Pure Isolation and Stabilization of Energetically Highly Disfavored Geometric Isomers by Controlling the Stereoselectivity of Supramolecular Interactions in Tailored Host−Guest Systems

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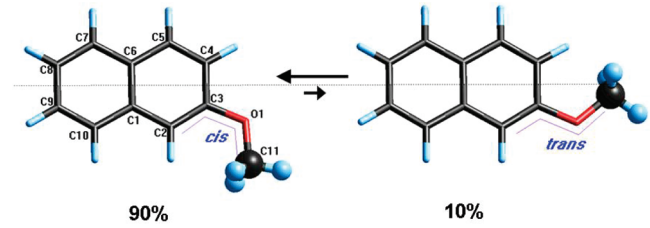
Energetically highly disfavored geometric isomers are present in only trace amounts in solution and hence cannot be clearly observed by conventional spectroscopic methods. Here, we provide spectroscopic evidence that a suitably sized/shaped cavitand (α-cyclodextrin) can discriminate distinctive stereochemical differences between all possible *cis*−*trans* stereoisomers of a qualified compound, showing selective recognition solely for the target unstable isomer. We tested a set of guests, and we were able to obtain, for each one separately, *purely* thermodynamic selectivity of the host for the energetically highly dispreferred stereoisomer among all other equilibrating geometric isomers under ambient conditions.

Introduction

To efficiently tailor host−guest supramolecular interactions requires as far as possible exact control of the size, shape, chemical complementarity, and functionality of the interacting components.[1] Combinations of the above factors may selectively facilitate screening, amplification, and prolongation of the lifetime of an unstable reactive conformation of the guest substrate inside the confined space of an appropriate cavitand.[2] In several cases, the trapped reactive conformation of the guest is kinetically stable (low energy) but exists in only trace concentration in the external medium due to its high reactivity toward decomposition, e.g., hydrolysis.[3] Container-like receptors, furthermore, functionalized with suitably stereodirectional active groups, can mimic biological macromolecules by amplifying and temporarily stabilizing concentrations of high-energy (kinetically labile) reactive intermediates of specific reactions.[2,4] Rebek's recent work also provides evidence that self-assembled capsules can shift the chemical equilibrium between two isomeric—via intramolecular cyclization—forms toward amplification of the energetically unstable structure.[5]

The influence of volume-restricted nanospaces on the geometric (*cis*−*trans*) isomerism of organic molecules is a field of wide interest, spanning from photoisomerization processes in proteins[6b,c] to nanomachinery.[1] *Cis*−*trans* stereoisomers of a given compound normally differ considerably in energy due to the unequal steric repulsions imposed by the different spatial arrangement of the bulky isomerizing group(s) with respect to the fixed molecular framework.[6a] Accordingly, energetically disfavored isomeric structures are present in trace concentrations in solution and, hence, cannot be clearly observed by conventional spectroscopic methods. In some cases, e.g., compound **1** here, the unstable isomeric form (*trans*) can be amplified photochemically via electronic excitation of the energetically preferred *cis* configuration (*cis** → *trans**) but is short-lived and observable only with time-resolved spectroscopic techniques.[7] It is interesting, therefore, if energetically highly disfavored geometric isomers could be isolated and stabilized by tailored supramolecular interactions. This can be achieved only if one obtains precise control on the thermodynamic selectivity of the host binding two or more stereoisomers of a given compound. First, an appropriately sized/shaped cavitand is required that must be able to discriminate distinctive stereochemical differences between all possible isomers, showing selective recognition solely for the unstable target species. Second, the desirable equilibrium must be thermodynamically favored; that is, the *free* energy of the selective association process must sufficiently compensate the energy gap between the equilibrating isomers in the external medium.

SCHEME 1: Geometric Isomers of 1[a]



[a] The *cis* (*syn*, $\varphi \approx 0°$) and *trans* (*anti*, $\varphi \approx 180°$) configurations are denoted by the dihedral angle φ(C2−C3−O1−C11) formed by the naphthalene plane and the O−Me bond vector. The ratio was determined by absorption spectroscopy.[7]

In this work, we tested the applicability of the above concepts using well-defined popular cavitands combined with suitably substituted aromatic guests that exhibit discrete geometric isomers. We choose as cavitands the water-soluble cyclodextrins (CDs).[8] These widespread receptors offer *well*-defined and *size*-adjustable cavities made up of between six and eight glucose units covalently linked to form open-ended macrocycles of a toroidally shaped truncated cone. We report experimental results supported by theory on the set of test guests: 2-methoxynaphthalene (**1**) and its disubstituted (centrosymmetrically) analogue 2,6-dimethoxynapthalene (**2**). These compounds can exist in discrete stereoisomers with *cis* and *trans* configurations[7,9] that differ considerably both in energy and stereodirectionality of the isomerizing methoxy group(s) (see Schemes 1 and 2). The *cis* and *cis,cis* configuration of **1** and **2** respectively represent the global energy minima in the ground state. These *cis* structures, as opposed to the *trans* analogues, are spatially

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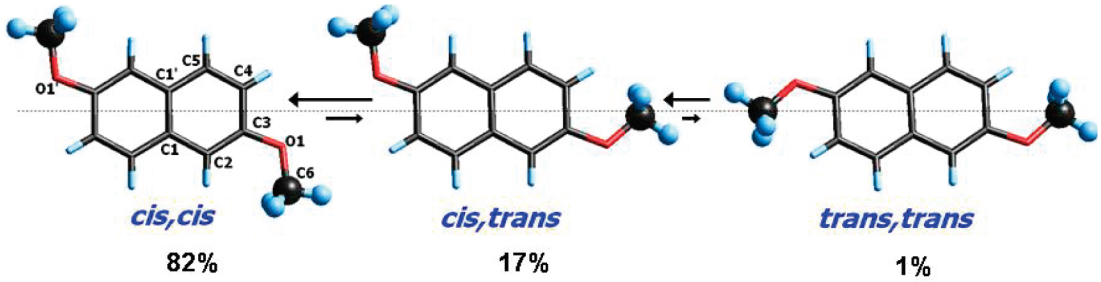
SCHEME 2: Geometric Isomers of 2[a]



[a] The approximate ratio between the *cis,cis* and *cis,trans* forms was determined experimentally.[9] The abundance of the highly unstable *trans,trans* isomer was predicted according to Boltzmann's distribution law.

volume-demanding toward long-axis inclusion within a suitable narrow cavity. We find that the energetically highly unstable *trans* isomers fit uniquely into the narrowest cavity of α-CD, leading to the pure thermodynamic selectivity of these forms over the *cis* analogues. On the contrary, the moderate cavity of *β*-CD can accommodate loosely the predominant stable *cis* stereoisomers. The wider cavity of *γ*-CD, finally, binds also the *cis* forms, forming initially simple 1:1 complexes which then self-assembled to form long-sized nanostructures.[10]

Experimental Section

Materials. 2-Methoxynaphthalene (**1**) and 2,6-dimethoxy naphthalene (**2**) were purchased from Sigma-Aldrich and cyclodextrins from Cyclolab. Purification methods of solvents and compounds are described elsewhere.[9]

Instrumentation and Methods. Absorption spectra were recorded on a Perkin-Elmer Lambda-16 spectrophotometer. Steady-state fluorescence spectra were accomplished by the Perkin-Elmer model LS-50B and the Edinburgh Instruments model FS-900 spectrofluorometer. Fluorescence lifetimes (τ) were determined using the time-correlated single-photon counter FL900, of the above Edinburgh Instruments setup. Details of the temperature dependent experiments and quantum yield estimations are given elsewhere.[7,9] All ^{1}H NMR spectra were recorded with a Bruker Avance DRX 500 spectrometer at 500 MHz and 25 °C. All computer fits and simulations, except those of time-resolved experiments, were performed using the program "Micro Math Scientist for Windows", version 2.01, of Micro Math. Quantum mechanical calculations were performed with the latest professional version 8.0 of the HyperChem molecular modeling program.

Results and Discussion

I. Compound 1 (2-Methoxynaphthalene). 1 exhibits geometric isomerism via rotation about the C_{Aryl}−O quasi-single bond both in the gas phase[11] and in solution.[12] These isomers have been assigned to a *cis* (*syn*, $\varphi = 0°$) and a *trans (anti*, $\varphi = 180°$) configuration (see Scheme 1) of which the *syn*-periplanar (*cis*) conformation was the one observed in the crystal structure.[13] We have further supported herein the above configurations computationally; fully relaxed torsional potentials were calculated with the MP2//RHF and DFT methodologies combined with the aug-cc-pVDZ Dunnin correlation-consistent basis set (see the Supporting Information for details, part S1).

Briefly, the calculations indeed give two minima on the potential energy surface of **1** in the ground state; these correspond to the planar structures depicted in Scheme 1. Both methods converge to following: (a) the oxygen atom exhibits considerably sp^2 hybridization, and (b) the planar *cis* configuration is the lowest energy structure (in consistency with the X-ray analysis[13] of **1**). The *trans* isomer lies higher in energy by 5.9 kJ/mol (∼490 cm^{-1}) than the *cis* analogue, and the barrier to rotation of the methoxy group is estimated to be 16.4 kJ/mol.

We have recently demonstrated that **1** exists in 3-methylpentane (3-MP) as a mixture of *cis* (major) and *trans* (minor) stereoisomers which can interconvert rapidly (dynamic isomers) both thermally and photochemically.[7] At 77 K, the only isomeric form observed is the thermodynamically stable *cis* form, as evidenced by the temperature dependence of the absorption spectrum (see Figure 1a). Upon progressively heating, the equilibrium is shifted gradually, albeit weakly, toward the *trans* isomer whose $S_1 \leftarrow S_0$ electronic origin transition—centered at 333.5 nm—is distinctly shifted to the red by ∼620 cm^{-1} with respect to the *cis* analogue. The equilibrium constant $K_{eq}^{S0} = [trans]/[cis]$ at room temperature in the electronic ground state was found to be[7] ∼0.1; this suggests an enhanced stability of ∼6.0 kJ/mol (∼500 cm^{-1}) for the *cis* over the *trans* form in excellent agreement with our calculations (5.9 kJ/mol). It is important also to note that environmental stimuli such as the solvent's dielectricity, proticity, and viscosity do not alter distinctly the position of the electronic spectra and the photophysical properties of the isomeric forms of **1** and **2** (except for a notable broadening of the spectra with respect to those observed in an inert hydrocarbon solvent, e.g., 3-MP; see part S2 of the Supporting Information).

The insets in Figure 1b show the dependence of the absorption spectrum of **1** (7.2×10^{-5} M) in water with varying amounts of added *γ*- and *β*-CD. Subtle spectral shifts by ∼1.5 nm (∼100 cm^{-1}) saturated at ∼10^{-2} M CDs were observed for both cases. The latter spectra coincide with that of the predominant *cis* form in THF in accord with the view that the polarity of the cyclodextrin cavity is similar to that of an etheric solvent.[8] These findings in conjunction with results obtained from fluorescence and ^{1}H NMR experiments show features consistent with loose inclusion of the predominant *cis* isomer within the cavity of *β*- and *γ*-CD, and details are given in part S2 of the Supporting Information. We note that, in the case of *γ*-CD, turbidity was observed after an induction period of ∼30 min. This phenomenon, albeit out of the scope of this presentation, is observed occasionally with *γ*-CD and rod-like guests, and it is attributed to the formation of long-sized tubular nanostructures growing by the self-assembly of the initially formed single 1:1 (host:guest) supramolecular subunits.[10]

In obvious contrast to the complexation scheme seen with *γ*- and *β*-CD, the narrowest cavity of α-CD exhibits a totally different inclusion motif. Interestingly, it shows purely thermodynamic selectivity toward preferential inclusion with the

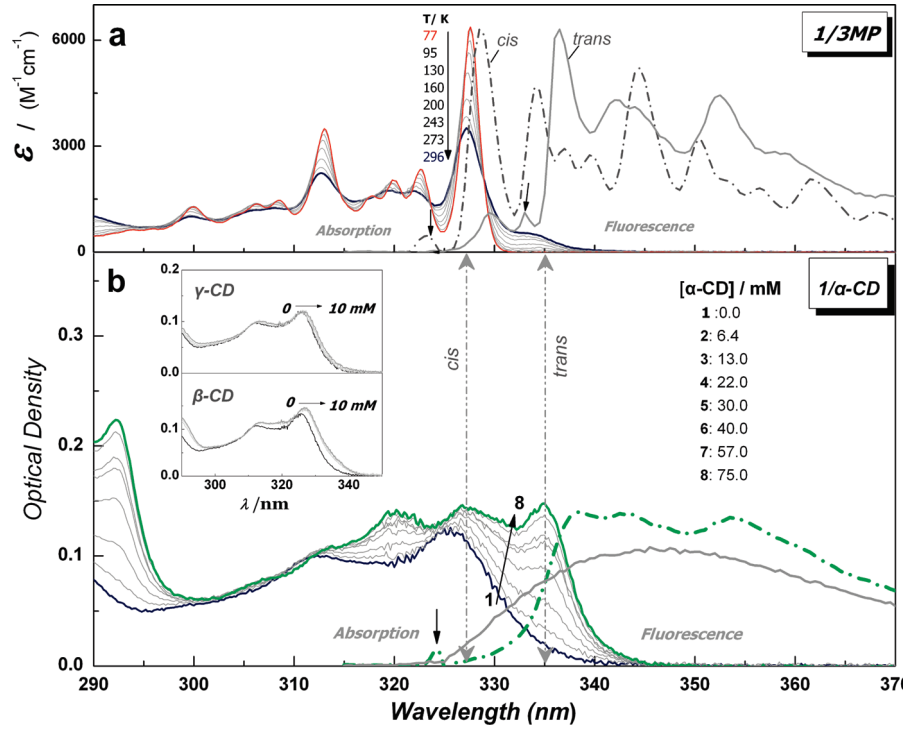


Figure 1. (a) Left: Absorption spectra of **1** in 3-MP (2×10^{-4} M) at varying temperatures.[7] Right: Pure emission spectra of *cis* and *trans* isomers obtained, respectively, at 77 and 160 K (see arrows for excitation). (b) Left: Absorption spectra of **1** (7.2×10^{-5} M) in water with varying amounts of added α-CD. Right: Fluorescence spectrum of **1** in pure water (solid gray curve) and of the encapsulated *trans* form of **1** (dotted curve) in α-CD (exc: 324 nm). Insets: Absorption spectra of **1** (7.2×10^{-5} M) in water vs [γ-CD] (upper) and [β-CD] (down).

TABLE 1: Fluorescence Quantum Yields (Φ); Lifetimes (τ); Radiative Rate Constants (k_f and k_f^{SB}) Obtained, Respectively, Experimentally and from the Strickler−Berg Formulation; Nonradiative Rate Constants (k_{nr}); Maxima of the Transition Origins (υ_{max}^{abs}); and Differences between Maxima of the Transition Origins ($\Delta\upsilon_{max}^{abs}$) and Oscillator Strengths (f) of the Geometric Isomers of Compounds 1 and 2 Obtained at Low Temperatures in 3-Methylpentane (3-MP) and 2-Methyltetrahydrofuran (2MTHF)

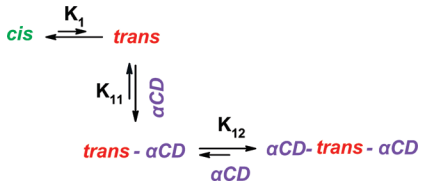
molecule	solvent	isomer	Φ^a	τ^b (ns)	k_f,^{b} 10^7 (s^{-1})	k_f^{SB}, 10^7 (s^{-1})	k_{nr},^{b} 10^7 (s^{-1})	υ_{max}^{abs} (cm^{-1})	$\Delta\upsilon_{max}^{abs}$ (cm^{-1})	f
1	3-MP	*cis*	0.36	13.0	2.90	2.88	4.80	30 520	0	0.017
		trans	0.40	13.0	2.90	2.88	4.80	29 985	535	
	2MTHF	*cis*	0.39	12.7	3.07	3.81	4.80	30 413	0	0.019
		trans	0.41	12.2	3.36		4.84	29 760	650	
2	3-MP	*cis,cis*	0.36	8.6	4.18	4.59	7.44	28 960	0	0.0313
		cis,trans	0.41	8.6	4.77		6.86	28 450	510	
	2MTHF	*cis,cis*	0.34	8.1	4.20	4.99	8.14	28 818	0	0.033
		cis,trans	0.39	8.5	4.59		7.17	28 246	572	

[a] Uncertainties in low temperature quantum yields of ∼10%. [b] Uncertainties in recovered lifetimes and rate constants of ∼5 and ∼10%, respectively.

energetically unfavorable *trans* isomeric form as manifested primarily by optical spectroscopic methods and ^{1}H NMR. Figure 1b shows the variation of the absorption spectrum of an aqueous solution of **1** (7.2×10^{-5} M) as the concentration of added α-CD increases. As becomes evident, the most dramatic changes are confined to the spectrally distinguishable first absorption band of the *trans* isomer centered at ∼335 nm. The optical density (OD_{335}) starts from a low value of about 0.014 (due to a minor population of ∼10% of the preexisting *trans* isomer thermally equilibrating with the *cis* analogue) and then grows with increasing [α-CD] until it reaches its maximum value of ca. 0.15 in the presence of an excess of α-CD (∼7.5×10^{-2} M). The selective binding of the *trans* stereoisomer of **1** with α-CD is further manifested by the steady-state and time-resolved fluorescence experiments. The most interesting features of these experiments are the following: First, the fluorescence spectrum of the caged form of **1** nearly matches that of the pure *trans* isomer (the pure emission spectrum of the *trans* form of **1** was obtained independently in 3-methylpentane at 160 K by photoexciting selectively its own first electronic transition origin at 333.5 nm; see Figure 1a). Second, as seen in Figure 1b, there is nearly perfect mirror symmetry between the absorption and fluorescence spectral features of the trapped isomeric form of **1**. Third, the emission spectrum profile of this isomeric form is found to be (a) independent of the excitation wavelength and (b) vibronically better resolved compared to the emission spectrum of **1** dissolved in pure water. Fourth, the fluorescence intensity decays monoexponentially (τ = 13.5 ns), while the absolute fluorescence quantum yield of the caged form of **1** is found to be similar to that measured for degassed dilute solutions[7] of **1** ($\Phi \approx 0.35$; see Table 1). The above facts conclusively demonstrate the presence of a single, insulated, and tightly trapped *trans* isomeric form in the supramolecular adduct(s). The presence of tight supramolecular interactions is further supported by the ^{1}H NMR spectra (see the Supporting Information, Figure S2-3).

When a curve fitting procedure was applied to the experimental data OD_{335} vs [α-CD], a unique fit was obtained (R^2 =

0.9998) only when the fitting model took into consideration the competitive equilibrium scheme given below The experimental



data OD_{335} vs [α-CD] were fitted to the following model:

$$OD_{335} = \varepsilon_{trans,free}[trans]_{free} + \varepsilon_{trans,1:1}[trans{-}\alpha CD] + \varepsilon_{trans,1:2}[\alpha CD{-}trans{-}\alpha CD] \quad (1)$$

The concentration of each species during the titration process is given by

$$[trans]_{free} = K_1[cis]_{free} \quad (2)$$

$$[trans{-}\alpha CD] = K_{11}[trans]_{free}[\alpha CD] \quad (3)$$

$$[\alpha CD{-}trans{-}\alpha CD] = K_{12}[trans{-}\alpha CD][\alpha CD] = K_{12}K_{11}[trans]_{free}[\alpha CD]^2 \quad (4)$$

$\varepsilon_{trans,free} = 2055$ L mol^{-1} cm^{-1} and $K_1 = 0.1$ are known quantities and were introduced to the fitting as fixed parameters. It was also assumed that $\varepsilon_{trans,11} \approx \varepsilon_{trans,free}$, whereas $\varepsilon_{trans,12}$ was introduced to the minimization process as a free parameter. The calculated $\varepsilon_{trans,12} = 2238 \pm 60$ L mol^{-1} cm^{-1} is highly consistent with the experimentally manifested slight amplification of the absorption spectrum.

The binding constants for the stereoselective complexation between the energetically disfavored *trans* isomer and α-CD were estimated to be $K_{11} = 188 \pm 40$ M^{-1} and $K_{12} = 86 \pm 30$ M^{-1} for the 1:1 and 1:2 (guest:host) supramolecular adduct, respectively. These estimates correspond to the free energies of association of $\Delta G_{trans\rightarrow 11}^{298K} \approx -13.0$ kJ/mol and $\Delta G_{11\rightarrow 12}^{298K} \approx -11.0$ kJ/mol which sufficiently compensate the energy gap between the *cis* and *trans* isomers in the external aqueous medium (~6.0 kJ/mol).

II. Compound 2 (2,6-Dimethoxynaphthalene). For the centrosymmetrically disubstituted derivative **2** (2,6-dimethoxynaphthalene), the present calculations yielded three minima on the potential energy surface of the ground state. These minima correspond to the planar structures shown in Scheme 2 (ordered with decreasing stability from left to right). The calculations predict that the planar *cis,cis* configuration is the lowest energy structure (global minimum) in consistency with the X-ray analysis of an analogue compound.[9] The equilibrium geometries of the *cis,trans* and *trans,trans* isomers are predicted to be higher in energy by 4.9 kJ/mol (~410 cm^{-1}) and 11.5 kJ/mol (~960 cm^{-1}), respectively, with respect to the global minimum (*cis,cis* configuration; see the Supporting Information, Table S1-2).

Compound **2** in solution, e.g., 3-MP exists as a mixture of rapidly interconverting *cis,cis* and *cis,trans* stereoisomers[9] (Figure 3a). At 77 K, the thermodynamically favorable *cis,cis* form was solely observed. Heating the sample results in the progressive formation of the energetically closest lying *cis,trans* isomer which appears as a weak shoulder at the red edge of the absorption spectrum. The electronic origin transition $S_1 \leftarrow S_0$ of the *cis,trans* isomer is centered at ~353 nm and is red-shifted distinctly by ~580 cm^{-1} relative to that of the predominant *cis,cis* form (~346 nm; Figure 3). The equilibrium constant between the above stereoisomers under ambient conditions was found to be[9] ~0.2, suggesting an enhanced stability of ~4.0 kJ/mol (~420 cm^{-1}) for the *cis,cis* over the *cis,trans* form in reasonable agreement with our calculations (4.9 kJ/mol). The energetically highly unfavorable *trans,trans* isomer was not clearly observed spectroscopically due to its very low abundance (~1% according to Boltzmann's distribution law).

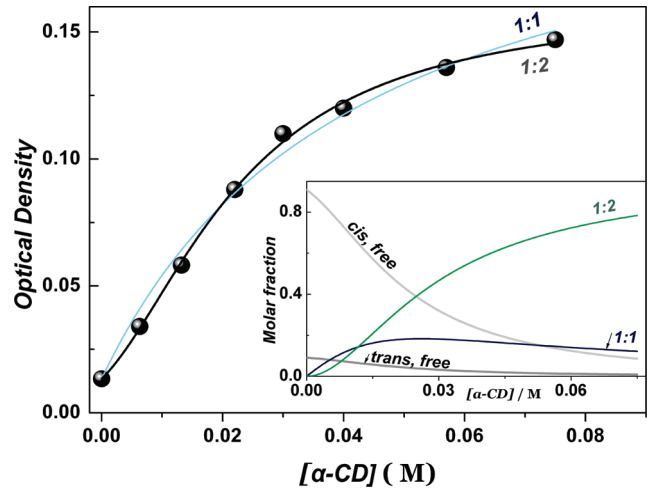


Figure 2. OD_{335} vs [α-CD]. The solid black line is the fitting curve according to the competitive equilibrium scheme given in the text. An unacceptable fit was obtained with 1:1 stoichiometry of complexation (light blue line). Inset: Molar fractions of the various adducts vs [α-CD].

Compound **2** is sparingly soluble in pure water ($\leq 2 \times 10^{-7}$ M). Concentrated aqueous solutions of CDs, however, can dissolve sufficient amounts of **2**, rendering the spectroscopic determination of **2** bound to the CDs possible. γ-CD binds the stable *cis,cis* configuration, forming—after a short induction period—extended nanotubular aggregates. β-CD accommodates the stable *cis,cis* isomeric form, as evidenced by the coincidence of the normalized absorption spectra between the caged form of **2** and the predominant *cis,cis* configuration in pure methanol or THF (Figure 3b). This conclusion is further supported by ^{1}H NMR (vide infra; see also Figure 4).

The above typical complexation motif is changed dramatically when **2** is bound to α-CD. Curiously, the encapsulated form of **2** elevates a new interesting, noticeably structured and significantly red-shifted by ~15 nm (~1200 cm^{-1}), absorption spectrum compared to that of the normal *cis,cis* form in methanol or β-CD (see Figure 3b). No energy loss (further than the typical Stokes' shift) and good mirror symmetry between absorption and emission is observed for the caged form of **2**. Furthermore, both the fluorescence quantum yield $\Phi = 0.55$ and lifetime $\tau \approx 17.0$ ns of the above form are practically independent of the excitation wavelength. The above conclusively demonstrate that the radiative rate constant of the trapped isomeric form $k_f = \Phi/\tau = 3.23 \times 10^7$ s^{-1} matches that of the isolated molecular unit of **2** (namely, the intrinsic radiative transition probability of **2**; see Table 1), suggesting absence of "aggregated" emission, e.g., interacting couples of **2** within the supramolecular adduct. In addition, the absorption and the emission-wavelength-dependent excitation spectra are essentially superimposable (see Figure S2-5 of the Supporting Information);

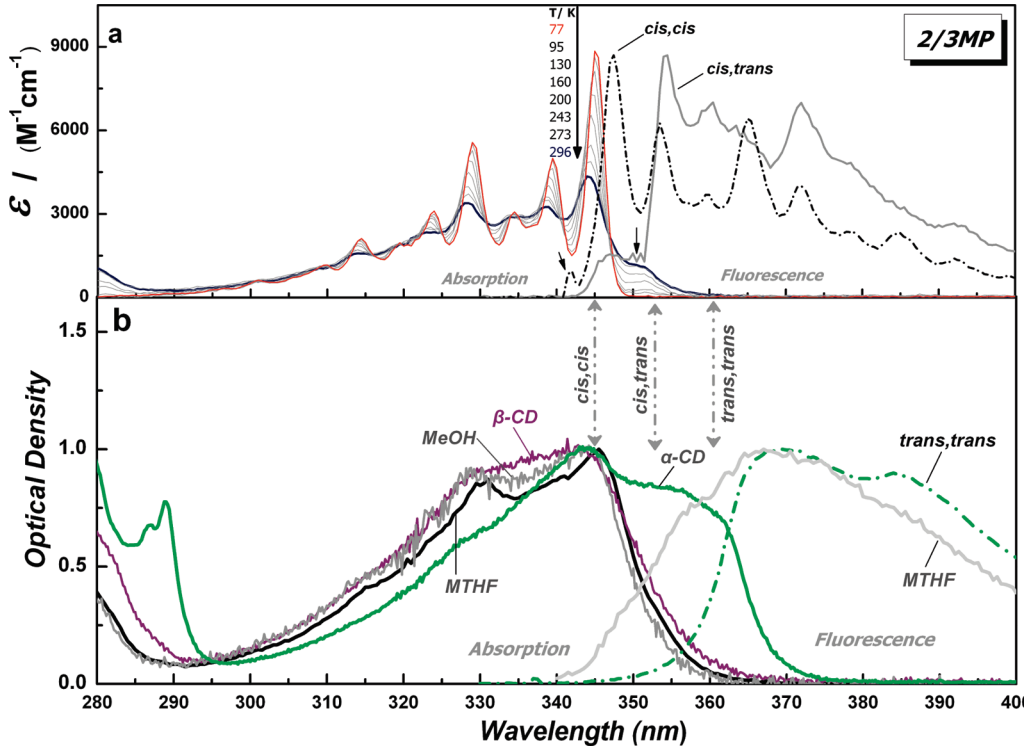


Figure 3. (a) Left: Absorption spectra of **2** in 3-MP (4.8×10^{-5} M) at varying temperatures.[9] Right: Pure emission spectra of *cis,cis* and *cis,trans* isomers obtained, respectively, at 77 and 160 K (see arrows for excitation). (b) Left: Absorption spectra of **2** in various solvents and in aqueous solutions of 10^{-2} M β-CD and 5×10^{-2} M α-CD. Right: Fluorescence spectra of **2** in 2-MTHF and in 5×10^{-2} M α-CD (exc: 337 nm).

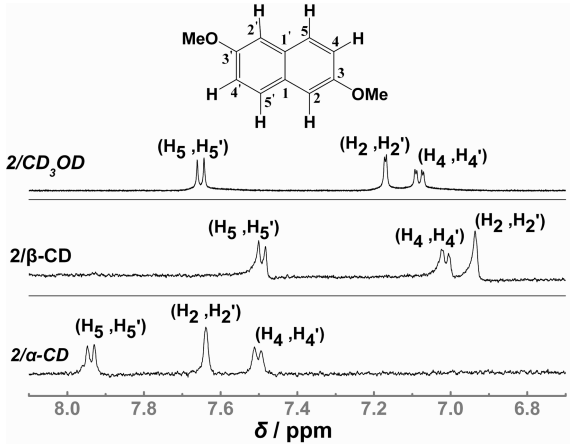


Figure 4. 500 MHz ^{1}H NMR spectra of **2** in CD_3OD and in aqueous D_2O solutions of 10^{-2} M β-CD and 5×10^{-2} M α-CD.

this feature is also typical of the presence of a single, kinetically trapped isomeric form of **2** inside the confined space of the receptor. We note that the lack of solubility of **2** in pure water renders impossible the determination of the exact stoichiometry of complexation and the corresponding binding constant(s) between **2** and α-CD(s) by means of a titration method. Nevertheless, addition of triethanolamine quencher to an aqueous solution of 0.05 M α-CD containing 3.3×10^{-5} M **2** did not result in a measurable quenching of the fluorescence signal of caged **2**. This feature strongly suggests complete protection of the substrate from the bulk solvent. Most likely, therefore, the trapped form of **2** is encapsulated within the inner space formed by two assembled α-CDs in a barrel-type configuration, as observed predominantly for the singly substituted compound **1**.

Given the spectral insensitivity of the isomeric forms of **2** to various environmental stimuli, the trapped form **2**/α-$CD_{(2)}$—spectroscopically quite distinguishable from the *cis,cis* and *cis,trans* configurations—should represent uniquely the energetically highly disfavored *trans,trans* stereoisomer as manifested further by ^{1}H NMR spectroscopy and supported also computationally. In particular, the *cis,cis* and *trans,trans* configurations are both centrosymmetrical and of C_{2h} point group symmetry, leading to crystallographic (*cis,cis*)[9] and magnetic equivalence between the two halves of the naphthalene ring. This equivalence is totally canceled in the *cis,trans* configuration owing to the fact that the symmetry (*Cs*) is reduced significantly (see Table S1-2 of the Supporting Information). Therefore, if the *cis,trans* form was to be kinetically trapped in the supramolecular adduct, then one would expect that each one of the six aromatic hydrogens would appear independently at its own chemical shift[14] (ppm). The above expectations are further supported computationally by the calculated ^{1}H NMR spectra (HyperNMR modulus of HyperChem 8.0 program). Specifically, the calculated chemical shift dispersion of the aromatic ^{1}H signals splits into six for the *cis,trans* and three signals for each one of the *cis,cis* and *trans,trans* configurations (see the Supporting Information, part S3). In effect, the experimental ^{1}H NMR spectra clearly certify the stereoselective trapping of a structurally highly symmetric isomeric form, obviously other than the stable *cis,cis* isomer. In other words, this experimental fact unambiguously proves that the trapped isomeric form within the confined space formed predominantly by two assembled α-CDs is the *trans,trans* stereoisomer and nothing else (see Figure 4).

This conclusion is further supported by theory. In particular, singly excited-state configuration interaction (CI) at the MP2//RHF/aug-cc-pVDZ level of theory predicts the $S_1 \leftarrow S_0$ adiabatic electronic transition of the *trans,trans* isomer to be distinctly shifted bathochromically by ~1000 and 500 cm^{-1} with respect to that of the *cis,cis* and *cis,trans* isomer, respectively. This is almost what we have observed spectroscopically; that is, a red-

shifted absorption spectrum of **2**/α-$CD_{(2)}$ by ∼1200 and ∼550 cm^{-1} relative to that of the aforementioned isomers (see Figure 3).

In conclusion, we provide here clear evidence on how control of steric hindrance and tightness in host−guest supramolecular interactions can lead spontaneously to the *pure* isolation and *permanent* stabilization of energetically highly disfavored geometric isomers which normally would not be detected appreciably in uninhibited fluid media. Our findings may appear useful for better understanding of *cis*−*trans* isomerization and for further investigations on the isolation of specific isomeric forms of various biologically interesting molecules, e.g., polyenes.

Supporting Information Available: Quantum mechanical calculations, additional experimental details, and calculated ^1H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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