

Electronic Supplementary Information

Regio- and stereospecific [2+2] photocyclodimerization of a crown-containing butadienyl dye *via* cation-induced self-assembly in solution

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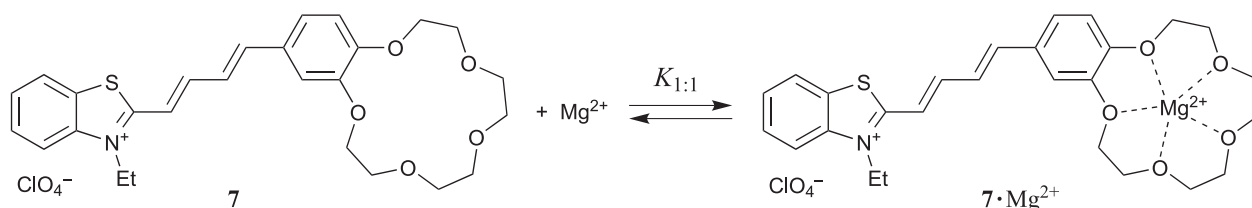
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1. Absorption spectroscopy data for a cationic analogue of dye 5

We have demonstrated previously¹⁸ that a cationic analogue of dye **5**, *viz.*, the crown-containing butadienyl dye **7**, binds Mg^{2+} in MeCN as 1:1 complexes ($7 \cdot \text{Mg}^{2+}$, Scheme S1).



Scheme S1 Complexation of crown-containing butadienyl dye **7** with Mg^{2+} in MeCN: $\lg K_{1:1} = 5.95$ at an ionic strength of 0.01 M.¹⁸

Figure S1 allows one to compare the absorption spectra of dyes **5** and **7**, complex $7 \cdot \text{Mg}^{2+}$ and supposed complex $(5 \cdot \text{Mg}^{2+})_2$. Uncomplexed forms of dyes **5** and **7** show almost identical spectra. The spectra of $7 \cdot \text{Mg}^{2+}$ and $(5 \cdot \text{Mg}^{2+})_2$ strongly differ from each other in the shape. The spectrum of $(5 \cdot \text{Mg}^{2+})_2$ has a specific profile with a pronounced long-wavelength shoulder. The spectral difference between $7 \cdot \text{Mg}^{2+}$ and $(5 \cdot \text{Mg}^{2+})_2$ resembles that between monomers and H-type aggregates of dyes. Stacking interactions in H-type dye aggregates commonly result in absorption band splitting;^{19a} in many cases, the weaker, lower-energy band is unresolved and reveals itself as a shoulder of the more intense, higher-energy band.^{19b} Thus, the specificity of the absorption spectrum of $(5 \cdot \text{Mg}^{2+})_2$ is likely to arise from stacking interaction between two identical chromophore units.

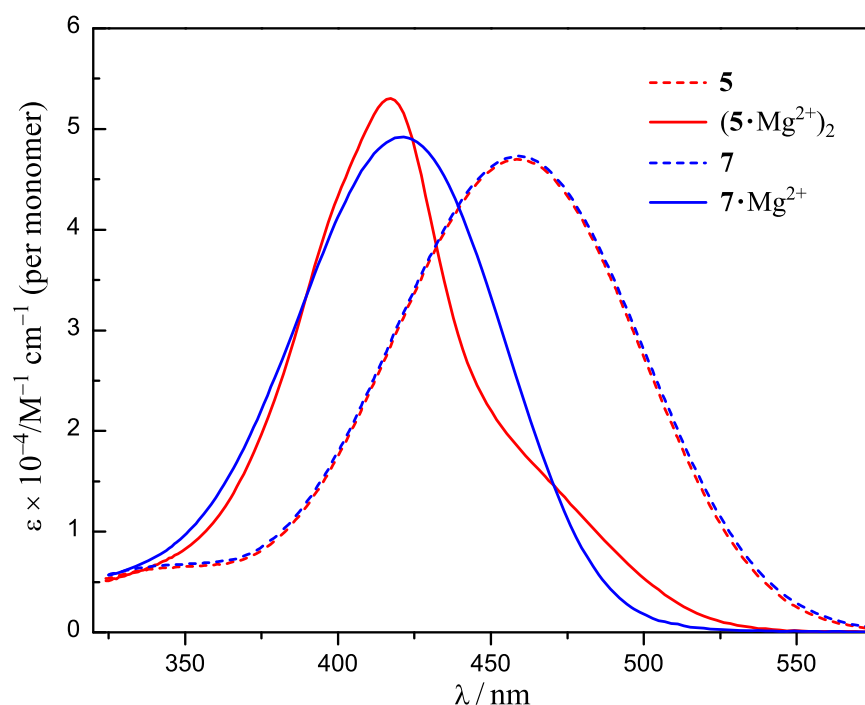


Fig. S1 Absorption spectra of dyes **5** and **7**, complex $7 \cdot \text{Mg}^{2+}$ and supposed complex $(5 \cdot \text{Mg}^{2+})_2$ in MeCN.

2. Global analysis of spectrophotometric titration data

Factor analysis

In order to estimate the number of absorbing components in the system **5**/Mg(ClO₄)₂, the absorption spectra represented in Fig. 1 together with a few spectra measured at intermediate values of Mg(ClO₄)₂ concentration were subjected to factor analysis.^{20a}

An $n \times m$ matrix **D** was constructed from the absorption curves measured at m different values of Mg(ClO₄)₂ concentration and containing the values of optical density at n different wavelengths. If there are k linear-independent absorbing components in the system, the experimental matrix **D** can be approximated, within instrumental error, by a theoretical matrix, whose columns are linear combinations of the k eigenvectors associated with k largest eigenvalues of the second moment matrix $\mathbf{M} = (\mathbf{D} \times \mathbf{D}^T)/m$, where \mathbf{D}^T is the transpose of **D**. The total residual error, σ_k , between matrix **D** and its best approximation is estimated by the formula

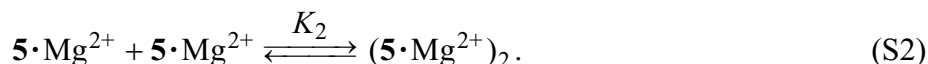
$$\sigma_k = \sqrt{\frac{\text{trace}(\mathbf{M}) - \sum_{i=1}^k r_i}{n-k}},$$

where r_i are the largest eigenvalues of **M**.

The experimental matrix **D** was approximated quite well by this method under the assumption that there are only two absorbing components in the system ($\sigma_k = 0.0012$ optical density units, when $k = 2$); the small value of σ_k suggests that the contribution from a third component to the total spectral variation can be neglected.

Complexation stoichiometry

The fact that dye **5** complexed with Mg²⁺ shows specific spectroscopic properties enabled us to assume the formation of 2:2 complexes between **5** and Mg²⁺. Then the complexation in the system **5**/Mg²⁺ can be represented by the following equilibria:



From the spectroscopic data obtained for the reference cationic dye **7** (Fig. S1) one can predict that complexes $\mathbf{5} \cdot \text{Mg}^{2+}$ and $(\mathbf{5} \cdot \text{Mg}^{2+})_2$ differ significantly from each other in the absorption spectra. This implies that in the system **5**/Mg²⁺ there are three linear-independent absorbing components: **5**, $\mathbf{5} \cdot \text{Mg}^{2+}$ and $(\mathbf{5} \cdot \text{Mg}^{2+})_2$. On the other hand, the results of factor analysis (see previous subsection) show that the spectral variations in this system (Fig. 1) can be approximated by two linear-independent absorbing components. We suppose that the contribution from monomers $\mathbf{5} \cdot \text{Mg}^{2+}$ to the absorption spectra represented in Fig. 1 is negligible due to a very high value of the equilibrium constant K_2

(presumably $\lg K_2 > 7$), *i.e.*, the equilibrium of eq S2 is shifted towards the dimers $(\mathbf{5}\cdot\text{Mg}^{2+})_2$ even at relatively low concentrations of $\mathbf{5}$ (10^{-6} – 10^{-5} M). This conclusion is supported by the following facts:

(i) The Debye-Hückel theory predicts that an increase in the ionic strength of solution will shift the equilibrium of eq S2 towards the dimers $(\mathbf{5}\cdot\text{Mg}^{2+})_2$. The spectrum of complexed form of $\mathbf{5}$ (spectrum B in Fig. 1) did not change on varying the ionic strength of solution between 10^{-4} and 10^{-2} M (supporting electrolyte Bu_4NClO_4). This observation is attributable to the fact that the equilibrium of eq S2 is strongly shifted towards the dimers even at relatively low ionic strengths.

(ii) The fact that the complexation of dye $\mathbf{5}$ with Mg^{2+} induces selective and very efficient [2+2] photocyclodimerization at very low concentrations of $\mathbf{5}$ (10^{-6} – 10^{-5} M) also corroborates the conclusion about a very high value of the equilibrium constant K_2 .

Parameterized modelling of absorption spectra

The parameterized matrix self-modelling (PMS)²⁰ is a very convenient method for treatment of spectroscopic data. This method allows one to verify the complexation model supposed, to estimate the equilibrium constants and to determine the unknown spectra of components.

The facts described in the previous subsections indicate that modelling of the absorption spectra represented in Fig. 1 in terms of the equilibria of eqs S1 and S2 is unreasonable because in the system $\mathbf{5}/\text{Mg}^{2+}$ the partial concentration of monomers $\mathbf{5}\cdot\text{Mg}^{2+}$ relative to dimers $(\mathbf{5}\cdot\text{Mg}^{2+})_2$ is negligibly small at all experimental values of $\text{Mg}(\text{ClO}_4)_2$ concentration. Therefore the experimental data were analysed by the PMS method in terms of the single equilibrium



where L is dye $\mathbf{5}$, M is Mg^{2+} , L_2M_2 is the dimeric complex $(\mathbf{5}\cdot\text{Mg}^{2+})_2$ and $K_{2,2}$ is the complex stability constant. The relationship between the concentrations of the species involved in the equilibrium of eq S3 is described by the law of mass action (eq S4) and the material balance equations (eqs S5 and S6):

$$[\text{L}_2\text{M}_2] = K_{2,2}[\text{L}]^2[\text{M}]^2, \quad (\text{S4})$$

$$C_{\text{L}} = [\text{L}] + 2[\text{L}_2\text{M}_2], \quad (\text{S5})$$

$$C_{\text{M}} = [\text{M}] + 2[\text{L}_2\text{M}_2], \quad (\text{S6})$$

where C_{L} and C_{M} are the total concentrations of $\mathbf{5}$ and Mg^{2+} , respectively.

The PMS process begins by postulating value of $K_{2,2}$ and solving the system of eqs S4–6 for [L] and $[\text{L}_2\text{M}_2]$ (this system can be solved only by a numerical method). The resulting values of [L] and $[\text{L}_2\text{M}_2]$ corresponding to m different values of C_{M} are used to construct a $2 \times m$ concentration matrix \mathbf{C} . This matrix is then used together with the experimental matrix \mathbf{D} to generate an $n \times 2$ theoretical matrix of molar absorption coefficients $\mathbf{E}_{\text{cal}} = \mathbf{D}\mathbf{C}^{\text{T}}(\mathbf{C}\mathbf{C}^{\text{T}})^{-1}$. A theoretical matrix of absorption spectra is calculated by the formula $\mathbf{D}_{\text{cal}} = \mathbf{E}_{\text{cal}}\mathbf{C}$. The stability constant $K_{2,2}$ is determined by minimizing the residual error, σ_{D} , between the experimental matrix \mathbf{D} and its approximation \mathbf{D}_{cal} :

$$\sigma_D = \sqrt{\frac{\sum_{i=1}^n \sum_{j=1}^m (D_{\text{cal}}^{ij} - D^{ij})^2}{n(m-2)}}$$

The experimental matrix \mathbf{D} was approximated quite well by this method when $\lg K_{2:2} > 20$ ($\sigma_D = 0.002$ optical density units). The value of σ_D is larger than the residual error for the approximation of \mathbf{D} by the factor analysis method because σ_D , in addition to instrumental errors, includes measurement errors for C_M and C_L . The experimental and reconstructed spectra for the system $5/\text{Mg}^{2+}$ are shown in Figure S2.

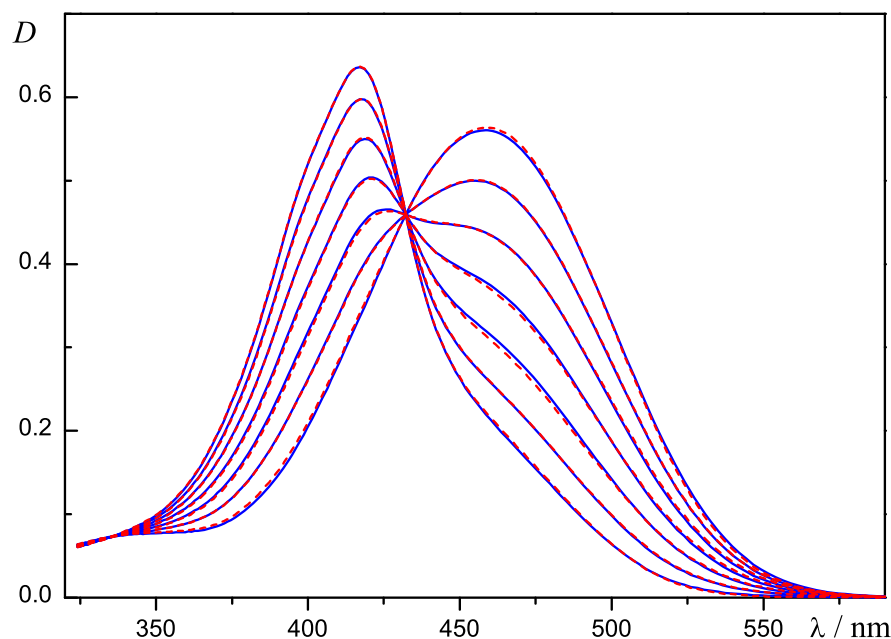


Fig. S2 Experimental absorption spectra of the system $5/\text{Mg}^{2+}$ (solid blue curves, correspond to the spectra represented in Fig. 1) and their approximation (dashed red curves) by the PMS method in terms of the equilibrium of eq S3 with $\lg K_{2:2} = 21$.

3. Molecular mechanics and DFT modelling of dimers $(5 \cdot \text{Mg}^{2+})_2$

Methods: Two principal conformers of $(5 \cdot \text{Mg}^{2+})_2$ with the *syn*- and *anti*-head-to-tail alignment of dye molecules were constructed from monomers $5 \cdot \text{Mg}^{2+}$. The single-bond rotamer of $5 \cdot \text{Mg}^{2+}$ that we used to construct the dimers was selected on the basis of the results of quantum chemical calculations published for complexes $7 \cdot \text{Mg}^{2+}$ (ref.¹⁸). Both of the principal conformers of $(5 \cdot \text{Mg}^{2+})_2$ were optimized by a conformational search method using the MMFF94 molecular mechanics model and Monte-Carlo algorithm. The number of conformers examined in each of two searches was 5000. The lowest-energy *syn*- and *anti*-head-to-tail conformers of $(5 \cdot \text{Mg}^{2+})_2$ were selected and then fully optimized by RI-DFT method with the PBE functional [1] and the def2-SV(P) basis set [2], using the

ORCA program [3]. To take into account dispersion forces, the Grimme's correction to DFT energy [4] was employed ('vdw' keyword in ORCA). Finally, single point calculations of the DFT energy in acetonitrile were carried out. The solvent was simulated using the COSMO model as implemented in ORCA [5].

Results: The DFT optimized geometries of the *syn*- and *anti*-conformers of $(\mathbf{5}\cdot\text{Mg}^{2+})_2$ are shown in Figure S3. The DFT energies for these structures in gas phase and acetonitrile are listed in Table S1. The calculations predict that the conformational equilibrium in acetonitrile is shifted toward the *anti*-conformer (the energy difference between the *syn*- and *anti*-conformers in this solvent is 2.6 kcal mol⁻¹). The *anti*-conformation of $(\mathbf{5}\cdot\text{Mg}^{2+})_2$ is topochemically much more favourable for the [2+2] photocyclodimerization of the butadiene moieties because the distance between reactive C=C bonds in the *anti*-conformer, $R = 5\text{--}6 \text{ \AA}$, is much shorter than that in the *syn*-conformer, $R \approx 9 \text{ \AA}$. The calculated structure of the *anti*-conformer is consistent with the structure of the photocycloadduct obtained from $(\mathbf{5}\cdot\text{Mg}^{2+})_2$ (cyclobutane isomer *rtct-6*, Scheme 3).

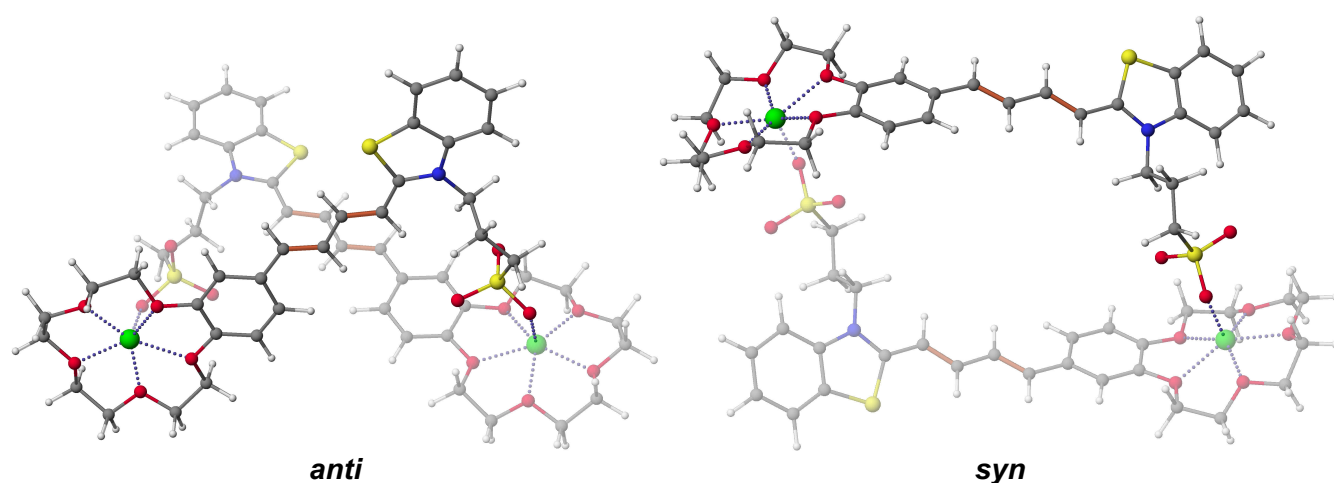


Fig. S3 DFT optimized conformers of $(\mathbf{5}\cdot\text{Mg}^{2+})_2$; the butadiene double bonds are shown as brown cylinders.

Table S1 DFT energies for the *syn*- and *anti*-conformers of dimeric complex $(\mathbf{5}\cdot\text{Mg}^{2+})_2$.

Conformer	DFT energy / au	
	Gas phase	Acetonitrile
<i>syn</i> -head-to-tail	-5470.6115	-5471.1520
<i>anti</i> -head-to-tail	-5470.6099	-5471.1562

References: [1] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; [2] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297; [3] F. Neese, *OCRA – an ab initio, density functional and semiempirical program package*, version 2.7; Universität Bonn: Bonn, Germany, 2009; [4] S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787; [5] S. Sinnecker, A. Rajendran, A. Klamt, M. Diedenhofen, F. Neese, *J. Phys. Chem. A.*, 2006, **110**, 2235.