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Kinetically trapped supramolecular assembly of perylene dianhydride derivative in methanol: optical spectra, morphology and mechanisms

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Abstract: Supramolecular self-assembly has attracted increasing attention as a breakthrough methodology in the fields of nanoscience and nanotechnology. In this study, a perylene dianhydride derivative (TP-PDA) self-assembles into well-defined nanospheres through a nucleation-growth process. The mechanisms of this process are explored by spectral analysis, dynamic light scattering (DLS) and scanning electron microscopy (SEM). Both insitu DLS and in-situ SEM reveal that the sizes of aggregated nanospheres increase with time until the formation of equilibrium Haggregates. It shows that TP-PDA undergoes a kinetically trapped assembly with a rapid transformation into the thermodynamically favoured form, and this process can be finely tuned by reduced concentration and increased temperature. Weak intermolecular forces such $\pi-\pi$ stacking, hydrogen bonding and solvophobic interactions play an important role in the formation of nanostructures. The work inspires us to explore other kinetically trapped supramolecular assemblies that might be easily ignored due to the short trapping time of commonly used experimental timescales.

Introduction

Self-assembly provides an attractive way to control the properties and performance of organic materials.^[1-7] The formation of complex nanostructures during self-assembly based on the delicate balance between various weak intermolecular forces have been studied as a function of the molecular building blocks and the processing conditions.^[8] Recent studies have shown that the first step of the self-assembly pathway can furnish kinetically trapped products.^[9-14] These observations inspired us to explore the growth of ordered nanostructures by controlling the "trapping" process.

Perylene carboxyanhydride and -imide dyes display exceptional chemical, thermal, and photochemical stability with high fluorescence quantum yields in organic solvents.^[15-18] Further, these chromophore systems exhibit rich self-assembly behaviour with H-aggregates as a common motif.^[19] Many research groups have investigated the π -stacking of perylene-based monoimides (PMIs) or -bisimides (PBIs) as a function of

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solvents and substitution type.^[20-21] a similar process has rarely been studied for perylene tetracarboxydianhydride (PDA). The latter serves as an important precursor of PMIs and PBIs,^[22-25] but is also an important chromophore in its own right. Its poor solubility and the lack of chemical functionalization ask for new suitably functionalized PDAs which then hold promise for a different assembly behavior.

In this work, we report a perylene tetracarboxydianhydride derivative bearing four phenyoxy groups in the bay-region (TP-PDA) (**Scheme 1**).^[26,27] This chromophore self-assembles into well-defined nanospheres through an autocatalytic process in polar protic solvent MeOH. The sizes of aggregated nanospheres increased with time. The mechanisms of supramolecular assembly were explored by optical spectra, suggesting the existence of kinetically trapped products.



Scheme 1. Molecular structure of TP-PDA, TTBP-PDA, TP-PMI and TP-PBI.

Results and Discussion

The introduction of substituents in the bay-region of PDA provokes a strong twist within the perylene ring and TP-PDA becomes soluble in a wide range of organic solvents,^[28] such as methanol (MeOH), dichloromethane (DCM), tetrahydrofuran, toluene and acetone. Remarkably enough, when the red solution of TP-PDA in DCM (10^{-3} M) was diluted with MeOH (5×10^{-6} M), the color turned to yellow after several hours (inset in **Figure 1**). Recovering the sample and re-dissolving it in DCM gave back the original red color (**Figure 2A**).

MALDI-TOF-MS spectra of TP-PDA in MeOH pointed toward unobstructed TP-PDA and excluded a chemical transformation (**Figure S2**), instead the color change must be attributed to the reversible formation of supramolecular assemblies. For the sake

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of comparison, TTBP-PDA, TP-PMI and TP-PBI (**Scheme 1**) were synthesized and investigated under the same conditions. Similar assembly phenomena were observed in a MeOH solution of TTBP-PDA that contains two carboxydianhydride groups, but not in a MeOH solution of TP-PMI or TP-PBI (**Figure S3**), suggesting the importance of two carboxydianhydride groups for the formation of supramolecular assemblies in MeOH.

In order to explore the underlying growth mechanisms, optical spectra were recorded in DCM and MeOH at 283K (5×10^{-6} M) (**Figure 1**). It appeared that the absorption and emission maxima had large blue-shifts (≈ 80 nm) which can readily explained by the formation of H-aggregates.^[29,30] We also measured the optical properties of TP-PDA in other solvents, but no similar blue-shifts were observed (**Figure S4**), indicating that this phenomenon was depended on solvents used.



Figure 1. UV-vis and fluorescence spectra of TP-PDA in (A) DCM, (B) MeOH at the concentration of $5\times10-6$ mol/L. Inset: the photographs of TP-PDA in (A) DCM, (B) MeOH.

The time dependent evolution of the color changes was monitored by the spectral changes (**Figure 2B**). When the solvent was switched from DCM (10⁻³ M) to MeOH (2×10⁻⁵ M), the absorption maxima shifted from 576 nm to 551 nm immediately, corresponding to monomer peaks of TP-PDA in DCM and MeOH, respectively. Within 4 minutes, the absorption maxima of TP-PDA in MeOH revealed a blue shift from 551 nm to 536 nm and then remained stable for a few minutes due to the formation of kinetically trapped aggregation.^[14] Then the intensity of the peak at 536 nm revealed a gradual decrease until stable. This process can be described as pre-equilibrium^[13] and the formation of equilibrium H-aggregates. According to the previous works,9-13 it can be concluded that the initial kinetically form is supposed to be disassemble at first, and there are interplay and balance between the disassembly and selfassembly into final H-aggregates. The titration experiments were performed to gain the information on this aggregation process and to study the solvent effect (Figure 3). A stock solution of TP-PDA in MeOH (2×10⁻⁵ M) or DCM (2×10⁻⁵ M) was prepared. The MeOH solution was titrated into the DCM solution to form a DCM/MeOH mixture. The ratio of DCM/MeOH was thus changed from 100:1 to 1:4. At the low amount of MeOH, there was no obvious change in the spectra. When the ratio of DCM/MeOH was increased up to 5:1, the monomer TP-PDA began to aggregate into trapped product since sufficient MeOH was needed to initiate The MeOH/DCM ratio affects the aggregation. thermodynamic equilibrium between the monomer and the final H-aggregate.



Figure 3. UV-Vis absorption spectra of titration experiments.



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Scheme 2. Self-assembly mode of TP-PDA in MeOH.



Figure 2. (A) Formation and transformation of supramolecular assembly of TP-PDA. (B) UV-visible spectra of TP-PDA in MeOH at 283K (concentration: 2×10⁻⁵ M) (C) SEM image of TP-PDA H-aggregates.

In order to monitor the aggregation process in MeOH, insitu dynamic light scattering (DLS) was employed.[31,32] The initial diameters of aggregates in MeOH were approximately 100 nm (Table S1), and then increased with time up to approximately 300 nm. The morphology of the obtained aggregates was further evaluated using scanning electron microscopy (SEM). TP-PDA formed a regular sphere with a diameter of about 600 nm in MeOH when it reached the equilibrium H-aggregate state (Figure 2C). Interestingly, the growth process could also be observed by in-situ SEM, the spheres with diameters of 100-400 nm formed at various time (Figure S5) upon fast evaporation of the solvent. This observation is consistent with the DLS result and supports the existence of a 'pre-equilibrium' as illustrated by Scheme 2. The aggregate morphologies of TP-PDA in DCM, acetone or tetrahydrofuran appeared as irregular bulk phases (Figure S6), again, indicating the important role of the solvent in regulating the assembly process. The photoluminescence quantum yield (PLQY) of TP-PDA in DCM (Φ_F =76%) was higher than that in MeOH

(Φ_F =68%), obviously a result of aggregation-induced quenching effects.^[33,34]

We deduce from the complex kinetic profile that there is interplay between two states involving the initially trapped aggregation and the final H-aggregates. In order to further explore this complexity, we investigated the spontaneous transformation of TP-PDA monomer to TP-PDA Haggregate. TP-PDA showed a relatively short trapping time (the TP-PDA trapping time in MeOH was measured at a concentration of 4×10⁻⁵ M at 283 K, Figure 4A). Under this condition the final equilibrium H-aggregate of TP-PDA was achieved after 1200 minutes, while the absorption peak remained 20 minutes at 536 nm due to the trapping process of TP-PDA monomer in MeOH (Figure 4B). During the measurements, the transformation from TP-PDA monomer to TP-PDA H-aggregate was accelerated by reduced concentration and increased temperature properly and could be completed even within several minutes. As shown in Figures 4C and 4D, the H-aggregate of TP-PDA in MeOH at a concentration of 1×10⁻⁵ M was achieved within

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60 minutes at 288K. Thus, a higher temperature led to a faster H-aggregation process in MeOH (**Figure 4E**).



Figure 4. (A) Time course of transformation from TP-PDA monomer to TP-PDA H-aggregate at 283 K (concentration: 4×10^{-5} M). (B) Constant plots of absorbance at the given wavelength as a function of time (A). (C) Time course of transformation from TP-PDA monomer to TP-PDA H-aggregate at 288 K (concentration: 1×10^{-5} M). (D) Plots of absorbance at the given wavelength as a function of time (C). Time course of the aggregate formation in MeOH (2×10^{-5} M) at different temperatures (E) and at different concentrations (298 K) (F).

Moreover, the H-aggregation time is dependent on the concentration (c_T) of TP-PDA since a higher c_T results in a longer aggregation time (Figure 4F). This concentrationdependent behaviour is consistent with that of a previously reported porphyrin-based system, in which the monomers are trapped as off-pathway aggregates.^[13] The transformation of TP-PDA monomer to TP-PDA H-aggregate occurred after a trapping time in accordance with a nonlinear sigmoidal transition (Figure 4E and 4F). This kinetic profile is characteristic of an autocatalytic (or self-replication) process including a nucleation and elongation processes.^[13,14,35-37] It is noteworthy that the transformation from TP-PDA monomer to TP-PDA H-aggregate can be tuned or accelerated by mechanical stir, adding an aliquot of TP-PDA H-aggregate solution, or increasing temperature (Figure S7). Given the unique evolution of monomeric to H-aggregated TP-PDA in MeOH with time for ca. 1200 minutes, the trapping time can be set to more than 20 minutes at an initial concentration of 4×10⁻⁵ M at 283 K in MeOH.

It appears reasonable that TP-PDA aggregation is dominated by particularly strong π - π stacking together with solvophobic interactions and hydrogen bonding in protic solvents.^[20] In order to verify this hypothesis, we considered the role of dibutylether

as solvent. The latter is non-protic, but has weak solvating power. No similar blue shift was observed in dibutylether (Figure S8), which indicated the existence of solvophobic interactions. The striking feature in Fourier transform infrared (FTIR) spectrum of TP-PDA in MeOH (Figure S9) was a stretching frequency at v(C=O) = 1680 cm⁻¹ corresponding to a hydrogenbonded carbonyl group, indicating the existence of hydrogen bonding between TP-PDA and MeOH molecule.[38] According to previous reports, the aggregation could be destroyed by stimuli such as temperature,^[13,14] concentration^[39] and acid-base^[40,41]. Here we tried to disintegrate the hydrogen-bonded supramolecular structure of TP-PDA in MeOH (5×10⁻⁶ M) by varying the pH through the addition of NaOH (1 M) or HCl (1 M). When the pH of the solution decreased to 2, the color changed to red. In contrast, when the pH value was adjusted to pH 7, the solution returned to yellow and exhibited a yellow fluorescence (Figure S10). Alkaline solutions were not considered because pervlene tetracarboydianhydrides are unstable under these conditions. When exciting the chromophore at 520 nm, a new peak at 600 nm appeared only under acidic conditions (pH=2) as seen by the fluorescence spectra of TP-PDA (Figure S11). This can be attributed to the disintegration of H-aggregate and the emergence of fluorescent TP-PDA monomer under acidic conditions. The absorption peak of the nanospheres was blueshifted in comparison with that of monomeric TP-PDA, indicating that in H-aggregates the TP-PDA molecules overlap with a faceto-face stacking.^[39] The internal structure of self-assembled nanostructures of TP-PDA was also investigated by X-ray diffraction (XRD) analysis (Figure 5).



Figure 5. X-ray diffraction patterns of the nanostructured TP-PDA from methanol (black), from DCM (red) and none on glass sheets

As shown in **Figure 5**, two strong peaks at 0.35 and 0.71 nm were observed in the XRD curve of TP-PDA in MeOH, but no peak can be detected in DCM. It was reported that the π - π plane distance ranged from 0.334 to 0.355 nm. The peak of 0.35 nm could be assigned to the distance of the single-layer of π -stacked perylene and the peak at 0.71 nm could be assigned to the distance of double-layer of π -stack.^[42] These results demonstrated that π - π stacking and hydrogen bond in protic solvents play an important role in the regulation of TP-PDA aggregates in MeOH.

Conclusions

In conclusion, we have described the supramolecular assembly of TP-PDA in MeOH. TP-PDA can self-assemble into regular nanospheres that grow with time until the formation of equilibrium H-aggregates, as revealed by DLS, SEM and UVvisible spectral analysis. TP-PDA undergoes a kinetically trapped assembly with a rapid transformation into the thermodynamically favoured form. The trapping time is relatively short and can be finely tuned by reduced concentration and increased temperature. Weak intermolecular forces such π - π stacking, hydrogen bonding and solvophobic interactions play an important role in the formation of nanostructures. This study not only presents a new supramolecular assembly system based on TP-PDA, but also inspires us to explore other kinetically trapped supramolecular assemblies that might be easily ignored due to the short trapping time of commonly used experimental timescales.

Experimental Section

Materials and characterization: Unless otherwise stated, reagents were commercially obtained and used without further purification. Reactions were monitored by TLC. Flash chromatography separations were carried out using silica gel (200-300 mesh). ¹H-NMR spectra were recorded on a Bruker 400 (400 MHz ¹H; 100 MHz ¹³C) spectrometer at room temperature. Mass spectra (MS) were measured with a XEVO-G2QTOF (ESI) (Waters, USA). X-ray diffraction (XRD) patterns of the powder were recorded using a Rigaku 2500VB2+PC diffractometer using the Cu Ka radiation (λ =1.541844 Å) at 40 kV and 50 mA with the step-scanned mode in 0.04° (20) per step and count time of 10s/step in the range from 5 to 40°. Fourier transform infrared (FT-IR) spectra were recorded using a Thermo Nicolet Nexus FT-IR devise with the Smart Golden Gate ATR attachment in the range of 4000-500 \mbox{cm}^{-1} with 2 \mbox{cm}^{-1} resolution. Fluorescence spectroscopic studies were performed on a fluorescence spectrophotometer (Horiba JobinYvon FluoroMax-4 NIR, NJ, USA). UVvisible spectra were obtained on a spectrometer (Cintra 20, GBC, Australia). The percentage contribution of each lifetime component to the total decay curve, photoluminescence quantum yield (PLQY) were Edinburgh recorded using an Instruments' FLS 980 fuorospectrophotometer. The surface morphology was investigated by a Zeiss Supra 55. Dynamic light scattering (DLS) was performed with an equipment composed of an ALV SP-86 goniometer, a Spectra Physics 2011-s Kr ion laser (637.2 nm wavelength, 500 mW output power) and an ALV-3000 correlator. pH was adjusted by dropwise adding NaOH (1 M) or HCl (1 M) aqueous solution using needle tubing and measurements were carried out using a pH meter (Mettler Toledo S40K).

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