Tetrahedron Letters 54 (2013) 143–146

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Triethynylmethane: a molecular unit inducing excimer-like emission in aggregated states of hydrocarbon fluorophores

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A R T I C L E   I N F O

Article history:
Received 26 September 2012
Revised 19 October 2012
Accepted 22 October 2012
Available online 5 November 2012

Keywords:
Fluorescent
Triethynylmethane
Excimer emission
Pyrene

A B S T R A C T

We report the synthesis of triethynylmethane (TEM) derivatives substituted with fluorescent aromatic hydrocarbons and the fluorescence properties in dilute aqueous solution and in spin-coated film. Pyrene-tethered TEM derivatives showed excimer-like fluorescence in 80% water in THF and spin-coated film. UV and ^{1}H NMR analyses showed the aggregation of TEM derivatives. Phenanthrene-tethered TEM also showed excimer-like fluorescence in high water content in THF. These data showed that TEM is a novel molecular unit inducing excimer-like emission in the aggregated states of aromatic hydrocarbon fluorophores.

Pyrene is a typical aromatic hydrocarbon showing concentration dependent fluorescence and aggregation caused quenching (ACQ) in condensed states and emitting excimer fluorescence with much decreased quantum yield than that of monomer emission due to the tendency of π–π stacking of these planar molecules.[1–4] However, it has been described in literatures that pyrenes incorporated into the polymer material and other organized media in an aqueous environment often produced the excimer-like fluorescence due to the ground state aggregation of pyrenes.[5–17] In contrast to ACQ-fluorophores, molecules exhibiting a totally opposite phenomenon termed as aggregation induced emission (AIE) show only weak or a little fluorescence in a dilute solution but became highly fluorescent in the aggregated or solid states.[18–20] It was recently demonstrated that ACQ-fluorophores could be transformed into the AIE-active fluorophores by tethering to the AIE unit tetraphenylethene[21–24] and other molecular systems.[25–27] The success of transformation of ACQ-fluorophores into AIE-active fluorophores in addition to the fact that ground state aggregates of pyrenes sometime emit excimer-like emission prompted us to explore the auxiliary molecular units that can induce the excimer-like emission in the aggregation state of ACQ-fluorophores.

Toward this end, we were interested in a triethynylmethane (TEM) unit involving the sp^3-hybridized carbon center that fixes three ethynyl groups extruding from the quaternary carbon center at the non-planar orientation. (Fig. 1) Structural characteristics of TEM are as follows; (1) various aromatic chromophores could be

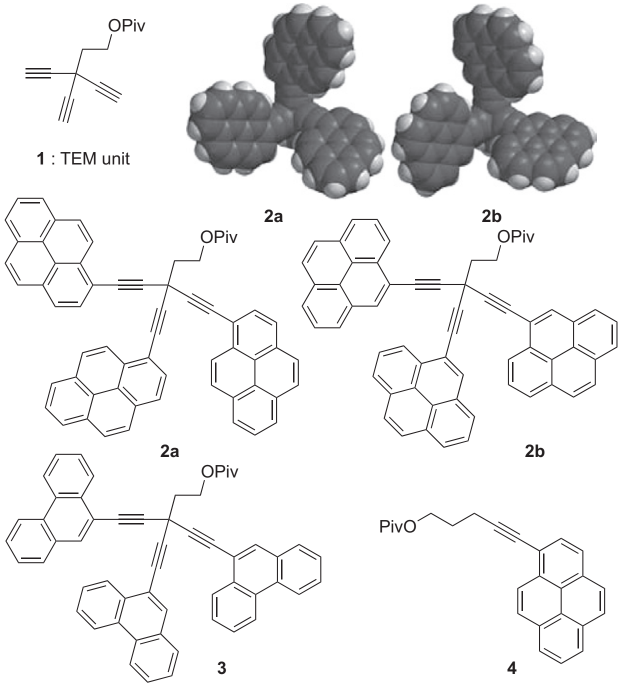

Figure 1. Chemical formulae of TEM unit **1**, TEMs tethered with 1-pyrene **2a**, 4-pyrene **2b**, and 4-phenanthrene **3**, and a reference pyrene monomer **4**. **2a** and **2b** were also shown by the space-filling model (top right, the pivaloyl group was omitted for clarity).

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0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2012.10.093

introduced into the terminal carbon of the ethynyl group by metal-catalyzed cross coupling, (2) due to the sp^3-hybridized carbon center, three aromatic chromophores are not on the same plane and have limited rotational freedom along the sp–sp carbon axis to allow little *intramolecular stacking*, (3) due to a concaved shape of TEM with three aromatic chromophores suggested by molecular modeling simulation, *intermolecular stacking* by hydrophobic interactions was anticipated. We here report that TEM is a novel molecular unit to which aromatic fluorescent hydrocarbons tethered produced excimer-like fluorescence in aggregated states with much higher quantum yield than that of excimer fluorescence. Since molecules that emit fluorescence at a different wavelength depending on the degree of molecular aggregation are potentially useful environment-sensitive ratiometric fluorescent sensors,[1,28–31] TEM unit may be useful for the novel design of environment-sensitive fluorescent sensors.

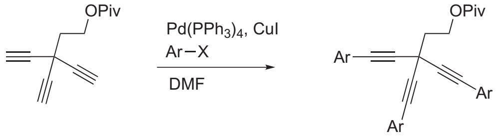
Due to the facile availability of triethynylmethanol, we first investigated the triethynylmethanol derivatives (Ar_3COH and Ar_3COR, where $R = CH_2CH_2OPiv$) substituted with pyrene and phenanthrene, but these molecules were found labile under photochemical conditions. Komatsu et al. have reported that triphenylethynylmethanol produced triphenylethynylmethyl carbocation under photoirradiation conditions.[32] The chemical instability of pyrene- and phenanthrene-substituted triethynlymethanol derivatives is most likely due to a facile formation of triarylethynylmethyl carbocation, suggesting the necessity of the quaternary carbon center for the chemically stable molecular unit. The TEM unit **1** we then investigated consisted of the sp^3-hybridized quaternary carbon center, and was synthesized from 3,3,3-tris(triethylsilylethynyl)propene,[33] of which synthetic application remained to be addressed. Hydroboration of the vinyl group and subsequent oxidative work-up followed by protection of the resulting primary alcohol as a pivalate provided TEM **1**. The pivalate is not essential but substantially decreased the handling difficulty caused by a low molecular weight of the unprotected alcohol.

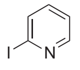
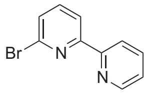
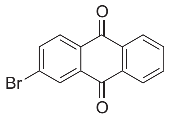
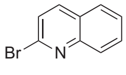
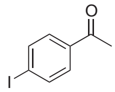
With the TEM unit **1** in hand, we first tethered the pyrene chromophore to the unit. Under the standard conditions, the coupling of **1** and 1-iodopyrene proceeded smoothly to give **2a** having three pyrene chromophores in 66% yield. Likewise, the coupling with 4-iodopyrene and 4-iodophenanthrene produced **2b** and **3** in 48% and 75% yields, respectively. Heterocycles having potential metal binding sites and aromatic molecules with electron withdrawing groups can be tethered to the TEM unit, demonstrating the availability of a variety of TEM derivatives with different chemical properties and functionalities (Table 1).

Having completed the synthesis of TEM derivatives with three aromatic chromophores, we then investigated the fluorescent properties of TEM possessing hydrocarbon fluorophores **2a**, **2b**, and **3**. In THF, the absorption maximum was observed at 366 nm. In a mixed solvent of THF and water, the absorption was found to decrease steadily as the water fraction increased, accompanied by the red shift of the absorption maximum by 6 nm and significant signal broadening. (Fig. 2a, For enlarged spectra, please see Fig. S1) An index P_A, the peak-to-valley intensity ratio obtained from the absorption intensity of the red-edge band (^1La) to that of the adjacent minimum at shorter wavelength was used for evaluating the association of pyrenes in the ground state,[34] and was 2.72 in THF and 1.27 in 80% water in THF. Responding to the absorption change, fluorescence spectra of **2a** were changed from its monomer emission to the excimer-like emission. (Fig. 2b) Thus, in THF solution, the fluorescence spectra of **2a** presented the typical spectra of the monomeric pyrene, with the (0,0) band at 385 nm. The peak intensity was first increased as the water fraction increased from 0% to 40%, and then decreased to the original level with the water fraction of 60%. Further increase of the water fraction to 80% resulted in a complete loss of the monomer emission and, instead, produced broad fluorescence centered at 502 nm, which resembled the emission from the pyrene excimer. The absolute quantum yield of excimer-like fluorescence reached as high as 0.27 in 80% water in THF. (Fig. 2c) The fluorescence change of **2a** solution (10 μM) from blue to greenish color depending on the water fraction in THF was clearly detected by naked eyes. (Fig. 2d) Excimer-like emission of **2a** was also clearly observed in the spin-coated film prepared from 10 mM toluene solution, whereas the spin-coated film of reference pyrene monomer **4** did not show any detectable fluorescence under the same conditions. (Fig. 2e) The fluorescence quantum yield of the **2a** film was 0.15 with spectra showing a peak top at 504 nm. (Fig. S2) To compare the excimer-like emission of **2a** in 80% water in THF, excimer fluorescence of **2a** was measured in 10 mM THF solution. The broad excimer emission of **2a** was observed at 493 nm accompanied by still intense monomer emission. (Fig. 2f, For non-normalized spectra, see Fig. S2c) The signal intensity of excimer emission in 10 mM THF was much weaker than that of excimer-like emission in 10 μM 80% water in THF.

Another pyrene derivative **2b** tethered to a TEM unit with pyrene substitution at the C4 position showed a broad excimer-like emission without monomer fluorescence at 493 nm in 80% water in THF. The UV spectra of **2b** also showed a significant peak broadening as the water fraction in THF increased. The P_A values changed from 1.83 in THF to 1.52 in 70% water in THF. In 80% water in THF (Fig. S3), the absorption spectrum of **2b** was too broad to identify the peaks for the P_A calculation. In separate experiments, we confirmed that reference compound **4** having only one ethynylpyrene

Table 1
Synthesis of TEM derivatives



Ar–X	Yield (%)	Ar–X	Yield (%)	Ar–X	Yield (%)
	74		51		37
	79		63		

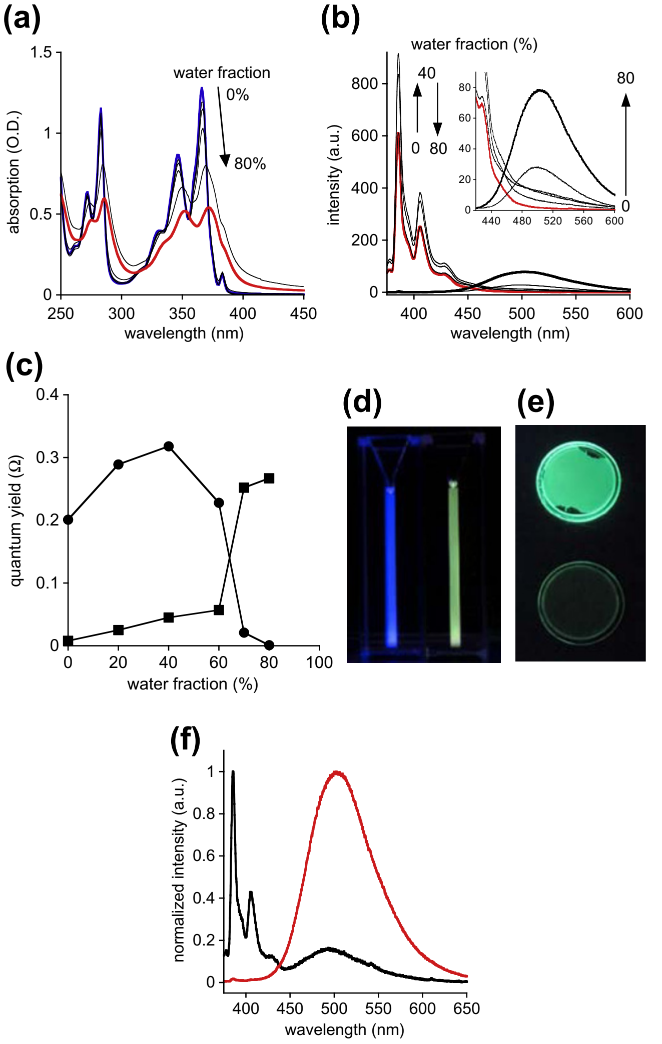
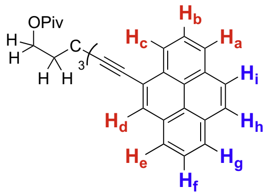


Figure 2. (a) UV–Vis spectra of **2a** (10 μM) in THF with the water fraction of 0%, 20%, 40%, 60%, 70%, and 80%. (b) Fluorescence spectra of **2a** in THF with the water fraction of 0%, 20%, 40%, 60%, 70%, and 80%. The excitation wavelength for fluorescence measurements was 366 nm. Inset: expanded spectra in the region of excimer-like emission. (c) The plots of quantum yield of **2a** in different water fractions in THF for monomer emission (calculated from 380–470 nm) (filled circle) and for excimer-like emission (calculated from 410–650 nm) (filled square). (d) A captured image of fluorescence change of **2a** (10 μM) in THF (left) and in 80% water in THF (right). (e) Fluorescence image of spin-coated films of 10 mM toluene solution of **2a** (top) and **4** (bottom). (f) Normalized fluorescence spectra of **2a** in 10 mM THF (black) and 10 μM in 80% water in THF (red).



	THF-d_8 / D_2O			
	100/0	50/50	30/70	20/80
H_a	8.43	8.43	8.41	8.40
H_b	8.26	8.16	8.13	8.11
H_c	9.10	8.95	8.94	8.93
H_d	8.77	8.63	8.59	8.57
H_e	8.42	8.36	8.34	8.33
H_f	8.19	8.20	8.19	8.19
H_g	8.44	8.44	8.43	8.43
H_h	8.30*	8.29*	8.28*	8.28*
H_i	8.28*	8.29*	8.28*	8.28*

Figure 3. Chemical shifts (ppm) of hydrogens of **2b** (10 μM) in THF-d_8 and D_2O in different fractions. Hydrogens that exhibited apparent up-field shift were shown in red, whereas other aromatic hydrogens were shown in blue. *These hydrogens were not identified.

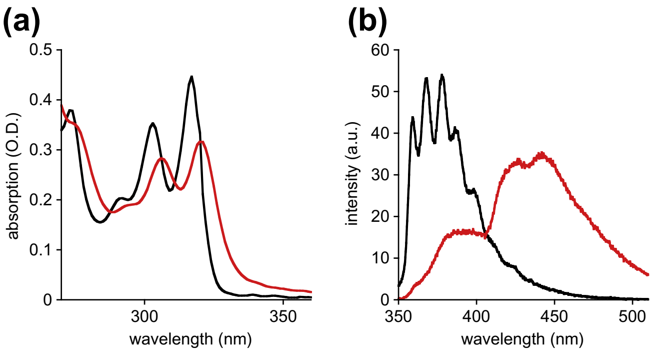


Figure 4. (a) UV–Vis and (b) fluorescence spectra of **3** (10 μM) in THF (black) and 80% water in THF (red).

unit did not show excimer-like fluorescence in 10 μM THF solution when the water fraction in THF was increased to 80%.

The absorption changes of **2a** and **2b** accompanied by the emission of excimer-like fluorescence in high water fraction in THF indicated the aggregation of these pyrene derivatives tethered to the TEM unit at a low concentration. To gain any insight into the aggregation of the pyrene-tethered TEM derivatives, ^1H NMR spectra of **2b** (10 μM) were measured in THF-d_8 with different D_2O fractions. (Fig. 3 and Fig. S4) As the D_2O fraction increased, an apparent up-field shift of the signals was observed for H_a, H_b, H_c, H_d, and H_e. Other four aromatic hydrogens H_f, H_g, H_i, and H_j showed a small up-field shift. The hydrogens showing apparent up-field shift were located on the molecular edge proximal to the TEM center, whereas the other four hydrogens are in the opposite edge. Since the intramolecular stacking of pyrene moieties in **2b** is not conceivable due to the restricted conformational freedom of pyrene moiety, the aggregation inducing the absorption, fluorescence, and ^1H NMR changes is most likely due to the intermolecular stacking of these pyrene-tethered TEM derivatives.

To know if the TEM unit could induce the emission of excimer-like fluorescence of other aromatic hydrocarbons in the aggregated state, 4-phenanthrene was introduced to the TEM unit, because excimer fluorescence was not observed for phenanthrene in solution at room temperature but does for phenanthrenophane, where two phenanthrene rings were fixed rigidly by covalent linkages.[35,36] Upon increasing the water fraction of the THF solution of **3** (10 μM), red shifting of the absorption maximum, decrease of P_A value, and signal broadening were observed (Fig. 4), suggesting the aggregation of **3** even in a dilute solution. The typical fluorescence of phenanthrene observed in THF disappeared in 80% water in THF, instead broad emission peaks centered at about 385, 425, and 440 nm appeared. It is reported that the wavelength of excimer emission in phenanthrenophane was sensitively dependent on the orientation of two phenanthrene rings and a degree of π-π stacking, ranging from 380 to 430 nm.[36] The observed broad peaks in fluorescent spectra of **3** in 80% water in THF are suggesting to involve different stacking orientations of phenanthrenes in the aggregation of **3**.

In conclusion, the hydrocarbon fluorophores tethered to TEM unit **1** aggregated even in a dilute THF solution of 10 μM concentration with high water content. The aggregates prepared in solution for pyrenes and phenanthrene and in spin-coated film of pyrene derivative **2a** emit excimer-like fluorescence. The excimer-like emission of phenanthrene chromophore could be also observed when the chromophore was tethered to the TEM unit. These results suggested that the TEM unit **1** is a novel molecular unit inducing excimer-like emission in aggregated states of hydrocarbon fluorophores.

Acknowledgments

We thank Professor Masahiko Yamaguchi of Tohoku University for kindly providing us detailed procedures for the synthesis of TEM precursor. We also appreciate the technical support for NMR measurements from the comprehensive analysis center of ISIR.

Supplementary data

Supplementary data (synthetic protocols of all compounds, a plot of fluorescent quantum yield of **2a** in different water fractions in THF, fluorescence spectra of **2a** film, UV, and Fluorescence Spectra of **2b** in different water fractions in THF, 1D, and 2D ^{1}H NMR of **2b**) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.10.093.

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