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COMMUNICATION

Alkylamide-Substituted Tetraphenylethylene: Three Modes of Fluorescence Based on a Hydrogen-Bonded Excimer

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Three modes of emission, with different intensities and wavelengths were observed in tetraphenylethylenetetraamide 1 depending on the solvent, concentration and continuous irradiation with light, where intermolecular hydrogen bonds 10 between amide units played a significant role. Limitation of the motility of the molecule 1 in excited state by intermolecular hydrogen bonding is the key for observation of fluorescence even in the solution and transformation to the corresponding 9,10-diphenylphenanthrene derivative.

- ¹⁵ Materials that exhibit aggregation-induced emission (AIE)¹ have attracted considerable interest not only from a fundamental perspective but also with regard to practical applications, such as in organic light-emitting diode devices.² In contrast to typical emissive polyaromatic hydrocarbons (PAH), which lose
- ²⁰ fluorescence with an increase in concentration, AIE luminophores show increased fluorescence. Whereas PAH easily form excimer in concentrated solution that lose photoexcitation energy by nonradiative processes, the rotation of the substituents in AIE luminophores is restricted in the aggregate, which suppresses ²⁵ nonradiative deactivation to increase the fluorescence intensity. A variety of AIE luminophores such as penta/hexaphenylsiloles,³ polyphenylenes,⁴ and arylenevinylenes⁵ have been reported.

Since the AIE phenomena reported so far have been examined in mixtures of a good solvent (generally THF) and a poor solvent ³⁰ (generally water),⁶ it is impossible to control the aggregation state

- and the degree of molecular motion in the aggregation state and the degree of molecular motion in the aggregate. In fact, the luminescence spectrum of AIE is generally broad, which suggests random molecular structures and the interaction of AIE molecules in the aggregate. If the manner of the aggregation of AIE
- ³⁵ molecules could be controlled, their fluorescence spectra may be sharpened and the fluorescence wavelength and intensity could be tuned depending on intermolecular interactions and the degree of allowed molecular motion, respectively.

To achieve this control, we envisioned the attachment of amide ⁴⁰ units with strong aggregation ability to the terminal positions of AIE luminophores. Benzeneoligoamide derivatives have been extensively studied from the perspectives of self-aggregation in solution, the formation of a liquid crystal (LC) and unique ferroelectric properties in the LC phase. For example, benzene-

⁴⁵ 1,3,5-tricaboxamide forms columnar self-aggregation even in dilute solution, which has been well characterized experimentally.⁸ It also forms a thermotropic hexagonal columnar

LC phase.⁹ Upon the application of an electric field, the amide units in the LC phase invert, which provides ferroelectricity.¹⁰ In ⁵⁰ each case, the intermolecular hydrogen bonding of amide units plays an important role.

In this study, we introduced four tetradecylamide units to tetraphenylethylene (TPE), which is a representative AIE luminophore.¹¹ We expect that the initial aggregation would

- ⁵⁵ occur in a well-organized fashion with molecular movement limited less in good solvents due to intramolecular hydrogen bonding, while aggregation with a random molecular arrangement and more limited molecular motion would occur in poor solvents. In addition, the intramolecular photocyclization of
- ⁶⁰ TPE derivatives with an electron-donating group has been reported.^{12,13} Thus, continuous photoirradiation might also alter the photophysical properties of tetradecylTPEtetraamide **1**.

Herein, we describe the preparation and photophysical properties of **1**. Fluorescence properties such as the wavelength and/or intensity of **1** could be transformed by characteristic and the

- 65 intensity of 1 could be tuned by changing the concentration and solvents. The high aggregation properties of this molecule enabled us to observe the fluorescence of hydrogen-bonded and well-organized aggregate 1 even in good solvents such as CHCl₃ and THF as well as typical AIE emission not only in aqueous
- ⁷⁰ medium but also in a mixed organic solvent of CHCl₃ (good solvent) and DMSO (poor solvent). Upon continuous irradiation with UV-light, intramolecular photocyclization occurred to give a new fluorescence peak in 1 even with an electron-deficient amide group. Intermolecular hydrogen bonding between amide units in ⁷⁵ the excited state decreased the motility of the molecule to induce this photocyclization. Since the wavelengths and intensities of these three modes of fluorescence of 1 are different, it may have potential as a multi-stimulus-responsive fluorophore.



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Figure 1 Molecular structure of 1 and illustration of the concept of dual enhancement of the fluorescence of 1 based on an aggregation/precipitation/photoisomerization strategy.

The preparation of tetraamide **1** is summarized in Scheme 1. We started the synthesis of **1** from tetraphenylethylene. Tetrabromide **2** was prepared as described in the literature.¹⁴ While the preparation of TPEtetracyanide **3** from its tetrabromide ²⁵ **2**¹⁵ has already been reported, modification of the work-up was necessary to obtain pure **3** (details in ESI). Hydrolysis of tetracyanide **3** under basic conditions^{15a} gave tetracarboxylic acid **4**, which was converted to the corresponding acid chloride by the reaction with thionyl chloride. The generated acid chloride was ³⁰ directly reacted with tetradecylamine in the presence of triethylamine to give tetraamide **1** as a white solid. For a comparison of photophysical properties, tetraester **5**, which is unable to form hydrogen bonds, was also prepared.



Scheme 1 Preparation of tetradecylTPEtetraamide **1** and tetraester ⁴⁵ **5**. (a) Br₂; (b) CuCN, DMF; (c) KOH, ethyleneglycol; (d) SOCl₂, (e) $C_{14}H_{29}NH_2$ (for **1**) or $C_{14}H_{29}OH$ (for **5**), Et₃N, THF.

The nature of the aggregation of **1** was examined by ¹H NMR and IR spectra. The ¹H NMR spectrum of **1** showed sharp signals of ⁵⁰ both aromatic and aliphatic protons. No concentration-dependence was observed in the ¹H NMR spectrum of **1**, which indicates that **1** has limited aggregation ability in the ground state. This is in sharp contrast to benzeneoligoamides¹⁰ and pyrenetetraamide,¹⁶ which exhibit broad signals of aromatic

⁵⁵ protons due to aggregation induced by strong intramolecular hydrogen bonds. This difference can also be confirmed by the IR spectrum in CHCl₃, where N-H stretching vibration of **1** was observed at 3450 cm⁻¹, whereas that of pyrenetetraamide was

- 3250 cm⁻¹.¹⁶ This indicates that TPEtetraamide **1** is isolated in ⁶⁰ dilute solution (less than 10⁻³ M) while it possesses hydrogen bonding units at the terminal position. The difference in aggregation properties between **1** and benzeneoligoamides and pyrenetetraamide is due to the difference in the degree of molecular motion of the central aromatic units. While the central ⁶⁵ units in planar benzeneamides and pyrenetetraamide are fixed by hydrogen bonds, the benzene rings of TPEcarboxamide can twist
- hydrogen bonds, the benzene rings of TPEcarboxamide can twist along the C_{sp2} - $C_{benzene}$ bond axis. (See Figure S5 in ESI.)



Figure 2 ¹H NMR (left, in CDCl₃) and IR [right, solid state (red) and in CHCl₃ (blue)] spectra of **1**.

Next, we examined the absorption and fluorescence properties of 1. Figure S1 in ESI shows the concentration-dependent UV-Vis spectrum of 1 in CHCl₃. The UV-Vis spectrum of 1 showed long wavelength absorption at 330 nm. No concentration-85 dependence was observed in the UV-Vis spectrum of 1, which is consistent with the results in the ¹H NMR and IR spectra. Figure 3 shows the fluorescent spectra of 1 in CHCl₃ and THF. It is well known that the parent TPE does not emit fluorescence because of efficient internal conversion due to high motility in solution. In 90 fact, nonsubstituted TPE and its ester derivative 5 did not emit any fluorescence at a concentration of 1x10⁻⁴ M. On the other hand, TPEtetraamide 1 showed significant, albeit very weak, fluorescence at around 500 nm even at a low concentration on the order of 10⁻⁵ M (Figure 3 and Figure S2 in ESI). The fluorescence 95 intensity against absorption 1-T (T: transmittance in the UV-Vis spectra, Figure S3 in ESI) shows linear relationship, indicating the emissive species are the same all over the concentration regime. In addition to this, we also observed large Stokes shift (170 nm, 1.26 eV; see Figure S2 in ESI) and the fluorescence 100 spectrum without vibronic structure in the solution of 1 in THF/CHCl₃. Based on these experimental results, we can conclude that the emission is solely derived from excimer. Dominant excimer emission even at lower concentration (~10⁻⁶ M) was also observed in the structurally similar pyrenetetraamide ¹⁰⁵ with hydrogen bonding ability.¹⁶ If we consider the NMR and IR spectra (vide ante), TPEtetraamide 1 should form a dimer or oligomer only in the excited state, where its motility is restricted by intermolecular hydrogen bonding to allow radiative irradiation. An increase in the concentration increases the population of 110 excimer to increase fluorescence. It is worth noting that the fluorescence spectrum of 1 in good solvents (THF, CHCl₃) was sharper and more bathochromic than that in a poor solvent (vide infra), which suggest that a well-ordered intermolecular hydrogen-bonded excimer was formed in equilibrium in a good 115 solvent.

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 $_{\rm 10}$ Figure 3 Concentration-dependent fluorescence spectra of 1 in $CHCl_3\,(left)$ and THF (right).

A drastic increase in fluorescence was observed upon the addition of a poor solvent (H_2O) to a solution of **1** in a good solvent (THF). 15 While weak, concentration-dependent fluorescence was observed at 500 nm in THF, broad and intense fluorescence emerged at around 450 nm upon the addition of H₂O. This observation is similar to the AIE of the parent TPE molecule. Since the emission of 1 in THF/H₂O was broad and strong, and the N-H stretching ²⁰ vibration of **1** in the solid state was at a lower wavenumber (3307 cm⁻¹) than that in good solvent, aggregation induced by the addition of a poor solvent should be unarranged with a more severe restriction of molecular motility and stronger hydrogen bonding between amide units compared with a hydrogen-bonded 25 excimer formed in a good solvent. Thanks to increased aggregation properties due to amide hydrogen bonding, the emission intensity of 1 was saturated at THF:H₂O =1:1, whereas 90% H₂O was necessary in the original TPE molecule. The strong aggregation properties of 1 enabled the observation of AIE even 30 in the mixed organic solvent CHCl₃:DMSO (1:9). Distinct

fluorescence of 1 in the solid state was also observed (Figure S4 in ESI).



⁵⁵ Figure 4 Changes in the fluorescence spectra of **1** (a) in THF upon the addition of H_2O and (b) in $CHCl_3$ upon the addition of DMSO. Photographic demonstration of change of fluorescence of **1** in (c) THF/H₂O and (d) in CHCl₃/DMSO.

60 An increase in fluorescence could also be triggered by continuous irradiation with UV light. Figure 5 shows changes in the fluorescence spectra of 1 upon irradiation with UV light. Moderate fluorescence at around 400 nm was continuously increased. This fluorescence was completely different from both 65 the weak fluorescence observed in good solvent at a high concentration and the strong fluorescence in a mixture of good/poor solvents. Since this emission property was similar to that of 9,10-diphenylphenanthrene, this change in the fluorescence spectrum of 1 upon irradiation with UV light could 70 be accounted for by a photocyclization reaction between the two benzene rings.^{12,13} Upon photocyclization, motility of the molecule decreased due to the connection between the two benzene rings by a covalent bond, which decreases the internal conversion of excited species. As a result, the intensity of 75 fluorescence is increased. It is worth noting that the corresponding ester 5 without a hydrogen-bonding unit did not show a change in its UV-Vis spectrum or exhibit fluorescence even after irradiation with UV light. This clearly indicates that the limited motility in the hydrogen-bonded excimer of 1 ⁸⁰ accelerated its photocyclization reaction. The photocyclization of TPEtetracarboxylate with limited motility on a cray surface, and the fluorescence spectrum of the cyclized product with an emission maximum of 400 nm were reported by George and coworkers.¹³ Although the clear changes of the UV-Vis and 85 fluorescence spectra of 1 upon irradiation of UV-light were observed at low concentration (Figure 5), we could not complete this photocyclization at higher concentration enough to take ¹H NMR spectrum (Figure S8 in ESI). Because of incompletion of photocyclization at high concentration, limited solubility of 1 and 90 difficulty in scale-up due to light source, we could not isolate the photocyclized product in pure form.





ESI for detail). (c) Photographic demonstration of change of fluorescence of ${\bf 1}$ in $CHCl_3$ upon irradiation of UV light.

In summary, we investigated the fluorescence properties of

- ⁵ TPEtetraamide 1, which can exhibit aggregation. While molecule 1 in solution is isolated in the ground state, it forms a well-ordered hydrogen-bonded excimer upon irradiation with UV light. As a result, weak, sharp and concentration-dependent fluorescence was observed at around 500 nm even in a good ¹⁰ solvent. Upon the addition of a poor solvent, broad and intense fluorescence was induced, which was ascribed to the AIE phenomenon of TPE derivatives. Continuous irradiation of a poor solvent.
- solution of **1** with UV light induced a photocyclization reaction to produce moderate emission at a shorter wavelength (around 400 ns nm). The hydrogen-bonded excimer of **1** plays an important role in limiting the motility of the molecule to induce photocyclization.
- Since the wavelength and intensity of the fluorescence emissions of **1** can be manipulated by the external environment, such as by solvents and light, it could serve as a multi-stimulus-responsible ²⁰ fluorophore. The modulation of physical properties based on the control of molecular motility should be an interesting approach^{16,17} for the creation of advanced materials, and is currently under investigation in our laboratory.
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Notes and references

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[†] Electronic Supplementary Information (ESI) available: Experimental procedures and characterization data for new compounds. UV-Vis and the procedures appeared to a f 1 in CUCI and TUE. Plots of the processor experiment

- $_{35}$ fluorescence spectra of 1 in CHCl₃ and THF. Plots of fluorescence against 1-T. Calculated dimer structure of 1. UV-Vis spectrum of 5. $^1{\rm H}$ NMR spectra of 1 before and after photoirradiation. $^1{\rm H}$ NMR spectrum of 3. $^1{\rm H}$ and $^{13}{\rm C}$ NMR spectra of 5. See DOI: 10.1039/b000000x/
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