A Hyperpolar, Multichromophoric Cyclodextrin Derivative: Synthesis, and Linear and Nonlinear Optical Properties

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Abstract: A chiral, highly polar, multichromophoric supermolecule has been designed by gathering seven push–pull chromophores onto a β-cyclodextrin assembling unit through covalent flexible linkers. The photophysical and nonlinear optical properties of this mutichromophoric conical bundle were investigated and compared with those of the monomeric chromophore. The strongly absorbing multichromophoric system combines interesting features: it has a high molecular first-order hyperpolarisability and a very large dipolar moment ($\mu = 38$ D) which reveal a self-arrangement of the dipolar chromophores within the supermolecule. The confinement of the push–pull chromophores within the nanoscopic bundle affects their optical properties and promotes interactions: the multichromophoric supermolecule is hypochromically and hypsochromically shifted with respect to its monomeric analogue. In addition, the close proximity promotes excitonic coupling, as well as excimer formation phenomena.

Keywords: chromophores · cyclodextrins · fluorescence · nonlinear optics · push–pull chromophores

Introduction

In the last twenty years, supramolecular chemistry has emerged as a major field of chemistry, owing to numerous applications such as selective recognition, ion complexation, sensing and transport.[1] Among the miscellaneous goals and strategies, one attractive approach is the design of "supermolecules" in which the assembly of several (identical or complementary) molecular components leads to an improved or specific function. Such an approach has been particularly successful in addressing, for instance, efficient electron or energy transfer.[2, 3]

In the present paper, we have been interested in the design and study of a supermolecule where seven "push–pull" chromophores (i.e. molecules that bear electron-donor (D) and electron-acceptor (A) groups connected through a π-conjugation path) are gathered by covalent grafting onto a β-cyclodextrin (β-CD) ring assembling unit. We investigated how this influences the optical (both linear and nonlinear) properties of the resulting multichromophoric supermolecule with respect to its monomeric counterpart.

Cyclodextrins are naturally occurring cyclic oligosaccharide backbones of widespread use in supramolecular chemistry.[4] These hollow chiral molecules exhibit interesting structural features such as characteristic sizes, polyfunctionality and symmetry, which makes them attractive for many applications. Cyclodextrins are mostly known for complexing organic substrates of suitable shape in aqueous solutions. In the last years, we have been concerned with the design, synthesis and physicochemical investigations of symmetrically derivatised cyclodextrins conceived as components for self-assembly in solution or as artificial antenna mimicking some of the events of photosynthesis.[5] During the latter studies, different aromatic chromophores were grafted onto the primary rim of the β-cyclodextrin to yield multichromophoric systems.[6] The absorption and emission properties of these bundles of covalently attached chromophores are sensitive to the molecular conformation. In fact, the average distance between individual chromophores is about one nanometer; this allows interactions involving the chromophores in their fundamental or their excited states to be revealed.[7]

In this paper, we focus on a multichromophoric β-CD bearing seven push–pull chromophores. Such chromophores exhibit an intramolecular charge transfer (ICT) between electron-releasing (D) and electron-withdrawing (A) end

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groups in the ground state, so that they have a significant ground-state dipole. This allows for strong dipolar interactions which can significantly affect both the conformation and the optical properties of the multichromophoric assembly. Push – push molecules are characterised in solution by an intense absorption band in the UV/visible region which is associated with an ICT phenomenon. By choosing suitable D and A groups, high transition dipole moments can be achieved. By grafting onto β-CD, seven push – pull chromophores that had higher transition dipoles than those of the chromophores used in the series of heptachromophoric cyclodextrin previously studied, we anticipated getting derivatives prone to exhibiting significant changes of their photophysical properties as a result of a conformational perturbation and of interactions between the chromophores. In particular, electronic interactions between the transition moments of close-packed chromophores within the supermolecule could allow for Frenkel-exciton-type coupling. A significant change in the absorption spectrum would then be observed.[8]

Such multichromophoric supermolecules also are of particular interest for nonlinear optics (NLO). Molecular NLO has attracted increasing interest over the past twenty years,[9–10] owing to numerous applications in various fields such as telecommunications, optical data storage, information processing and microfabrication. Molecular engineering of push – pull compounds[11] has been a very active area in recent years and has led to compounds displaying huge quadratic β[12] and/or cubic hyperpolarisability.[13] We note that β-cyclodextrin has also been used as a chiral complexing agent to allow the creation of second-harmonic generation-active solids through the formation of inclusion complexes of *p*-nitroaniline.[14]

Recently, several studies have addressed the potentials of multichromophoric dipolar systems for NLO. Highly promising results have been obtained when four push – pull chromophores are incorporated in calix[4]arenes; this leads to supermolecules that show intriguing second-order nonlinearities both at the molecular and macroscopic levels.[15] Interesting results have also been obtained with model trischromophoric dipolar compounds built from triphenylcarbinol.[16] Bis-chromophoric systems derived from binaphtyl have been extensively investigated over recent years.[17] The NLO properties of these preorganised, bis-dipolar systems have been shown to be strongly dependent on both the close proximity of dipolar chromophores and on their relative orientation. The dihedral angle between subchromophores plays a significant role. Dendrimers that incorporate numerous chromophores have lately emerged as fascinating systems.[18] For instance, multichromophoric dendrons that include up to 15 dipolar chromophores have been designed and shown to promote coupling enhancement of the molecular hyperpolarisability.[18b]

Results and Discussion

Design: We sought a cyclodextrin derivative that would be soluble in organic environments and whose photophysical features could possibly be modified by a change of microenvironment, such as solvent polarity. Consequently, we designed derivatives that should be soluble in a wide range of organic solvents. We focused on the functionalisation of cycloheptaamylose β-cyclodextrin[19] by seven push – pull chromophores bearing a dimethylanilino electron-releasing moiety connected to a rhodanyl electron-releasing moiety. Such chromophores were grafted to the primary rim of β-CD through a short spacer (one methylene unit) by using an ester linkage. These chromophores show significant molecular nonlinearity and intense absorption in the visible-blue region.[20]

Synthesis: The synthesis of the push – pull chromophore 1-[5-(4-dimethylamino-benzyliden)-4-oxo-2-thioxo-thiazolidin-3-yl]-acetic acid (**1**) bearing a pendant acid moiety was easily achieved by a Knoevenagel condensation (Scheme 1), under standard experimental conditions.[12e] Then the reaction between the per-2,3-*O*-acetyl-β-cyclodextrin[21] and **1** yielded the target derivative **2CD** by using previously reported conditions.[22] For comparison purposes, the model compound **2M** resulting from the condensation of **1** with ethanol was also synthesised (Scheme 1).

Absorption: Chromophore **2M** and multichromophoric **2CD** both have a large and intense absorption band in the visible region, shown in Figure 1. As exemplified in Table 1, both compounds exhibit positive solvatochromic behaviour: a bathochromic shift of the absorption band is observed with increasing solvent polarity. This is typical of an ICT transition with an increase of dipolar moment upon excitation,[20b, 23] which results in a larger stabilisation of the more polar excited state in polar solvents, and consequently in a red shift of the absorption band.

Table 1. Absorption properties of **2M** and **2CD** in different solvents: maximum absorption wavelength (λ_{max}), molar extinction coefficient (ε_{max}) and oscillator strength *f*.

	λ_{max} [nm]	ε_{max} [$10^4\,\mathrm{M^{-1}cm^{-1}}$]	*f*
2M			
Cyclohexane	447	4.5	0.64
Toluene	465	4.8	0.68
Chloroform	475	4.4	0.64
DMSO	486	4.7	0.68
2CD [a]			
Toluene [b]	436	12.8	2.38
Chloroform	468	15.7	2.87
DMSO	474	19.6	3.78

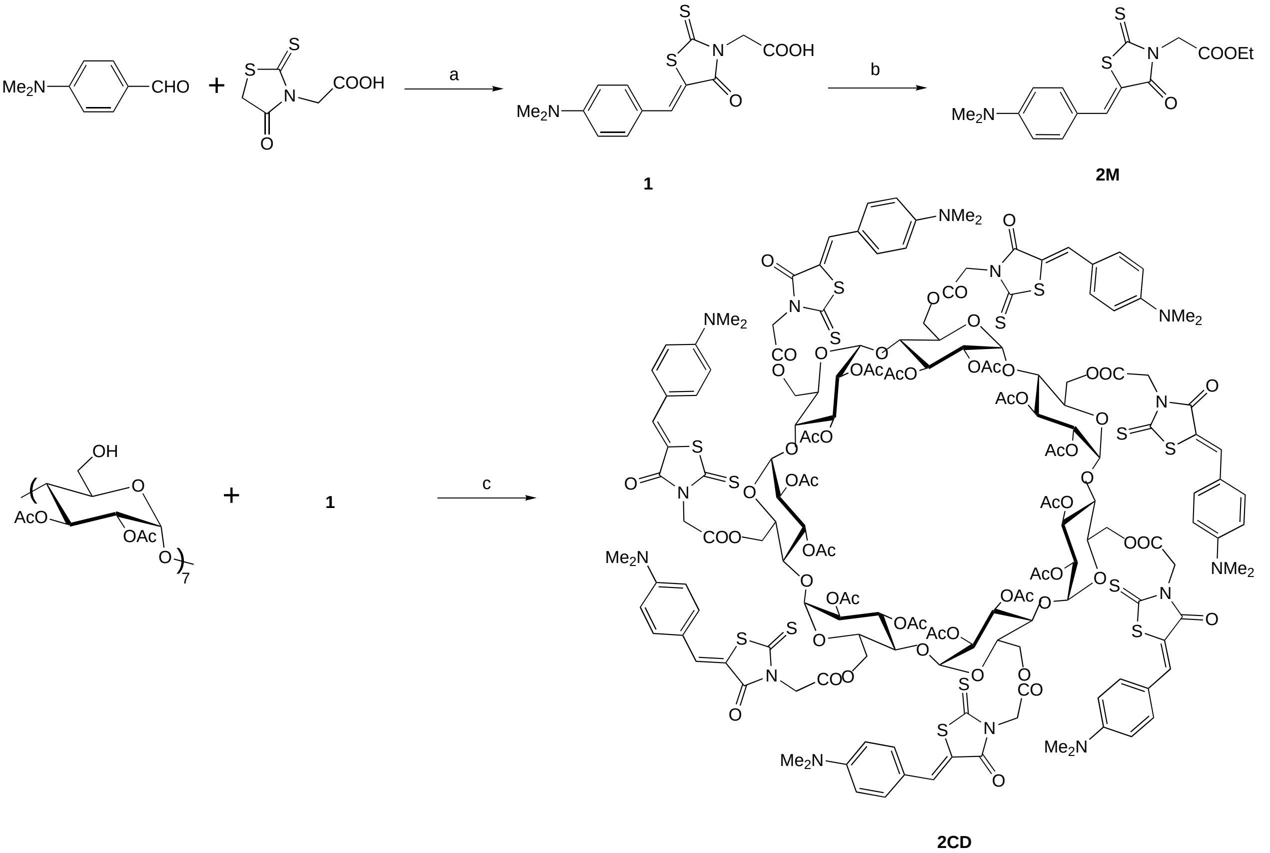
[a] **2CD** is insoluble in cyclohexane. [b] **2CD** is poorly soluble in toluene at room temperature. The sample was prepared at 80 °C and then cooled to room temperature.

Comparison of the absorption characteristics of **2M** and **2CD** reveals that the multichromophoric assembly **2CD** shows definite hypsochromic and hypochromic shifts (see Table 1) as well as a broadening of the absorption band, relative to its monomeric counterpart **2M**. Although the mutichromophoric species maintains a very high molar extinction coefficient (with typical $\varepsilon_{\max}$ values higher than $10^5\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$), the resulting $\varepsilon_{\max}$ value, as well as the integrated absorption coefficient (or equivalently the oscillator strength f), is much smaller than that expected for completely independent chromophores (i.e. seven times that of **2M**), as clearly seen from comparison of Figure 1a and b. In addition, this net hypochromic effect seems more pronounced in apolar solvents: **2M** presents similar $\varepsilon_{\max}$ and f values in solvents of different polarities, whereas **2CD** shows increasing $\varepsilon_{\max}$ and f values with increasing solvent polarity (Table 1).

Such changes of absorption characteristics provide evidence that the gathering and confinement of push–pull chromophores within **2CD** results in a modification of their optical properties as compared with monomeric chromophores in similar solvents. The hypsochromic shift can originate from several causes including interactions between individual chromophores within the supermolecule (such as electrostatic or π–π cofacial interactions[16d, 24]), excitonic coupling,[8, 25–26] hindered solvation or aggregation effects.

Oscillator strengths are rather similar for **2M** in the different solvents investigated. In contrast, lower solvent-dependent values are observed for **2CD**. The latter observation strongly supports the idea that other mechanisms than exciton coupling are also active in **2CD** samples. We note that the hypsochromic and hypochromic shifts are definitely more pronounced in toluene with the distinct emergence of a dominant blue-shifted shoulder at 436 nm. On considering the structure of **2CD** and the sample preparation in toluene, which required solvent heating, intra- and intermolecular aggregation might be considered to account for the pronounced hypochromism observed in that particular case. The large dipole moment of the multichromophoric bundle **2CD** (vide infra) should result in strong intermolecular dipolar interactions and could possibly promote formation of intermolecular aggregates. We anticipate such effects to be more important in solvents of low polarity, such as toluene.

Circular Dichroism: The cyclodextrin backbone is chiral. This feature is a distinct advantage for NLO and for detecting excitonic coupling between the individual chromophores borne by the primary rim of **2CD**. It is usually simple to detect excitonic coupling in a dimer made of two identical chromophores from the circular dichroism (CD) spectrum. In contrast to the absorption spectrum, the CD spectrum contains two bands of opposite signs.[7] Figure 2 displays the CD spectra of **2CD** in toluene and dimethysulfoxide, together with the absorption spectra.[27] Both spectra exhibit a similar excitonic coupling, as revealed by the comparable intensity of the CD spectra and excitonic splitting ($\Delta\varepsilon_{(\mathrm{L\text{-}R})}(\max) \approx 10^3\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$ and $\Delta\lambda \approx 40$ nm), crossing the x axis at 442 nm in toluene and at 458 nm in dimethylsulfoxide. In the present system, the quantitative analysis of the experimental data cannot easily be performed in order to derive a reasonable estimate of the average conformation of **2CD**. In fact, too many unknown parameters (e.g. distribution of interchromophoric distances, relative orientations of the chromophores) control the circular-dichroism spectrum.[7] Finally, the circu-



Scheme 1. a) EtOH, 80 °C, 83 %; b) EtOH, DCC, DMAP, CH_2Cl_2, 92 %; c) DCC, DMAP, CH_2Cl_2, 85 %.

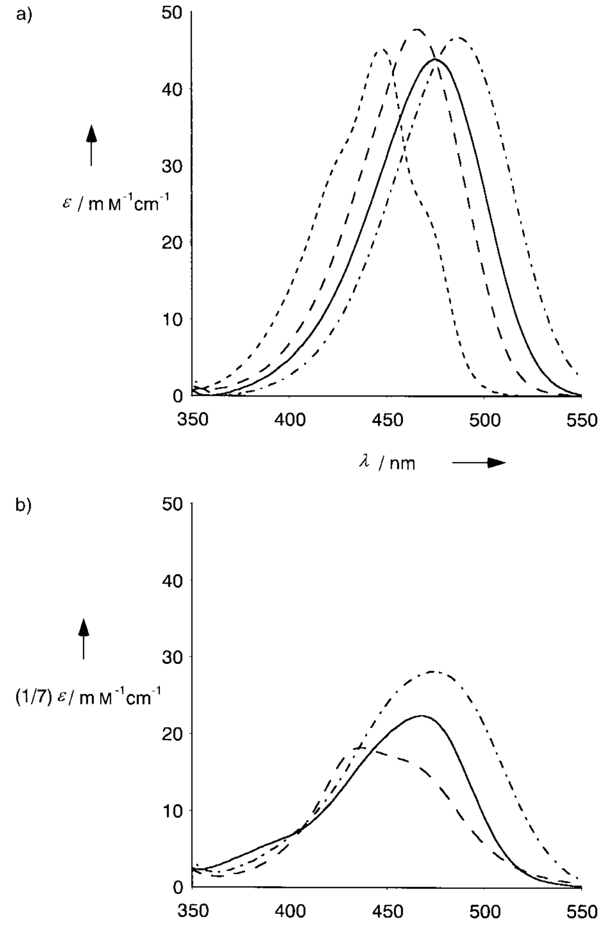


Figure 1. UV/Vis absorption spectra of a) **2M** and b) **2CD**. In the latter case, the molar absorption coefficient was divided by a factor of seven for comparison purpose. Solvents: cyclohexane (- - - -), toluene (– – –), chloroform (——), dimethylsulfoxide (–•–•–).

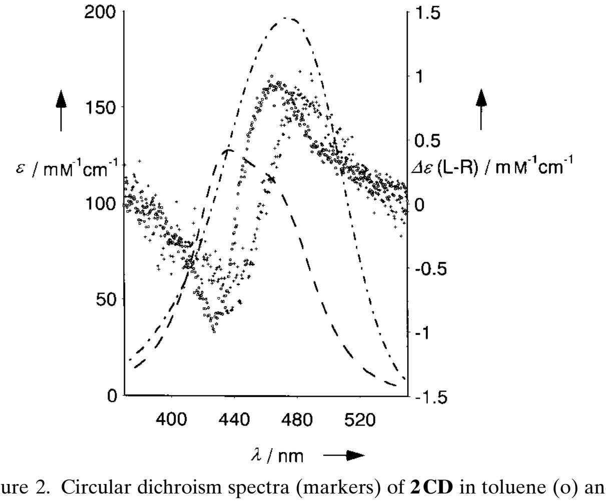


Figure 2. Circular dichroism spectra (markers) of **2CD** in toluene (o) and dimethylsulfoxide (+). The UV/Vis absorption spectra of **2CD** is given for comparison (toluene: – – –, dimethylsulfoxide: –•–•–).

lar-dichroism spectra suggest that the excitonic coupling within the bundle of covalently linked chromophores of **2CD** do contribute to the strong perturbation of the **2CD** absorption spectra compared with the **2M** ones.

Dipole moment: The dipole moments μ of the chromophores **2M** and **2CD** were determined from dielectric and refractive index measurements in solutions of decreasing concentration of the dipolar molecules in chloroform. From experimental data, the dipole moment can be inferred by using Equation (1), equivalent to the Debye equation:

$$\mu^2 = \frac{27kT}{4\pi N_A C}\frac{(\varepsilon - n^2) - (\varepsilon_1 - n_1^2)}{(\varepsilon_1 + 2)(n_1^2 + 2)} \qquad (1)$$

in which N_A is the Avogadro number, ε and n are the dielectric constant and the refractive index of the solution of concentration C, respectively, and ε_1 and n_l are the dielectric constant and the refractive index of the pure solvent. The dipole moment is determined from the slope of the graph of $\Delta = (\varepsilon - n^2) - (\varepsilon_1 - n_1^2)$ as a function of C, as $C \rightarrow 0$.[28]

Compound **2CD** shows a very large dipole moment (38.3 D), which is more than four times that of its monomeric counterpart **2M** (9.3 D). This very large dipole moment deserves a special comment. Our previous studies, carried out with several multichromophoric cyclodextrins bearing naphthalene units, demonstrated that the individual chromophores along the cyclodextrin were randomly oriented.[29] Consequently, except for a possible minor contribution resulting from the small number of chromophores that limits averaging, the dipole moment of the multichromophoric cyclodextrins bearing naphthaline units should be close to zero. On the other hand, in the present multichromophoric cyclodextrin **2CD**, one could imagine that the much larger dipole moment of the individual chromophores causes a preferential sheaf-type self-arrangement that leads to a large dipole moment for the multichromophoric bundle. By using the dipole-moment values of **2M** and **2CD**, an average tilt angle of 54° can be derived for each single push–pull chromophore with respect to the symmetry axis of the conical cyclodextrin.

Optical nonlinearities: The first hyperpolarisabilities β of molecules **2M** and **2CD** were determined by using the Harmonic Light Scattering (HLS) experiment, first introduced by Terhune and Maker.[30] The HLS technique, which is based on analysis of the incoherent, scattered second harmonic signal from an isotropic medium, has recently attracted strong interest for studies addressing octupolar molecular structures.[31–32] This method also provides the advantage over the electric-field-induced-second-harmonic (EFISH) technique of allowing direct measurement of the magnitude of the first-order hyperpolarisability. As it results from an incoherent process, the scattered nonlinear intensity $I^{2\omega}$ can be expressed as Equation (2):

$$I^{2\omega} = G(N\langle\beta^2\rangle + N_1\langle\beta_1^2\rangle)(I^{\omega})^2 \qquad (2)$$

for a solution with N (or N_l) chromophores (solvent molecules) per mL of solution, where the G coefficient embodies geometrical factors and experimental correction terms, and the brackets refer to statistical isotropic orientational averaging. G evaluation proceeds from the calibration of the experiment by means of a reference CCl_4 solution with $\sqrt{\langle\beta^2\rangle} = 0.26 \times 10^{-30}$ esu.

The $\sqrt{\langle\beta^2\rangle}$ value of the solute molecules can be inferred from the determination of the linear dependence of the harmonic intensity as a function of the square of the I^{ω} fundamental intensity for different molecular concentrations. Measurements were carried out in chloroform with pure solvent (leading to $\sqrt{\langle\beta_1^2\rangle} = (0.19 \pm 0.03) \times 10^{-30}$ esu[33] and different concentrations of the solute chromophores. HLS experiments were performed at 1.32 μm in order to locate the second harmonic signal in the transparency region of the chromophores and to avoid contamination by two-photon fluorescence.[34–35]

The experimental HLS results obtained for the reference chromophore **2M** and the multichromophoric bundle **2CD** are collected in Table 2. We note that the multichromophoric molecule **2CD** shows a significant first-order hyperpolarisability that leads to a molecular quadratic nonlinearity more than three times larger than its monomeric counterpart **2M**. This confirms that the polar chromophores are not randomly oriented around the cyclodextrin, but rather self-arranged within the multichromophoric supermolecule. By using the $\beta(0)$ values derived from HLS measurements for **2M** and **2CD**, an average tilt angle of 61° is obtained for the push–pull chromophores ICT axis with respect to the axis of the conical cyclodextrin. This is close to the tilt-angle value derived from dipole measurements, and suggests that the seven chromophores contribute in a roughly additive way to the nonlinearity of the multichromophoric molecule. On the other hand, the close proximity of other dipolar chromophores can affect the individual contribution; this leads to a reduction of intramolecular charge transfer.[36] We note that such a reduction of ICT could also be at the origin of the blue-shifted absorption.[37]

The sheaf-type self-arrangement of the push–pull chromophores in the multichromophoric cyclodextrin derivative is of interest for quadratic nonlinear optics. This is clear from the $\mu\beta(0)$ value estimated for the supermolecule **2CD**. The $\mu\beta(0)$ value, which is the relevant molecular figure of merit for the preparation of poled polymers with large electrooptic coefficients, is more than ten times larger that the experimental value determined for the benchmark dipolar chromophore Disperse-Red 1 (450×10^{-48} esu)[38] We note that **2CD** leads to both slightly superior nonlinearity and transparency than **DR1**;[39] this suggests that the multichromophoric strategy may be a promising approach. It remains to validate such an approach by studying the incorporation of such supermolecules into poled-polymers or ordered films.

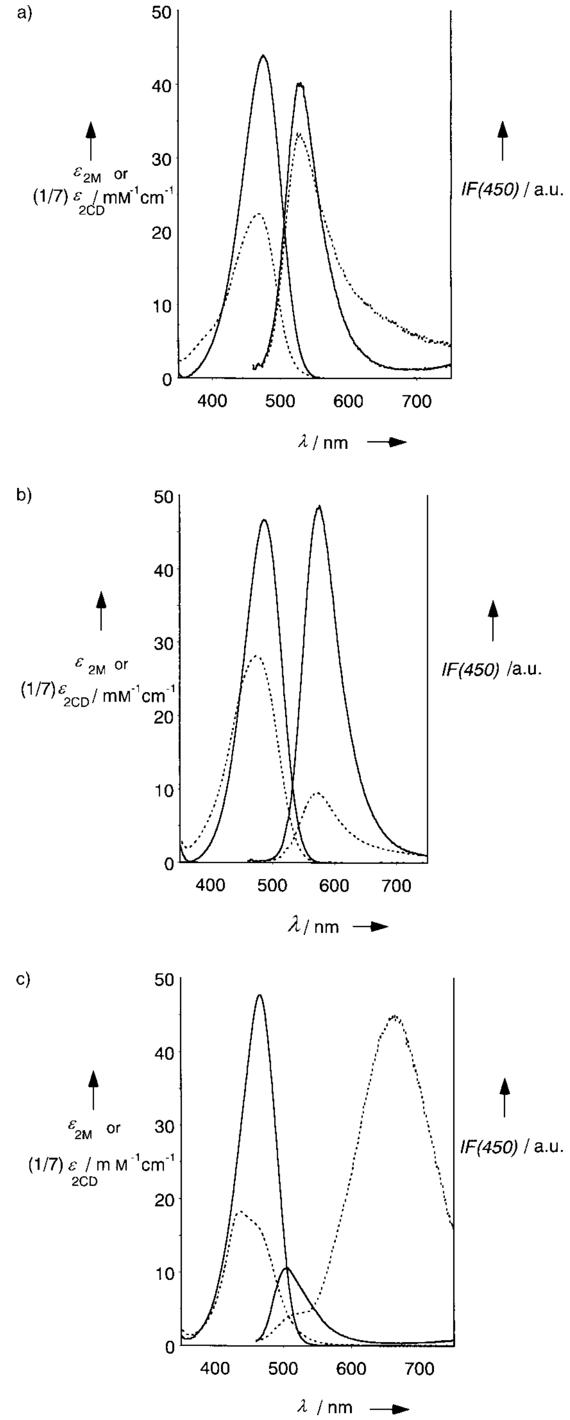


Figure 3. Corrected fluorescence emission spectra and absorption spectra of **2M** (——) and **2CD** (----) in a) chloroform, b) dimethylsulfoxide and c) toluene. In each solvent, the emission spectra have been normalised at the same absorbance for comparison purpose.

Fluorescence emission: Figure 3 displays the emission spectra of both **2M** and **2CD** in chloroform, dimethylsulfoxide and toluene, while Table 3 summarises the results. Upon increasing solvent polarity, **2M** fluorescence emission is increased and becomes red-shifted. The positive solvatochromism, as well as the increase of the Stokes shift with solvent polar-

Table 2. Dipole moment values for molecules **2M** and **2CD**, and experimental results of HLS experiments conducted at 1.32 μm in $CHCl_3$ leading to the HLS molecular averaged hyperpolarisability $\beta_{HLS} = \sqrt{\langle\beta^2\rangle}$.[a]

	μ [D]	λ_{max} [nm]	β_{HLS} [10^{-30} esu]	$\beta_{HLS}(0)$ [10^{-30} esu]	β_{zzz} [10^{-30} esu]	$\beta_{zzz}(0)$ [10^{-30} esu]	$\mu\beta_{zzz}(0)$ [10^{-48} esu]
2M	9.3	477	43	19	104	46	427
2CD	38.3	468	143	64	345	154	5920

[a] For typical one-dimensional dipolar chromophores, the dominant component β_{zzz} along the ICT axis is evaluated from $\sqrt{\langle\beta^2\rangle}$ according to $\beta_{zzz} = \sqrt{35/6}\,\beta_{HLS}$.[33] The corresponding static values were calculated by using the two-level dispersion factor.[42]

Table 3. Emission properties of **2M** and **2CD** in several solvents.

	Cyclohexane		Toluene		Chloroform		DMSO	
Compound	λ_{em} (I_r(450))[a] [nm]	SS[b] [cm^{-1}]	λ_{em} (I_r(450))[a] [nm]	SS[b] [cm^{-1}]	λ_{em} (I_r(450))[a] [nm]	SS[b] [cm^{-1}]	λ_{em} (I_r(450))[a] [nm]	SS[b] [cm^{-1}]
2M	–[c]		505 (0.63)	1700	529 (1.0)	2150	574 (7.2)	3150
2CD	–[d]		661 (2.7)[e]	–	530 (0.8)	2500	572 (1.4)	3600

[a] Absorbance-corrected relative intensity of fluorescence emission after excitation at 450 nm. The absorbance-corrected intensity of **2M** in chloroform was arbitrarily fixed at 1. [b] Stokes shift $= 1/\lambda_{max} - 1/\lambda_{em}$. [c] Very weak emission. [d] **2CD** is insoluble in cyclohexane. [e] **2CD** is poorly soluble in toluene at room temperature. The sample was prepared at 80 °C and then cooled to room temperature.

ity (which accounts for the more pronounced solvatochromism of fluorescence relative to absorption), is consistent with a significant increase of dipole moment upon excitation, leading to a highly polar excited state. For such a derivative, an increase of dipole of about 12 D is expected based on electro-optical absorption measurements in solution.[20b]

The **2CD** fluorescence emission exhibits both similarities to and differences from **2M**. The cases of chloroform and dimethylsulfoxide will be discussed first. In these solvents, the maxima of **2CD** fluorescence emissions are close to the **2M** ones. This observation suggests that the solvent shells around an excited chromophore in **2CD** or an excited **2M** molecule compare well. Thus, despite the large local chromophore concentration in **2CD**, no steric hindrance that leads to constraints on solvent configuration can be observed from **2CD** emissions in chloroform or dimethylsulfoxide. In contrast, **2CD** exhibits excimer formation as revealed by the existence of noticeable tails in the red tail of the emission spectra when compared with **2M**. Such excimer formation has already been observed in previous series.[6] It results from the close proximity of the chromophores in the multichromophoric molecules derived from β-cyclodextrin. The more pronounced excimer formation in chloroform than in dimethylsulfoxide can be explained by the lower polarity and viscosity of the former solvent. Both features should favour the formation of excited states of chromophore dimers.

The spectrum of **2CD** fluorescence emission in toluene is striking. It has its maximum at 661 nm, compared with 505 nm for **2M**. The corresponding red-shift probably results from the abundant formation of excimers. In addition to the poor solubility in toluene and the large perturbation of the absorption spectrum, the latter observation suggests that these excimers are most probably intermolecular and, at least partially, preformed. Nevertheless, the absence of any light scattering from the **2CD** toluene solution indicates that the aggregates remain smaller than the wavelength of the visible light. Interestingly, **2CD** emission is the strongest in toluene despite i) the observed trend for **2M** that should make us anticipate a low-intensity emission; ii) the excimer formation, which often leads to fluorescence quenching.

Conclusion

The mutichromophoric bundle obtained by the covalent linking of seven dipolar chromophores on the primary rim of a β-cyclodextrin shows intriguing features. The absorption, circular dichroism and fluorescence investigations reveal that the confinement of the push–pull chromophores within the nanoscopic supermolecule affects their optical properties and promotes electrostatic/electronic interactions. A blue-shifted absorption and hypochromic effect is obtained compared with isolated chromophores in a similar solvent environment. In addition, excitonic coupling and excimer-formation phenomena are observed.

The very large dipole moment (38 D) and the significant molecular first-order hyperpolarisability of the multichromophoric bundle indicate a spontaneous self-organisation of the dipolar chromophores within the supermolecule. Such chiral hyperpolar multichromophoric assemblies are promising candidates for nonlinear optics.

Experimental Section

Spectroscopic measurements: All experiments were performed at 25 °C. The solvents were of spectroscopic grade. The UV/Vis absorption spectra were recorded on a Kontron Uvikon 930 spectrophotometer and the CD spectra on a Mark V Jobin-Yvon spectrometer. Corrected fluorescence spectra were obtained with a PTI spectrofluorometer.

Dipole measurements: Dielectric constants were measured by using a WTW dipolemeter (type DM 01) made of a capacitance cell for liquids and a capacitance-measurement electronic bridge. From capacitance values of solutions, we can deduce the dielectric constant after a calibration process involving various solvents with different dielectric constants. Refractive indexes in the visible range were measured at 643 nm with a Carl–Zeiss–Abbe refractometer and a Cadmium spectral lamp as the visible source. Both measurements were performed at 25 °C; the solutions are maintained at this temperature by using a water flow driven by a thermostatic bath.

NLO measurements: HLS measurements were conducted with a Q-switched Nd^{3+}:YAG laser emitting pulses of about 40 ns duration at 1.32 μm. These experiments were performed by using solutions of increasing concentration in chloroform for each molecule. The experimental accuracy ranges between 5 and 10 %.

Synthesis

General P*rocedures*: Microanalyses were performed by the Service de Microanalyses de l'Université Pierre et Marie Curie (Paris). Melting points were determined with a Büchi 510 capillary apparatus. ^1H and ^{13}C NMR spectra were recorded at room temperature on Bruker AM 250 or AM 400 spectrometers; chemical shifts are reported in ppm with protonated solvent as internal reference (^1H, $CHCl_3$ in $CDCl_3$ $\delta = 7.27$, CHD_2SOCD_3 in CD_3SOCD_3 $\delta = 2.49$; ^{13}C, $^{13}CDCl_3$ in $CDCl_3$ $\delta = 77.0$, $^{13}CD_3SOCD_3$ in CD_3SOCD_3 $\delta = 39.6$); coupling constants J are given in Hz. Mass spectra (chemical ionisation with NH_3 or positive FAB) were performed by the Service de Spectrométrie de Masse de l'Ecole Normale Supérieure (Paris). Column chromatography was performed on silica gel 60 (0.040–0.063 mm) Merck. Analytical or preparative thin-layer chromatography (TLC) was conducted on Merck silica gel 60 F254 precoated plates. Commercially available reagents were used as obtained.

Acid ***1***: A solution of *p*-dimethylaminobenzaldehyde (2.73 g, 18.3 mmol) and rhodanine-3-acetic acid (3.50 g, 18.3 mmol) in absolute ethanol (250 mL) was heated under reflux for 18 h. After cooling, the crystalline red precipitate was filtered and washed with a little ethanol to yield pure acid **1** after drying under vacuum. Yield: 4.90 g, 83 %; m.p. 235 °C (lit.[40]

235 °C); ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C): $\delta = 2.95$ (s, 6H; 2CH$_3$), 3.25 (brs, 1H; COOH), 4.61 (s, 2H; CH2), 6.74 (d, ^{3}J(H,H) = 9.0 Hz, 2H; H-ar), 7.40 (d, 2H, ^{3}J(H,H) = 9.0 Hz, 2H; H-ar), 7.64 (s, 1H; HC=); ^{13}C NMR (62.90 MHz, [D$_6$]DMSO, 25 °C): $\delta = 40.0$, 45.3, 112.6, 113.7, 120.1, 133.8, 135.7, 152.5, 166.8, 167.6, 192.9.

Monomeric model chromophore ***2M***: Dicyclohexylcarbodiimide (DCC, 1.09 g, 5.3 mmol) was slowly added to a solution of absolute ethanol (370 µL, 6.3 mmol), **1** (1.70 g, 5.3 mmol) and 4-(dimethylamino)pyridine (DMAP; 0.644 g, 5.3 mmol) in anhydrous dichloromethane (100 mL). After being stirred overnight at room temperature and under protection from light exposure, the solution was filtered to eliminate the 1,3-dicyclohexylurea (DCU) formed and then evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (2:1) to give **2M** as red crystals after recrystallisation in ethanol. Yield: 1.66 g, 90%; m.p. 144–145 °C; ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): $\delta = 1.29$ (t, ^{3}J(H,H) = 7.2 Hz, 3H; CH$_3$-CH$_2$-O), 3.09 (s, 6H; N(CH$_3$)$_2$), 4.23 (q, 2H; CH$_3$-CH$_2$-O), 4.86 (s, 2H; N-CH$_2$-COO), 6.73 (d, ^{3}J(H,H) = 9.0 Hz, 2H; H-ar), 7.42 (d, 2H, ^{3}J(H,H) = 9.0 Hz, 2H; H-ar), 7.72 (s, 1H; HC=); ^{13}C NMR (62.90 MHz, CDCl$_3$, 25 °C): $\delta = 14.1$, 40.0, 44.9, 61.9, 112.1, 115.3, 120.8, 133.3, 135.4, 152.0, 166.2, 167.4, 193.1. MS (CI/NH$_3$): *m/z*: 368 $[M+NH_4]^+$; elemental analysis calcd (%) for $C_{16}H_{18}N_2O_3S_2$ (350.47): C 54.83, H 5.18, N 7.99; found: C 54.82, H 5.13, N 8.12.

Heptachromophoric supermolecule ***2CD***: Dicyclohexylcarbodiimide (DCC, 629 mg, 3.0 mmol) was slowly added to a solution of 2^A, 2^B, 2^C, 2^D, 2^E, 2^F, 2^G, 3^A, 3^B, 3^C, 3^D, 3^E, 3^F, 3^G-tetradeca-*O*-acetyl-β-cyclodextrin (300 mg, 0.17 mmol), **1** (983 mg, 3.0 mmoles, 2.5 eq) and DMAP (372 mg, 3.0 mmol) in anhydrous dichloromethane (55 mL). After the same work up as for **2M**, the crude residue was purified by chromatography on silica gel with dichloromethane/gradient of ethanol to give **2CD** as orange crystals after recrystallisation in dichloromethane/ethanol (1:30). Yield: 570 mg, 85%; m.p. 225 °C; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 2.09$ (s, 3H; OAc), 2.16 (s, 3H; OAc), 2.93 (s, 6H; N(CH$_3$)$_2$), 3.83 (t, ^{3}J(H,H) = 8.1 Hz, 1H; H-4), 4.24 (d, 1H, ^{3}J(H,H) = 8.1 Hz, 1H; H-5), 4.56 and 4.64 (2d, ^{2}J(H,H) = 11.0 Hz, 2H; N-CH$_2$-COO), 4.83 (d, ^{2}J(H,H) = 16.7 Hz, 1H; H-6b), 4.94 (dd, ^{3}J(H,H) = 8.4 Hz and ^{3}J(H,H) = 3.1 Hz, 1H; H-2), 4.96 (d, ^{2}J(H,H) = 16.7 Hz, 1H; H-6a), 5.11 (d, ^{3}J(H,H) = 3.1 Hz, 1H; H-1); 5.35 (t, ^{3}J(H,H) = 8.4 Hz, 1H; H-3), 6.48 (d, ^{3}J(H,H) = 7.9 Hz, 2H; H-ar), 7.14 (d, ^{3}J(H,H) = 7.9 Hz, 2H; H-ar), 7.46 (s, 1H; HC=); ^{13}C NMR (100.624 MHz, CDCl$_3$, 25 °C): $\delta = 20.8(2)$, 39.8, 44.6, 63.8, 69.7, 70.1, 71.0(3), 76.8, 97.2, 111.7, 114.2, 120.3, 133.3, 135.6, 151.6, 165.7, 166.8, 169.5, 170.5, 192.6; MS (FAB+): *m/z*: 3854.54 $[M+H]^+$; elemental analysis calcd (%) for $C_{168}H_{182}N_{14}O_{63}S_{14}$ (3854.33): C 52.35, H 4.76, N 5.09; found: C 50.68, H 4.65, N 5.02.[41]

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