S1 In the crystal $(\text{E})\text{-1c}\cdot\text{C3}\cdot2.67\text{C}_6\text{H}_6$: (a) disorder of stilbene molecule and (b) cyclic trimer $(\text{1c})_3\cdot(\text{C3})_3$ (the disorder of stilbene molecules is not shown). The additional letters “A”, “B”, “C”, “D”, and “E” indicate that atoms belong to symmetrically related positions. Most of the hydrogen atoms, perchlorate anions and solvate molecules are omitted for clarity. Hydrogen bonds are drawn with thin dash lines.

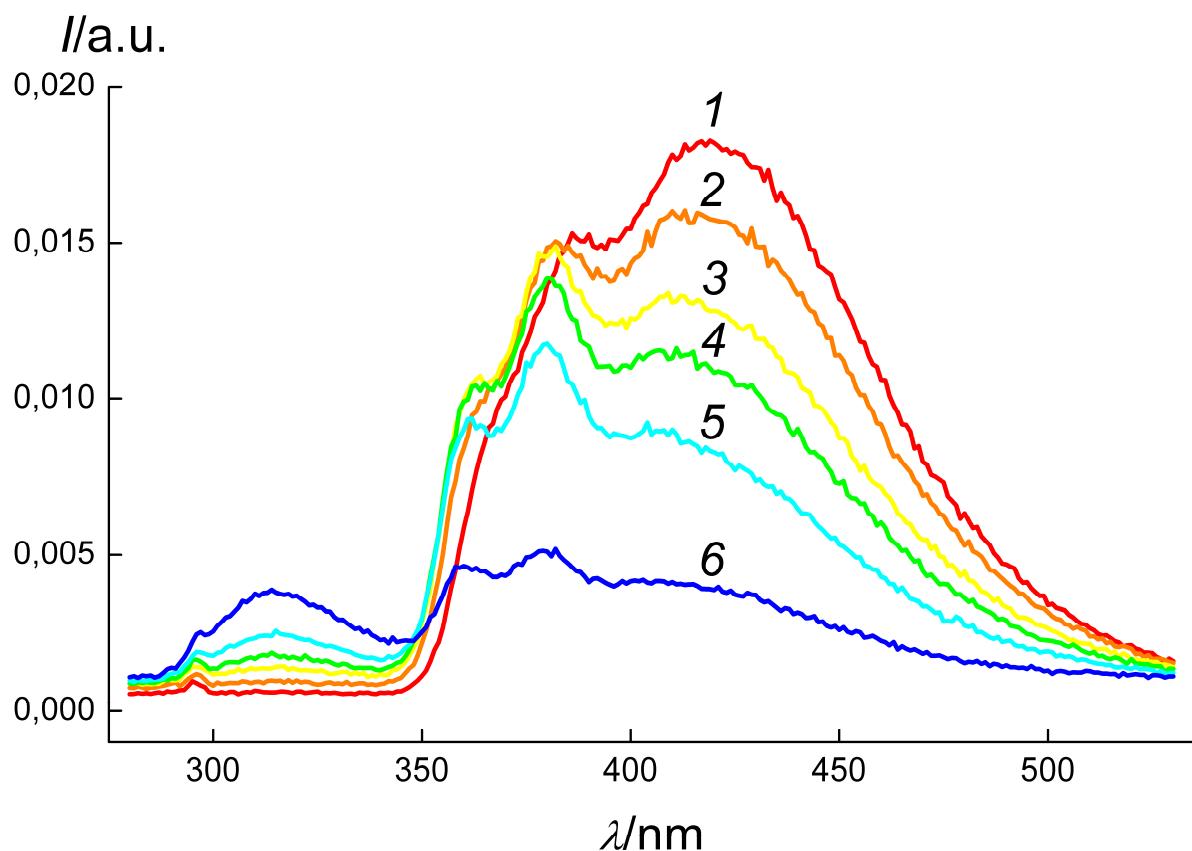


Fig. S2 Emission spectra of (1) equimolar mixture of (*E*)-**1b** and $\text{Ba}(\text{ClO}_4)_2$ ($C = 1 \cdot 10^{-5}$ M, MeCN, 1-cm cell, ambient temperature) and its photolysates after irradiation over (2) 0.8, (3) 2, (4) 3, (5) 5, and (6) 25 s; excitation at 270 nm.

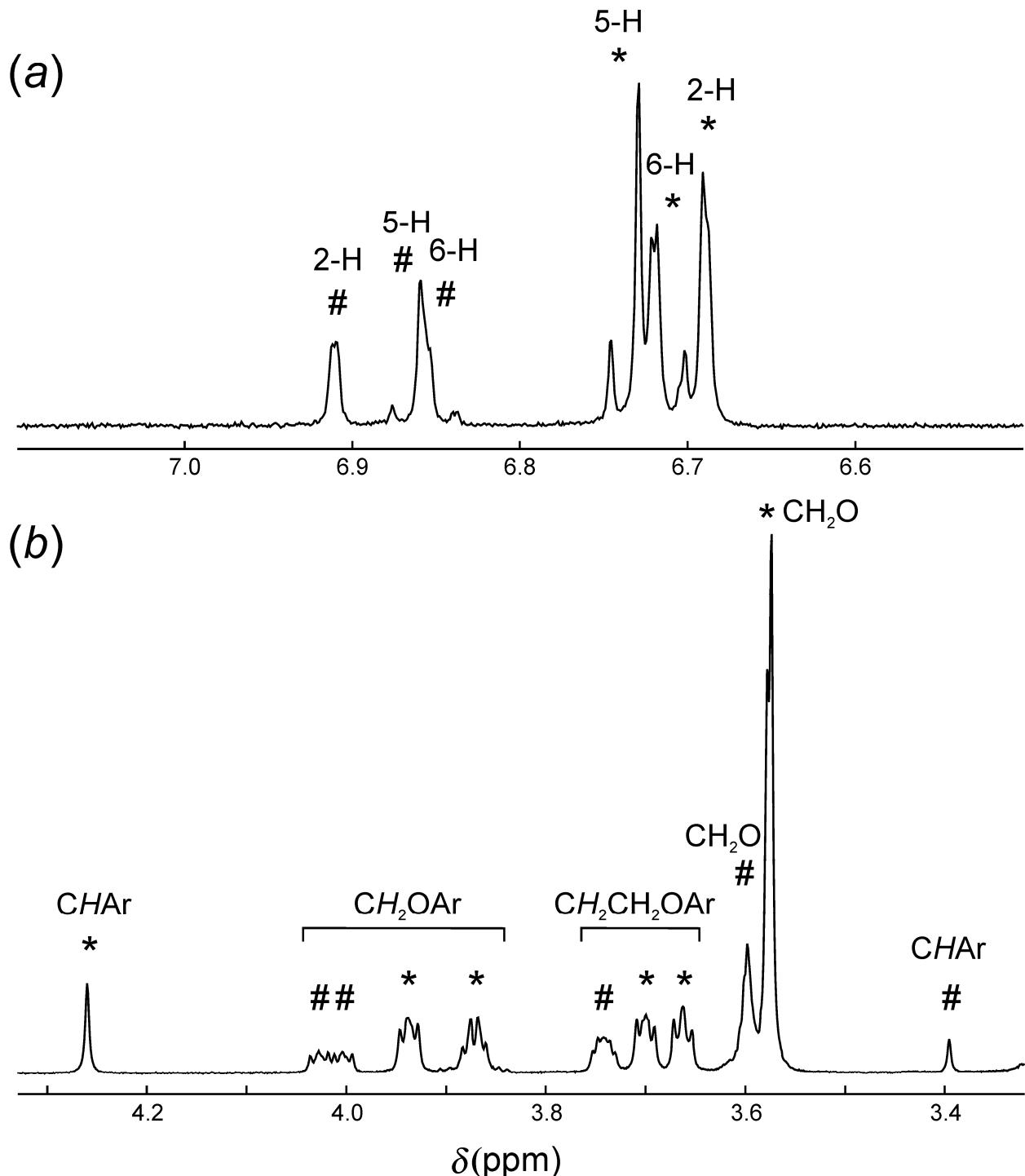


Fig. S3 ^1H NMR spectrum (the regions for (a) aromatic and (b) aliphatic protons) of the reaction mixture after photolysis in system (*E*-**1b**/Ba(ClO₄)₂ (500 MHz; DMSO-*d*₆; 30 °C). The proton signals are marked with asterisk for *rctt*-**4b** and with # for *rtct*-**4b**.

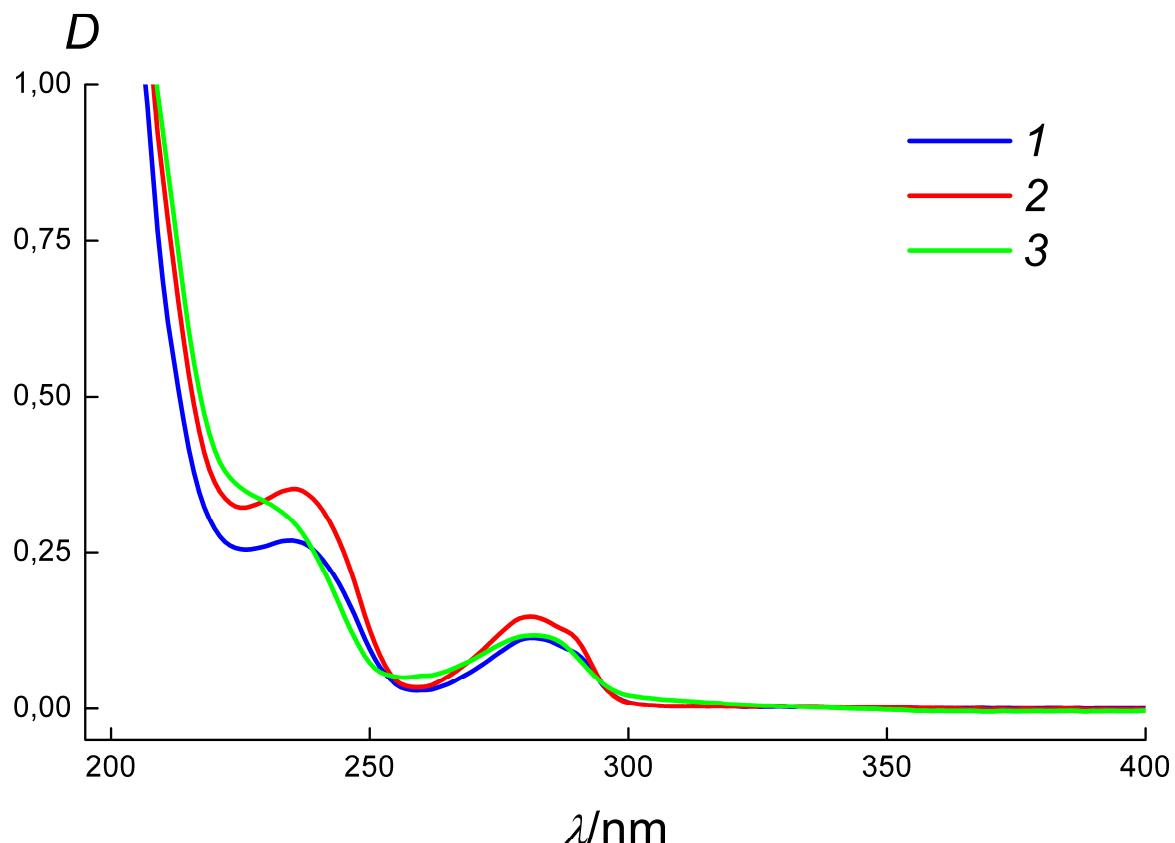


Fig. S4 Absorption spectra of (1) *rctt*-**4b**·(KClO₄)₂, (2) *rctt*-**4c**·(CsClO₄)₂, and (3) 2.4:1 mixture of *rctt*-**4a**·[Ba(ClO₄)₂]₂ and *rtct*-**4a**·[Ba(ClO₄)₂]₂ (MeCN, $C = 1 \cdot 10^{-5}$ M, 1-cm cell, ambient temperature).