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UV-visible Absorption Study of the Self-association of Non-ionic Chromonic Triphenylenes TP6EOnM (n = 2, 3, 4) in Dilute Aqueous Solutions: Impact of Chain Length on Aggregation

Antoine Herbaut and Etienne Baranoff*

Abstract: A series of triphenylenes with oligoethoxy chains of various length, TP6EOnM with $n = 2, 3, 4$, has been synthesised and purified by HPLC. The self-association of these disc-shaped molecules in dilute aqueous solutions ($\sim 10^{-7}$ to $\sim 4 \times 10^{-4}$ M) has been studied by UV-visible absorption spectroscopy. The free energy of association decreases as the length of the chains increases. As a result, for a given concentration, the average size of aggregate diminishes as the chain length increases. While the absorption properties of the monomer are identical for the three molecules, the extinction coefficients of solutions of the three triphenylenes at a given concentration are significantly different and are directly linked to the average size of the aggregates. The change of epsilon values upon aggregation could explain the trend generally observed with dyes for solar cells substituted with chains of increasing length showing increasing extinction coefficient values.

Keywords: Aggregation · Self-association · TP6EO2M · Triphenylene · UV-visible absorption

1. Introduction

The aggregation of molecules in solution is of great interest for a broad variety of topics including biology, drugs, inks, and organic electronics. Among all supramolecular architectures, there is a growing interest in chromonic liquid crystals because of numerous potential applications including the fabrication of polarizing films.^[1]

Chromonic liquid crystals are a particular class of lyotropic liquid crystals that aggregate in solution without a crit-

ical micelle concentration.^[1] Chromonic mesogens are formed of a rigid and solvophobic core, generally aromatic, surrounded by solubilising groups. An important difference with thermotropic liquid crystals, in which LC behaviour is controlled solely by temperature, is that the molecular organisation in chromonic liquid crystals is also dependent on the concentration. As the concentration increases, the molecules spontaneously aggregate into columnar stacks. As stacks grow, they become ordered and form the liquid crystalline phases.

2,3,6,7,10,11-hexa(2-(2-methoxyethoxy)-ethoxy)triphenylene (TP6EO2M, Fig. 1) is a triphenylene-based chromonic mesogen with six peripheral 2-(2-methoxyethoxy)ethoxy chains acting as the solubilising groups.^[2] When mixed with D₂O at room temperature, TP6EO2M forms a nematic columnar phase for concentration above ~20wt% and a columnar hexagonal phase at higher concentration. This behaviour has been studied by X-ray diffraction and ¹H NMR^[3] and results are well supported by theoretical studies.^[4] However, only limited studies of the aggregation at low concentration exist, as only one NMR study is reported.^[5] Based on this study relating the average aggregate length to the concentration, the photophysical properties, absorption and emission, of TP6EO2M have been investigated to show that the exciton hops along the columnar aggregate at a rate of at least 10^{11} s⁻¹.^[6]

TP6EO3M does not display liquid crystalline properties in water because the additional ethyleneoxy unit provides too much hydrophilic character.^[3a] It can therefore be safely assumed that TP6EO4M, which has a further additional ethyleneoxy unit, would also not show liquid crystalline properties with water. Consequently the aggregation properties of these compounds in dilute aqueous solution have not been studied.

The three molecules TP6EOnM, $n = 2, 3, 4$, have a common aromatic core with

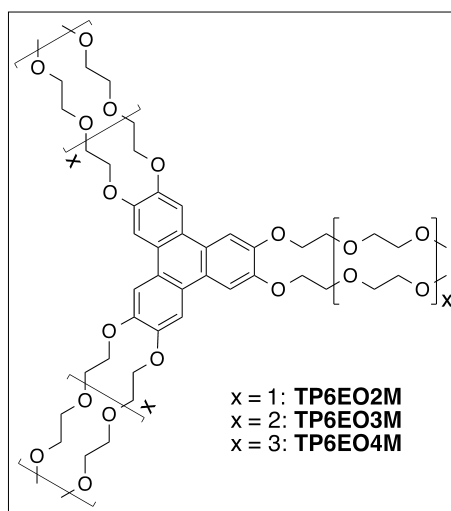


Fig. 1. Chemical structures of TP6EOnM ($n = 1, 2, \text{ and } 3$).

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well studied photophysical properties and therefore can be considered as a very good model to study the impact of chains on aggregation and on the absorption properties of the aggregates. The relation between aggregation size and absorption properties would be important in areas related to sensing and dyes chemistry and applications, *e.g.* solar cells.

Herein we have prepared a series of TP6EOnM ($n = 2, 3, 4$) and investigated by UV-visible absorption the self-association of these three triphenylene derivatives in dilute aqueous solution (concentration between $\sim 10^{-7}$ and $\sim 4 \times 10^{-4}$ M). We have found that the purity of the materials strongly influences the aggregation at very low concentration but not at higher concentration. Considering the aggregation process of such molecules as isodesmic and using an exciton-coupling model to link the absorption of the solution to the state of aggregation, we show that the 'bonding energy' between molecules in the aggregates decreases as the length of the chains increases. The main conclusion of this work is that the extinction coefficient of solution of TP6EOnM ($n = 2, 3, 4$) will be similar when the size distribution of aggregates is similar, not when the concentrations are the same. In the broader context of dyes for solar cells, this would explain the trends of increasing extinction coefficient as the length of pendent alkyl chains increases.

2. Results and Discussion

2.1 Synthesis

The series TP6EOnM was prepared following literature procedures with slight modifications. Briefly, trimerisation of veratrole using FeCl_3 gave 2,3,6,7,10,11-hexamethoxytriphenylene, which is reacted with HBr to provide 2,3,6,7,10,11-hexahydroxytriphenylene. Reaction with the required oligoethoxy alcohol activated

with a mesyl group results in the crude TP6EOnM compound.^[3a,7] Purification is crucial to perform reliable aggregation study. We have therefore evaluated the purity of the triphenylene derivative by HPLC. TP6EO2M is discussed as a representative example. After extensive column chromatography on silica gel (eluent: CHCl_3 to $\text{CHCl}_3/\text{MeOH}$ 5%), two impurities remain in the product (Fig. 2). Analysis of these impurities by mass spectrometry revealed that the impurity at ~ 35 min is the triphenylene with only five 2-(2-methoxyethoxy)ethoxy chains. This impurity originates from incomplete substitution of the hexahydroxytriphenylene. The second impurity very close to the TP6EO2M is a triphenylene with a methoxy instead of one 2-(2-methoxyethoxy)ethoxy chain. It originates from an incomplete cleavage of the methoxy groups of hexamethoxytriphenylene. We could fully remove these impurities only by HPLC, which gave us 'HPLC grade' materials. This purifica-

tion step is key for the aggregation study as the impurities have a clear impact on the self-association of the triphenylene at very low concentration. Indeed we have also isolated by HPLC a 'technical grade' TP6EO2M containing only a small amount of the second impurity and compared its aggregation in water with the 'HPLC grade' TP6EO2M (see below).

2.2 UV-visible Absorption.

The absorption spectra as a function of concentration of TP6EO2M, TP6EO3M and TP6EO4M in H_2O are shown in Fig. 3. The measurements were taken at 20°C . The spectra at the lowest concentration ($\sim 10^{-7}$ M) are virtually identical for the three compounds. By analogy with hexa-alkoxytriphenylene derivatives, the main absorption band at 276 nm has been attributed to the allowed $S_4 \leftarrow S_0$ transition and the broad band at 306 nm to the allowed $S_3 \leftarrow S_0$ transition.^[6,8] As the concentration increases, the shape of the

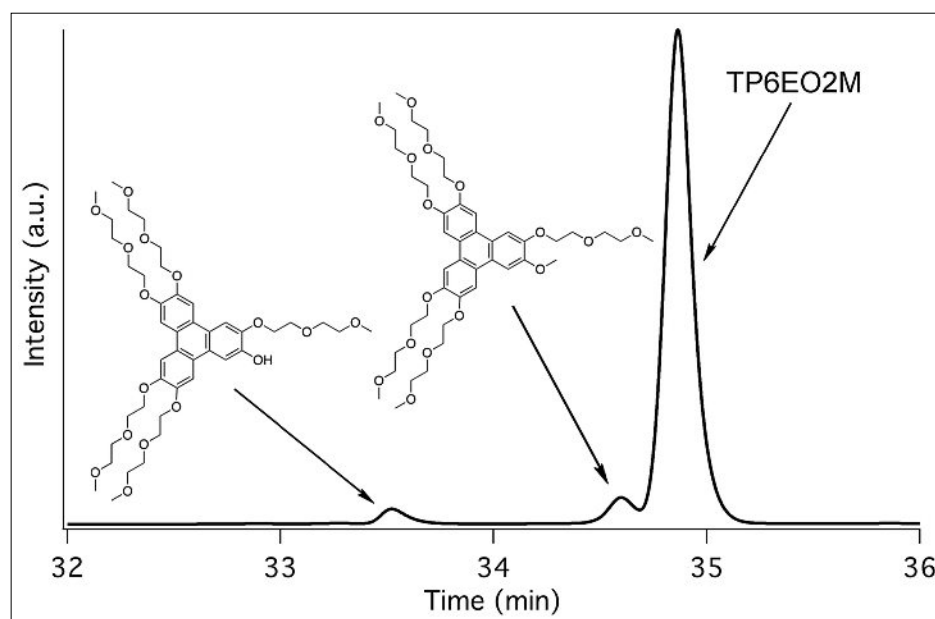


Fig. 2. HPLC trace of TP6EO2M after column chromatography.

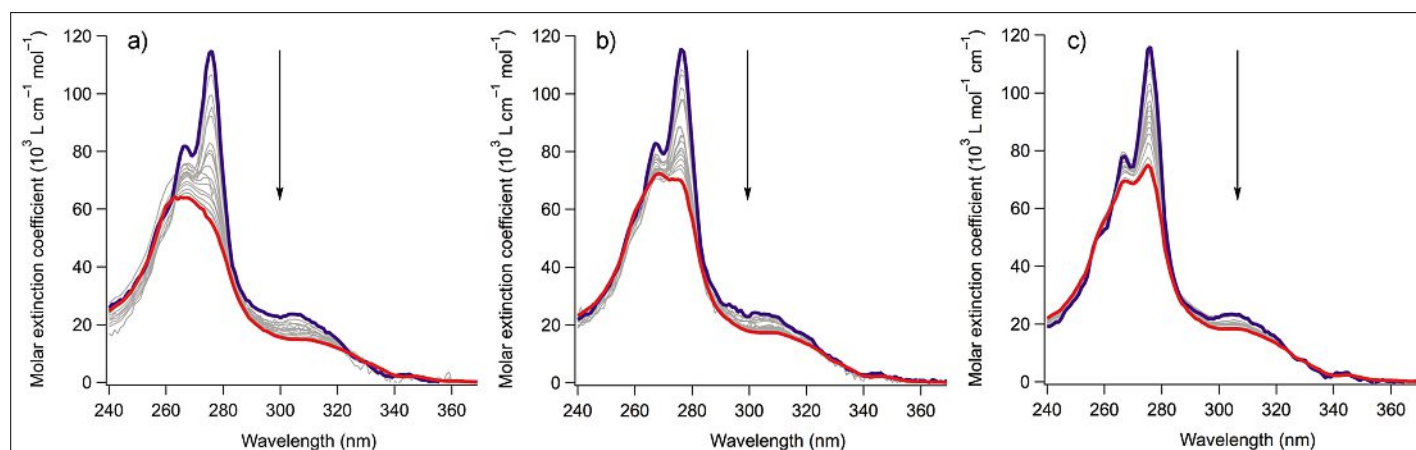


Fig. 3. UV-visible absorption spectra of increasing concentration in H_2O of a) TP6EO2M from 1.02×10^{-7} to 3.99×10^{-4} M; b) TP6EO3M from 1.01×10^{-7} to 2.86×10^{-4} M; c) TP6EO4M from 1.00×10^{-7} to 3.86×10^{-4} M.

spectra gradually changes because of the formation of columnar aggregates of larger size. In the aggregate, the chromophores are interacting with neighbouring molecules, which impact the properties of the excited chromophore.

2.3 Aggregation

The plots of extinction coefficient as a function of concentration are shown in Fig. 4. To analyse the change of extinction coefficient as a function of the concentration we used a known model of isodesmic aggregation.^[9] In short, the aggregation of molecules *A* can be described by successive equilibria of the form $A_{n-1} + A_1 \rightleftharpoons A_n$ ($n = 2$ to infinity), with equilibrium constants of the form $K_n = [A_n]/(K_2 K_3 \dots K_{n-1} [A_1]^n)$. In the simplest aggregation model, all equilibrium constants are equal, which means that the energy of interaction between two molecules, α , is independent of the size of the aggregate. To link the distribution of aggregates with the absorption properties of the solutions, we have considered exciton coupling theory as previously done for other small molecules, including chromonics.^[9c,10] The fits are plotted in Fig. 4 and fitting parameters are summarised in Table 1. In this preliminary study, we focus on the ‘bond energy’, α , and the absorption coefficient of the monomer, ϵ_{mono} .

The ‘bond energy’ is the free energy of association between two molecules; in the isodesmic self-association considered here, α is independent of the size of the aggregate. For TP6EO2M, α was found to be 12.6 ± 0.2 kT, which is similar to the value found by NMR (14 kT) and by atomistic simulations (14.7 kT using OPLS force field).^[4d,5] The NMR study was performed at 17 °C, which is a slightly lower temperature than our study (20 °C) and can explain our lower values. On going to TP6EO3M and TP6EO4M, α decreases to 11.4 and 9.3 kT respectively. Compared to TP6EO2M, the longer chains of TP6EO3M and TP6EO4M allow for additional water molecules to interact with the oxygen atoms of the oligoethoxy chains, hence increasing the hydrophilic character of the triphenylene.^[4c,d] This means that, for a given concentration, as the length of the chains increases, the distribution of aggregates moves towards smaller average size of aggregates.

Importantly, the distribution of aggregate size has a significant effect on the extinction coefficient of the solutions: as the average size of aggregates increases, the extinction coefficient decreases. As a result, solutions of different TP6EOnM with similar extinction coefficient will be obtained at different concentration but will have similar distribution of aggregates. For example, a 10^{-5} M solution of TP6EO2M (average size of aggregates ~ 2) has a

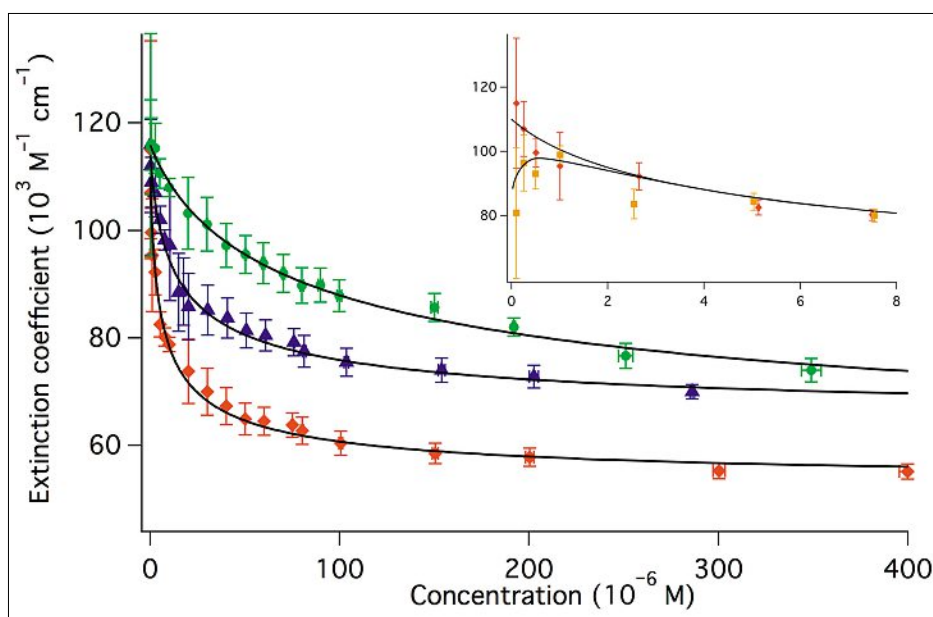


Fig. 4. Epsilon at 276 nm as a function of concentration in H₂O of TP6EO2M (◆), TP6EO3M (▲), and TP6EO4M (●). Black lines are from the fits (see text). Inset: comparison between TP6EO2M ‘HPLC grade’ (◆) and TP6EO2M ‘technical grade’ (■) between 0.1 and 8 mM. The black line for the latter has no physical meaning and is simply a guide for the eye.

Table 1. Fitting parameters for the extinction coefficient of solution of TP6EOnM ‘HPLC grade’ in H₂O as a function of concentration.

	α [kT] ^a	β ^b	ϵ_{mono} [10 ³ M ⁻¹ cm ⁻¹] ^c
TP6EO2M	12.6 ± 0.2	-28600 ± 1000	110 ± 2
TP6EO3M	11.4 ± 0.2	-24600 ± 800	114 ± 1
TP6EO4M	9.3 ± 0.2	-29800 ± 1000	116 ± 1

^aBond energy between two molecules in an aggregate. ^bCoupling constant of the exciton.

^cExtinction coefficient of the monomer.

similar epsilon value ($\sim 80,000$ M⁻¹ cm⁻¹) as a 15×10^{-5} M solution of TP6EO4M (average size of aggregates ~ 2). The approximation made is that the coupling constant β would not vary with a change of chain length. This aspect is outside the scope of the present study; as a simple note, the exciton coupling value is expected to vary with the interdisc distance, which is anticipated to increase slightly as the length of the chains increases by analogy with hexa-alkoxytriphenylenes.^[11]

Furthermore, it should be emphasised that the impact of aggregate size distribution on the extinction coefficient is stronger as the concentration decreases. For example, the average size of aggregates for TP6EO2M increases from just above 1 to ~ 1.1 molecule per aggregate on going from $\sim 10^{-7}$ to $\sim 10^{-6}$ M. In this range of concentration, the extinction coefficient significantly drops from $\sim 120,000$ M⁻¹ L⁻¹ to $\sim 85,000$ M⁻¹ L⁻¹. This result can simply explain the trend in extinction coefficients of series of organic dyes with increasing pendent chains.^[12]

The impact of aggregate size distribution on the extinction coefficient can also

explain the results obtained with the ‘technical grade’ TP6EO2M, which still contained minute amounts of the 2-methoxy-3,6,7,10,11-pentakis(2-(2-methoxyethoxy)ethoxy)triphenylene impurity (see HPLC trace in the Supplementary Data). Comparing the extinction coefficient of this ‘technical grade’ TP6EO2M with the ‘HPLC grade’ TP6EO2M at concentrations below 2×10^{-6} M (inset in Fig. 4), it is clear that the ‘technical grade’ TP6EO2M has an abnormal behaviour as the epsilon values are decreasing as the concentration decreases. The two grades of TP6EO2M behave the same at concentrations above 4×10^{-6} M. These measurements are reproducible over time using the same solutions and also when preparing new solutions from the same batch. As the present impurity has one methoxy group instead of one 2-(2-methoxyethoxy)ethoxy chain, it will be less hydrophilic than TP6EO2M. The lower hydrophilicity will favour aggregation hence larger size aggregates compared to the pure compound, which leads to lower extinction coefficient. As the concentration increases, the impurities will be buried inside larger size aggregates

and less accessible to water molecules^[4d] so that the effect of lower hydrophilicity on aggregates size will become marginal.

Finally it should be noted that the experimental extinction coefficients of the $\sim 10^{-7}$ M solutions are the same for the three triphenylenes pointing to the existence of only the monomeric species at this concentration. The drop in epsilon values is faster than expected from the isodesmic self-association model for concentrations up to $\sim 3 \times 10^{-7}$ M. This means that, at these concentrations, there are larger size aggregates than anticipated by the model. We attribute this observation to a larger 'bond energy' for the formation of the dimer as pointed out by theoretical calculations^[4d] but never observed experimentally for TP6EOnM systems. Further studies at very low concentration are required to confirm this hypothesis. The use of a self-association model in which the equilibrium constant for the formation of the dimer is different to the equilibrium constant of association with larger size stacks^[9a,13] will then allow for a study of the impact of chain length on exciton coupling constant β .

3. Conclusion

We report the synthesis and careful purification of a series of triphenylenes with oligoethoxy peripheral chains of increasing length, TP6EOnM with $n = 2, 3, 4$. We have studied by UV-visible absorption the self-association of these triphenylenes in dilute aqueous solution with concentrations between $\sim 10^{-7}$ to $\sim 4 \times 10^{-4}$ M, a much larger range of concentration than previously reported for TP6EO2M only. In this preliminary study, we analysed the aggregation behaviour using a simple isodesmic self-association model.

The 'energy bond' between two TP6EO2M molecules is found to be ~ 12.6 kT, close to reported values for this system. The study confirms that the 'energy bond' decreases as the chain length increases, which leads to smaller size aggregate distribution for a given concentration as the length of the chains increases. At concentrations $\sim 10^{-7}$ M the experimental values of extinction coefficients depart from the values expected by the isodesmic model. This would be the first experimental observation of the higher energy of dimerization compared to stack elongation for these triphenylenes.

In the broader context of dyes for solar cell applications, the results could provide a very simple explanation for the trends often observed that, at a given concentration, dyes with longer alkyl chains have higher extinction coefficients. We would attribute this mainly to the formation of aggregates of different size in solution. Indeed minute

changes of average size of aggregates lead to a significant decrease of extinction coefficient. In short, dyes with longer alkyl chains have higher extinction coefficients because, at a given concentration, they form smaller size aggregates than dyes with shorter alkyl chains.

4. Experimental

Detailed experimental methods and additional figures can be found in the Supplementary Data.

4.1 Materials

Dichloromethane, methanol, N,N'-dimethylformamide, acetic acid and sulphuric acid were purchased from Fisher. Diethyl ether was purchased from Sigma Aldrich. Hydrobromic acid was purchased from Alfa Aesar. All solvents were used without further purification. Chromatography columns were carried out on silica gel 60 [Alfa Aesar, 0.040-0.063 mm]. Reaction progress was followed with TLC plate on aluminium support (Alumina: Fluka; Silica: Alugram® SIL G/UV₂₅₄).

4.2 HPLC

Analytical chromatograms were recorded on a Shimadzu device using a Phenomenex Kinetex 5 μ m, C18, 100 Å column at a constant temperature of 35 °C and a flow rate of 1 mL/min. All samples were filtered through a 0.45 μ m Acrodisc® syringe filter (Supplier: Pall Corporation) before injection. Injection volume was 20 μ L. Detection was made by UV-visible absorption at a wavelength of 254 nm. Compound purities were calculated from the HPLC relative areas assuming that the impurities have the same absorption behaviour as the compound.

Preparative HPLCs were done using a Kinetex 5 μ m C18 100A, AXIA Packed, equipped with a Security Guard PREP Cartridge Core-Shell C18. Experiments were carried out at room temperature and at a flow rate of 10 mL/min. All samples were filtered through a 0.45 μ m Acrodisc® syringe filter (Supplier: Pall Corporation) before injection. Injection volume was 2 mL. Detection was made by UV-Visible absorption at a wavelength of 254 nm.

4.3 NMR Spectroscopy

NMR spectra were recorded on a Bruker Avance III 400 (¹H 400 MHz, ¹³C 101 MHz) instrument and are reported relative to the residual deuterated solvent as the internal standard (CDCl₃: δ [¹H] = 7.26 ppm; δ [¹³C] = 77.16 ppm; DMSO-d₆: δ [¹H] = 2.50 ppm; δ [¹³C] = 39.52 ppm, 74.40 ppm). Coupling constants are expressed in Hz.

4.4 UV-visible Spectroscopy

TP6EOnM ($n = 2, 3, 4$) solutions were prepared in distilled water at a concentration from $\sim 1 \times 10^{-7}$ M to $\sim 10^{-4}$ M. UV-Visible spectroscopy was carried out on a Cary 50 Spectrophotometer at a temperature of 20 ± 1 °C. 0.1 cm, 1 cm (from Starna scientific) and 5 cm (from Agilent Technologies) length path quartz cuvettes were used. Absorption spectra were recorded from 200 to 400 nm. Molar extinction coefficient ϵ was taken at $\lambda = 276$ nm.

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