Highly Blue Luminescent Triazine−Amine Conjugated Oligomers

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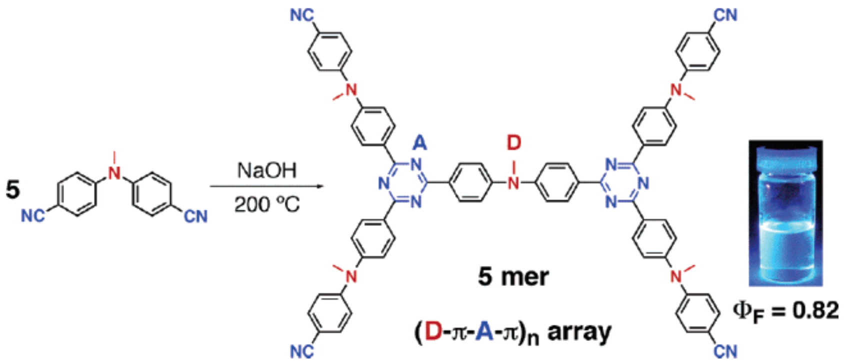

The novel synthetic strategy and optical properties of highly fluorescent, triazine−amine conjugated oligomers are described herein. Under basic conditions, aromatic dinitrile compounds, NC−C_6H_4−X−C_6H_4−CN (X = NMe, O, CH_2), underwent cyclic trimerization of the cyano groups at both ends to give a series of triazine-containing oligomers. The oligomers can be expressed as ($2n + 1$) mer, where n represents the number of triazine rings in the oligomer. The absorption maximum of an amine-conjugated trimer (X = NMe, $n = 1$) was outstandingly red-shifted as compared with those of the other trimers (X = CH_2, O). In acidic media, the amine-conjugated trimer showed two-step bathochromic shifts caused by protonation. The absorption maxima of the amine-conjugated ($2n + 1$) mers (X = NMe, $n = 1−4$) did not depend on n; instead, shoulder peaks appeared in the long-wavelength region when $n \geq 2$. The oligomers involving alternate conjugation of triazines and NMe groups through phenylene groups showed strong fluorescence in chloroform. In particular, the pentamer was the most efficient blue emitter ($\Phi_F = 0.82$). The other triazine-containing oligomers (X = CH_2, O) did not show fluorescence at all. Therefore, it is concluded that the emission properties are due to the strong electron-donating and accepting abilities of the NMe and triazine moieties, respectively.

Introduction

Electron donor (D)−electron acceptor (A) interactions play a fundamental role in organic chemistry. The reactivities and physical properties of organic compounds largely depend on the strength of the D−A interactions. Among a variety of electron-accepting functionalities, 1,3,5-triazine (hereafter simply "triazine") is a fascinating and interesting π-electron-deficient aromatic compound. Triazine possesses the largest nucleophilic susceptibility among various nitrogen-containing heteroaromatic six-membered ring compounds.[1] The π-electron deficiency of triazine is useful in organic synthesis, and 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) is a valuable reagent not only for synthesizing a lot of triazine derivatives but also as a coupling reagent in the formation of macrocyclic lactones[2] and β-lactams.[3] The π-electron-accepting ability of triazine remarkably affects optical properties. It was reported that 2,4,6-tris[*p*-(di-2-pyridylamino)phenyl]-1,3,5-triazine emitted a blue color both in solution and in the solid state, where the fluorescence quantum yield (Φ_F) in dichloromethane solution was high ($\Phi_F = 0.78$).[4] This feature is attributed to the chemical structure substituted by electron-donating aromatic amines at 2,4,6

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(1) Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V. In *Comprehensive Heterocyclic Chemistry II*; Boulton, A. J., Ed.; Pergamon: New York, 1996; Vol. 6, Chapter 6.12.

(2) Cossy, J.; Pete, J. P. *Tetrahedron Lett.* **1986**, *27*, 2369.

(3) Huang, H.; Wu, S. *Gaodeng Xuexiao Huaxue Xuebao* **1987**, *8*, 4341.

(4) Pang, J.; Tao, Ye.; Freiberg, S.; Yang, X.-P.; D'Iorio, M.; Wang, S. *J. Mater. Chem.* **2002**, *12*, 206.

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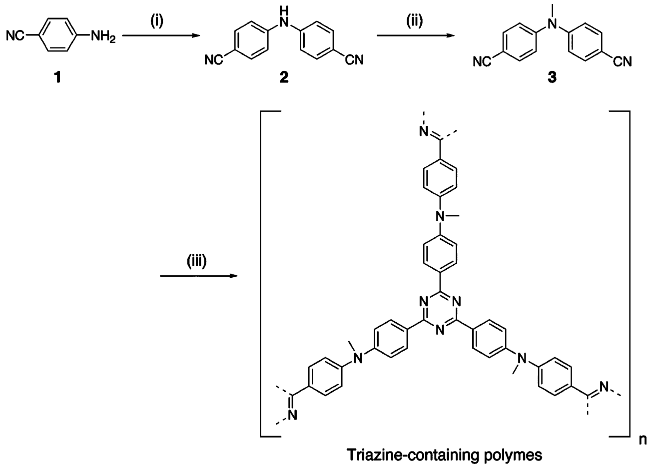
positions, resulting in efficient electron transfer in the compound. The connection of amine (D) and triazine (A) by a π-conjugated bridge to form the D−π−A structure is considered to be an effective way to improve nonlinear optical properties.[5] From the viewpoint of materials chemistry, triazine is known to serve as a core of liquid crystals.[6−9] In this way, triazine is important in many applications.[10−14]

The method for synthesizing triazine derivatives can be classified into two ways: one is, as mentioned above, nucleophilic displacement of chlorine atoms, in a stepwise manner, from cyanuric chloride; the other is trimerization of nitriles. The latter is featured by the direct formation of an aromatic ring (triazine) and is a simple and efficient method for preparing symmetrical 2,4,6-trisubstituted 1,3,5-triazines.[1] Various methods have been developed for trimerization of nitriles.[15−23] It is readily suspected that, under similar conditions, dinitriles lead to triazine-containing polymers by repeating the trimerization of nitriles. Some papers have suggested the existence of triazine-containing polymers.[24−29] However, the characterization is only the confirmation of triazine rings by the IR spectrum, and there are no reports on the isolation of individual oligomers from polymer mixtures. Moreover, despite the strong electron-accepting ability of triazine moieties, the optical properties of triazine-containing oligomers have not been investigated at all. It is anticipated that fluorescent compounds with a high Φ_F value are obtained when electron-donating parts are incorporated into triazine-containing oligomers.

SCHEME 1. Synthesis of Triazine-Containing Polymers[a]



[a] Reagents and conditions: (i) p-fluorobenzonitrile, t-BuOK, DMSO, rt, 75%. (ii) CH_3I, K_2CO_3, DMF, 130 °C, 92%. (iii) NaOH, neat, 200 °C.

In the present study, we report a novel one-step preparation of triazine−amine conjugated oligomers, composed of alternatingly arranged D (amine) and A (triazine). The oligomers are obtained by trimerization of aromatic dinitriles and separated by chromatography. Then, the electronic and optical properties, including absorption and emission, as well as redox properties, are investigated by means of cyclic voltammetry and UV−vis and fluorescence spectroscopy. Their properties will be discussed, noting the structures of oligomers.

Results and Discussion

Synthesis. The simplest amine derivative in aromatic dinitriles is 4,4′-dicyanodiphenylamine **2**. As shown in Scheme 1, dinitrile **2** was readily prepared by the reaction of p-aminobenzonitrile (**1**) with p-fluorobenzonitrile in a moderate yield (75%).[30] The melting point of **2** was high (258 °C) despite a relatively small molecular weight, and the solubility was very low in common organic solvents except for aprotic polar ones. These properties are undesirable for the synthesis of triazine-containing polymers because a high-concentration condition is indispensable for the synthesis of triazine derivatives via trimerization of aromatic nitriles. The best method is to carry out the trimerization in the molten state at high temperature without solvents. Moreover, good solubility is required for triazine-containing oligomers to separate them into their components. To remove these drawbacks, dinitrile **2** was converted to N-methylamino derivative **3** by heating it with methyl iodide and K_2CO_3 in DMF. In contrast to compound **2**, dinitrile **3** was readily soluble in common organic solvents such as chloroform, and the melting point of **3** (156 °C) was considerably lower than that of **2**. Therefore, dinitrile **3** was chosen as a suitable precursor for the triazine−amine conjugated polymers.

The trimerization of aromatic dinitrile **3** was conducted in the presence of NaOH at 200 °C. To prevent **3** from hydrolyzing into the amide, the dinitrile **3**, NaOH, and

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(5) Meng, F.; Li, B.; Qian, S.; Chen, K.; Tian, H. *Chem. Lett.* **2004**, *33*, 470.

(6) Lee, C.-H.; Yamamoto, T. *Tetrahedron Lett.* **2001**, *42*, 3993.

(7) Lee, C.-H.; Yamamoto, T. *Mol. Cryst. Liq. Cryst.* **2002**, *378*, 13.

(8) Lee, C.-H.; Yamamoto, T. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 615.

(9) Lee, S. J.; Chang, J. Y. *Tetrahedron Lett.* **2003**, *44*, 7493.

(10) Nishimura, N.; Kato, A.; Maeba, I. *Carbohydr. Res.* **2001**, *331*, 77.

(11) Burkhard, K.; Steward, M.; Barret, M. P.; Brun, R.; Gilbert, I. H. *J. Med. Chem.* **2001**, *44*, 3440.

(12) Iino, Y.; Karakida, T.; Sugamata, N.; Andoh, T.; Takei, H.; Takahashi, M.; Yaguchi, S.; Matsumo, Y.; Takehara, M.; Sakato, M.; Kawashina, S.; Morishita, Y. *Anticancer Res.* **1998**, *18*, 171.

(13) Paul, P.; Tyagi, B.; Bilakhiya, A. K.; Dastidar, P.; Suresh, E. *Inorg. Chem.* **2000**, *39*, 14.

(14) Santra, P. K.; Sagar, P. *J. Mol. Catal. A: Chem.* **2003**, *197*, 37.

(15) Bengelsdorf, I. S. *J. Am. Chem. Soc.* **1958**, *80*, 1442.

(16) Matsumoto, K.; Sera, A. *Synthesis* **1985**, 1.

(17) Martin, D.; Bauer, M. *Russ. Chem. Rev.* **1978**, *47*, 975.

(18) Anderson, H. L.; Anderson, S.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2231.

(19) Forsberg, J. H.; Spaziano, V. T.; Klump, S. P.; Sanders, K. M. *J. Heterocycl. Chem.* **1998**, *25*, 767.

(20) Xu, F.; Sun, J.-H.; Yan, B.-H.; Shen, Q. *Synth. Commun.* **2000**, *30*, 1017.

(21) Xu, F.; Zhu, X.-H.; Shen, Q.; Lun, J.; Li, J.-Q. *Chin. J. Chem.* **2002**, *20*, 1334.

(22) Deng, Z.; Qiu, W.; Li, W.; Li, Y. *Chin. Sci. Bull.* **2004**, *49*, 127.

(23) Antonio, H.; Roberto, M.-A.; Pedro, R.; Mourad, C.; Rachid, C. *Synthesis* **2004**, 503.

(24) William, G. T.; San, R. Polymerization of Aromatic Nitriles. U.S. Patent 3,060,179, 1962.

(25) Bartlett, R. K.; O'Neil, G.; Savill, N. G.; Thomas, S. L. S.; Wall, W. F. *Br. Polym. J.* **1970**, *2*, 225.

(26) Herward, A. V.; Oakdale, T. Poly(arylene *s*-triazines). U.S. Patent 3,654,192, 1972.

(27) Klaus, H. G.; Gillette, N. J. Polymerization of Aromatic Nitriles in 2-Pyrrolidinone as Solvent and Catalyst at Elevated Temperatures. U.S. Patent 3,678,049, 1972.

(28) Gordon, H. M. Polymerization of Aromatic Nitriles. U. S. Patent 3,775,380, 1973.

(29) Huang, Z.; Wang, L.; Wang, J. In *Proceedings of China-U. S. Bilateral Symposium on Polymer Chemistry and Physics*; Beijing, China, Oct 5−10, 1979; Science Press: Beijing, 1981; p 358.

(30) John, H. G. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1331.

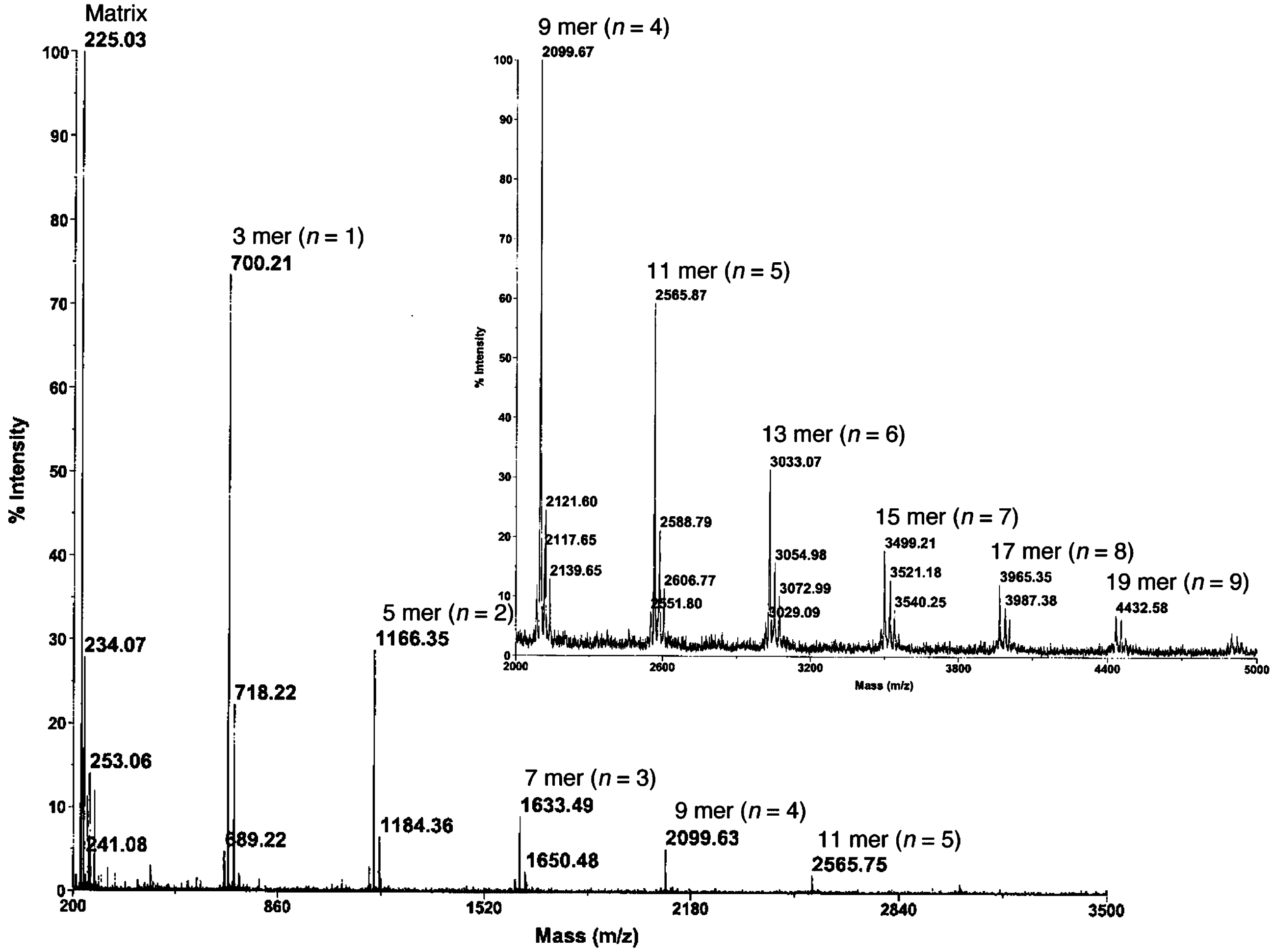

FIGURE 1. MALDI-TOF mass spectra of the obtained triazine−amine conjugated polymers.

the reaction vessel were sufficiently dried under vacuum before use. Other bases (nucleophiles), such as sodium methoxide ($NaOCH_3$), were less effective than NaOH. The acidic condition using compounds such as trifluoromethanesulfonic acid (CF_3SO_3H) and zinc chloride ($ZnCl_2$) is known as another effective way for preparing triazine-containing compounds.[26−29] However, such conditions were not appropriate in the preparation of the triazine−amine conjugated polymers.

The obtained reaction mixtures (triazine-containing polymers) were partially soluble only in chloroform and dichloromethane and were subjected to MALDI-TOF mass spectroscopy to clarify the degree of the trimerization (Figure 1). Prominent peaks appeared at regular intervals, whose intensities gradually decreased with enlarging structure. The triazine-containing oligomer can be expressed as "($2n$ + 1) mer" (n = 1 (trimer), 2 (pentamer), 3 (heptamer), ...), where n represents the number of triazine rings in the oligomer. The existence of 19 mer ($n = 9$) was confirmed from the spectrum. In each triazine formation process, a cyano group in the $2n + 1$ mer reacts with two monomers, giving $2(n + 1) + 1$ mer. Thus, the oligomer always involves an odd number of monomer units. From $2n + 1$ mer, $2(n + 1)$ mer with an even number of monomer units can be formed only if two cyano groups in the $2n + 1$ mer simultaneously participate in triazine formation with a cyano group of a monomer. However, such oligomers were not detected, indicating that the pseudointramolecular reaction did not occur. In addition to the desired oligomer peaks, hydrated species, in which the terminal cyano groups were partly hydrolyzed to amide groups, were also detected. Formation of such byproducts with high polarity is responsible for poor solubility and inhibits further trimerization reaction. According to previous reports, triazine-containing polymers were insoluble in any organic solvent. Therefore all triazine-containing polymers prepared previously are supposed to have amide structures in parts at the terminal, resulting in insoluble solids.[31]

After separation and purification by column chromatography and gel permeation chromatography (GPC) employing chloroform as an eluent, a series of triazine-containing oligomers ($n = 1−4$) were isolated as yellow powders. GPC separation is a powerful method for triazine-containing oligomers because the oligomer sizes dramatically increase with the increasing number of triazine rings they possess. MALDI-TOF mass analysis verified the isolation and purity of the triazine-containing oligomers, whose structures are shown in Figure 2. Whereas no isomers exist for trimer **4**, pentamer **5**, and

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[31] Some papers said the IR spectra of triazine-containing polymers showed the disappearance of the nitrile absorption around 2220 cm^{-1}. This means that the terminal cyano groups were fully hydrolyzed to amide ones and that the trimerization of nitriles was stopped.

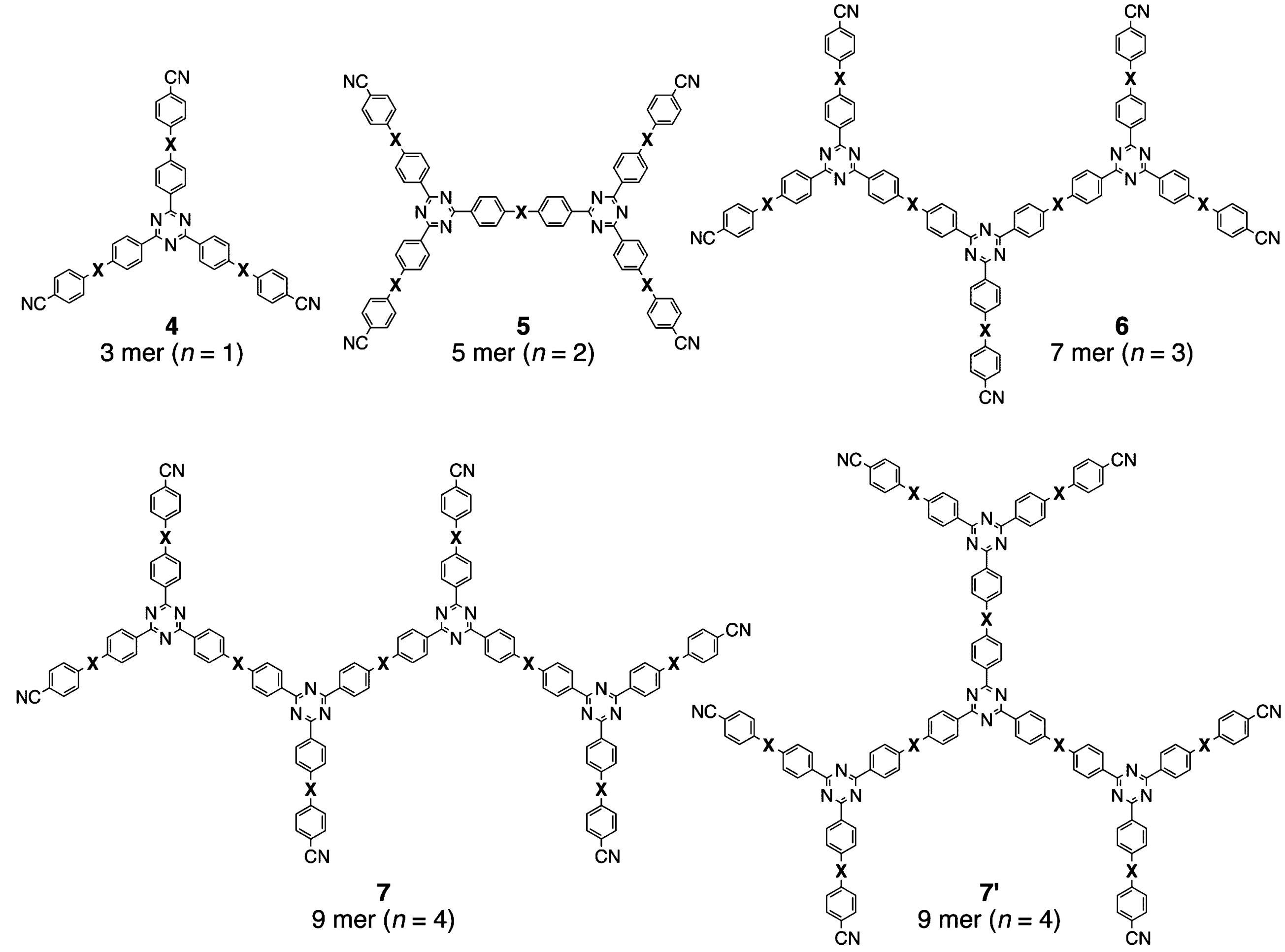

FIGURE 2. Triazine−amine conjugated oligomers (X = NMe).

heptamer **6**, there are two structural isomers for the nonamer (i.e., **7** and **7′**), which cannot be distinguished by MALDI-TOF mass spectroscopy. The isolated yields of trimer **4**, pentamer **5**, heptamer **6**, and nonamer **7** or **7′** were 11%, 6.7%, 3.6%, and 2.8%, respectively. The low yields of the triazine-containing oligomers are ascribed to the large amount of unreacted monomer (**3**) and the formation of byproducts (triazine-containing oligomers with amide structures). Larger oligomers ($n \geq 5$) could not be isolated.

NMR Characterization. Both the electronic property and structural information are provided by ^{1}H NMR spectroscopic analysis (Figure 3a). Considerable downfield shifts of the aromatic protons adjacent to the triazine rings (8.7−8.8 ppm) were observed ($\Delta\delta = 1.2$ ppm for monomer **3**), which was attributed to the strong deshielding effect of the triazine ring. These protons provide useful information to identify each oligomer. The peak patterns are in good agreement with their symmetry: they were simple up to pentamer **5** but became complex in heptamer **6** and nonamer **7**. For the nonamer, five sets of partially overlapped doublet peaks (Figure 3b) were consistent with the structure of **7**, but not with the structure of **7′**, which should reveal only three sets of doublet peaks. In the triazine-containing oligomers isolated in this work, since the connection of the triazine rings in **4**−**7** are not branched, they can be drawn as the general formula shown in Figure 3c.

The N*Me* protons also provided structural information. For example, two methyls were observed for pentamer **5** at δ = 3.5 and 3.6 ppm in a 4:1 ratio: the former is substituted by cyanophenyl, while the latter is not. For heptamer **6** and nonamer **7**, the ratio was 5:2 and 6:3 (2:1), respectively, consistent with the ratio of the peripheral (cyanophenyl-subsutituted) amino groups to the other ones.

Electronic Absorption Spectra. The most intriguing feature of oligomers **4**−**7** is the triazine (acceptor)−amine (donor) conjugation through phenylene groups. The optical absorption spectrum of trimer **4** in $CHCl_3$ is shown in Figure 4a. For comparison, the spectra of the other trimers, **4′** (X = O) and **4″** (X = CH_2), are also shown. The absorption maximum (λ_{max}) of **4** (387 nm) was outstandingly red-shifted as compared with those of the other trimers **4′** and **4″** (299 and 287 nm, respectively). This red shift is not due to the conjugation of the amino nitrogen with the adjacent phenylene rings alone because the conjugation of **4** is the same as that of **4′**, where the ether oxygen is conjugated with the phenylene rings. The triazine ring and the adjacent rings are almost coplanar,[32] resulting in the efficient conjugation. Therefore,

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[32] The coplanarity of one triazine ring and three directly attached benzene rings can be estimated by the crystal structure of 2,4,6-triphenyltriazine-based compounds. See: (a) Hayami, S.; Inoue, K. *Chem. Lett.* **1999**, *28*, 545. (b) Kusukawa, T.; Fujita, M. *J. Am. Chem. Soc.* **2002**, *124*, 13576.

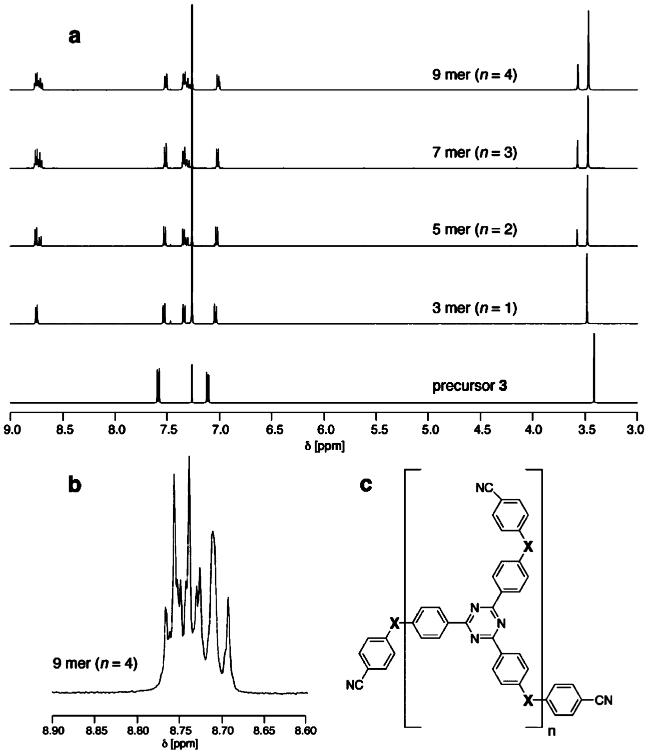

FIGURE 3. (a) ^{1}H NMR spectra of precursor **3** and triazine−amine conjugated oligomers. (b) ^{1}H NMR spectra of nonamer (n = 4) in the low field (8.6−8.9 ppm). (c) General formula of the obtained triazine-containing oligomers (X = NMe).

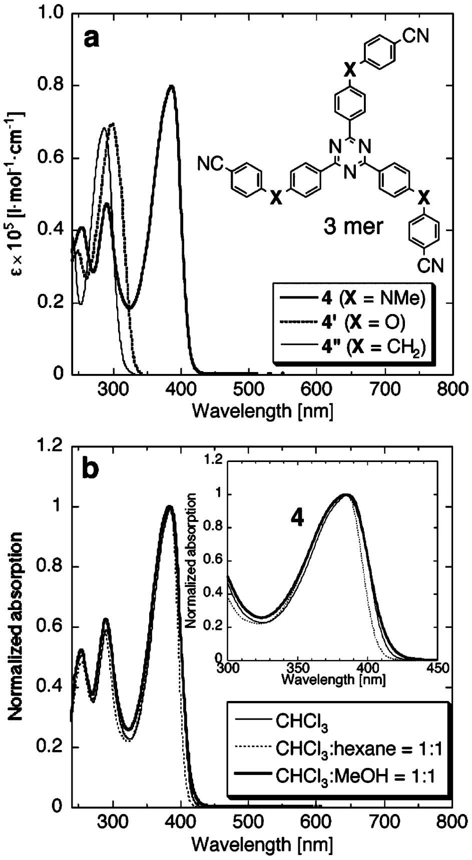

FIGURE 4. UV−vis absorption spectra of (a) trimer (X = NMe, O, CH$_2$) in CHCl$_3$ and (b) trimer **4** (X = NMe) in other solvent systems. The inset shows the magnification of the absorption spectra of **4**.

TABLE 1. Absorption Property of Trimer 4 in Various Solvent Systems

solvent	λ_{max} [nm]
CHCl$_3$	255, 291, 387
CHCl$_3$/cyclohexane = 1:1	255, 288, 385
CHCl$_3$/hexane = 1:1	254, 288, 384
CHCl$_3$/CCl$_4$ = 1:1	290, 387
CHCl$_3$/toluene = 1:1	290, 387
CHCl$_3$/dioxane = 1:1	254, 289, 386
CHCl$_3$/ethyl acetate = 1:1	289, 385
CHCl$_3$/CH$_3$CN = 1:1	254, 290, 385
CHCl$_3$/MeOH = 1:1	254, 291, 385

the maximum absorption band in **4** can be assigned as an intramolecular charge transfer (ICT) band from the amino nitrogen (donor) to the triazine/cyanophenyl moiety (acceptor).[1] Unlike ordinary CT absorption, this ICT absorption was very strong. This is attributed to the interactions between the strong electron-donating and accepting moieties.

The optical absorption spectra of trimer **4** in various solvent systems are shown in Figure 4b. Trimer **4** is soluble only in CHCl$_3$ and CH$_2$Cl$_2$. Therefore, various solvents were examined as 1:1 mixed solvents with CHCl$_3$. The absorption maxima are collected in Table 1. In a polar solvent system (CHCl$_3$/MeOH = 1:1), the ICT absorption band was broadened a little relative to that only in CHCl$_3$. However, the absorption maxima varied only slightly. The same phenomenon was observed in the other polar solvent system (CHCl$_3$/CH$_3$CN = 1:1). On the other hand, in a nonpolar solvent system (CHCl$_3$/hexane = 1:1), the ICT absorption band was slightly blue-shifted. These results suggest that the electronic and structural nature of the ground and Franck−Condon (FC) excited states responsible for ICT absorption do not vary much with solvent polarity. This tendency is quite similar to that observed in the *N*,*N*-dimethylamino (D) and cyano (A) substituted tetrahydropyrene derivative.[33]

The addition of trifluoroacetic acid (TFA) to a CHCl$_3$ solution of trimer **4** led to significant two-step bathochromic shifts caused by protonation (Figure 5). The intensity of the first ICT band (387 nm) decreased and that of the second ICT band (~480 nm) increased with increasing concentration of TFA, and the color of the solution changed from colorless to yellow-orange. Further addition of TFA caused a decrease of the second ICT band accompanied by red-shifting and the appearance of a third ICT band (577 nm). The solution color finally turned wine-red.

To elucidate the mechanism of the solvatochromic (acidochromic) behavior, pH-dependent ^{1}H NMR spectra were studied (Figure 6).[34] In the yellow-orange solution, the aromatic protons adjacent to the triazine ring were upfield-shifted, while those adjacent to cyano groups were downfield-shifted. The former is attributed to the decrease in the deshielding effect of the triazine ring by the protonation on the triazine, and the latter is at-

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(33) Sumalekshmy, S.; Gopidas, K. R. *J. Phys. Chem. B* **2004**, *108*, 3705.

(34) Meier, H.; Holst, H. C.; Oehlhof, A. *Eur. J. Org. Chem.* **2003**, *21*, 4173.

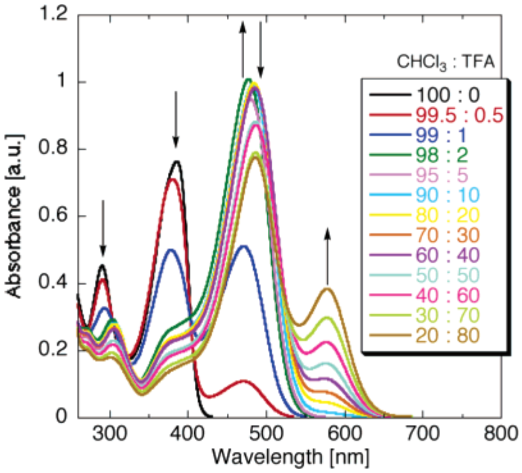


FIGURE 5. Change in the UV–vis absorption spectra of trimer **4** in $CHCl_3$ with varying concentrations of TFA. Concentration: 1.0×10^{-4} M solution of **4** in $CHCl_3$/TFA mixed solution (1 mm cell, 0.4 mL).

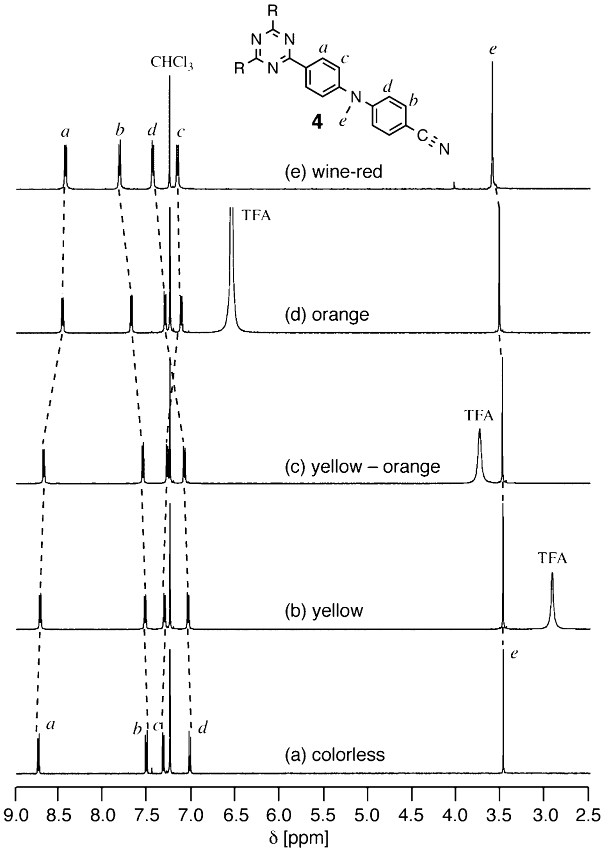


FIGURE 6. ^{1}H NMR spectra of trimer **4** in (a) $CDCl_3$, (b) $CDCl_3$/TFA = 100:0.2, (c) $CDCl_3$/TFA = 100:0.4, (d) $CDCl_3$/TFA = 100:1, and (e) $CDCl_3$/TFA = 100:100. Concentration: 2.4×10^{-3} M solution of **4** in $CDCl_3$/TFA mixed solution (0.6 mL).

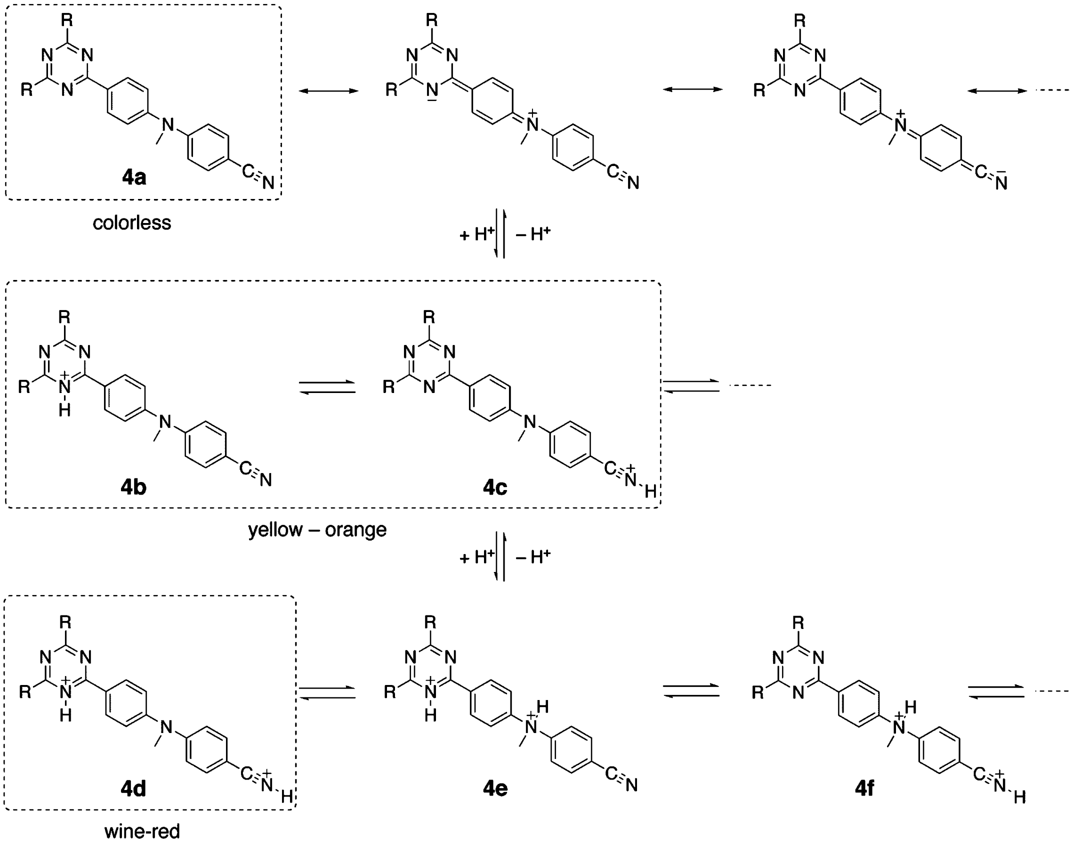
tributed to the decrease in the electron density of the cyanophenyl moiety by the protonation on the cyano group. Scheme 2 shows the mechanism of the protonation of trimer **4**. The proton exchanges among the existing species are rapid on the NMR time scale, and the spectra were averaged. The protonation on a triazine ring or a cyano group increases the degree of their electron-accepting properties. Therefore, the second ICT appeared in the long-wavelength region. The peak of the N*Me* protons did not change in the yellow-orange solution. This suggests that the protonation on the amino nitrogen does not take place in this step. It is impossible to determine whether **4b** or **4c** is the dominant species in the yellow-orange solution. With increasing concentration of TFA, both a triazine ring and a cyano group were protonated, enhancing the A–D–A character. The third ICT band and the resulting wine-red solution are responsible for the species **4d**. The aromatic protons adjacent to the cyano groups are considerably downfield-shifted, while those adjacent to the triazine ring were almost unaffected. This means that the triazine ring is more easily protonated than the cyano group. In the wine-red solution, the peak of the N*Me* protons was slightly downfield-shifted because of the protonation on the amino nitrogen. The protonation on the amino nitrogen reduces its electron-donating property and disrupts the D–A push–pull effect. Therefore, the ICT bands are expected to disappear. However, the intensity of the third ICT band increased with increasing concentration of TFA. This means that **4e** and **4f** are minor species and hardly contribute to the proton exchange.

Figure 7 shows the optical absorption spectra of **4**–**7**. The absorption maxima of the ICT band did not change with enlarging structures, suggesting that the π-electron conjugation was not extended all over the structure and the ICT was very strong. A shoulder peak appeared in the long-wavelength region when $n \geq 2$, whose intensity increased with increasing n number (Figure 7, inset). These shoulder peaks are supposed to be another ICT band. Probably, the primary ICT comes from peripheral $NC-C_6H_4-NMe-C_6H_4-$triazine segments (A) while the secondary ICT (shoulder) comes from internal triazine$-C_6H_4-NMe-C_6H_4-$triazine segments (B). Both ends of segments A and B consist of electron-accepting parts (triazine ring/cyano group). Trimer **4** is composed of only segment A, while pentamer **5**, heptamer **6**, and nonamer **7** are composed of segments A and B (Table 2). The ratio of B to A in the triazine–amine conjugated oligomers increases with enlarging structures. Therefore, it is concluded that segments A and B contribute to the primary and secondary ICT, respectively.

Electrochemical Properties. To examine the electrochemical properties of the triazine–amine conjugated oligomers, cyclic voltammetry (CV) experiments were carried out in CH_2Cl_2 solution at room temperature using Bu_4NPF_6 as the supporting electrolyte (Figure 8). All oligomers showed quasi-reversible oxidation peaks, and the results are summarized in Table 3. The first oxidation wave was almost overlapped with the second one in all oligomers, and the anodic and cathodic peaks were determined by separating two peaks. Judging from the fact that the second oxidation wave is close to the first one, the sequential removal of electrons from the arylamino groups occurred in triazine–amine conjugated oligomers.

Oligomers **5**–**7** were oxidized at a lower potential than trimer **4**, and the first arylamine oxidation potential was not essentially affected by the sizes of the oligomers. These results are in good agreement with the observation in the absorption spectra and suggest that, upon the incorporation of segment B into the triazine–amine

SCHEME 2. Mechanism of the Protonation of Trimer 4 in $CHCl_3$/TFA Mixed Solution[a]



[a] R represents the three equal arms of **4**.

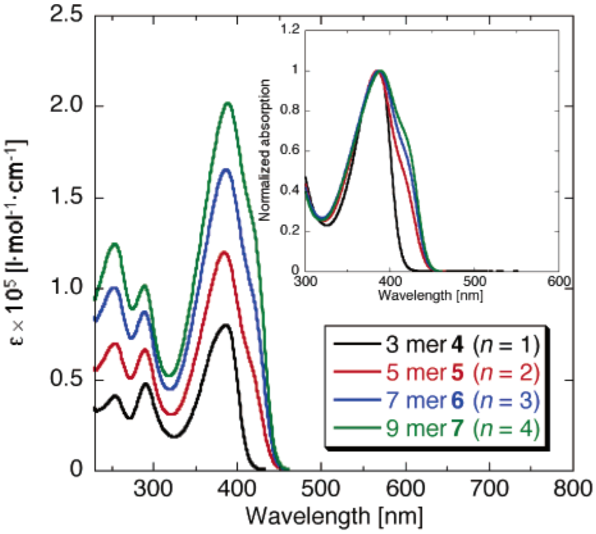
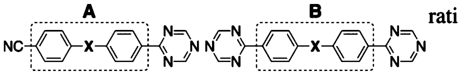


FIGURE 7. UV−vis absorption spectra of triazine−amine conjugated oligomers **4**−**7** in $CHCl_3$. The inset is the normalized absorption spectra of oligomers **4**−**7**.

TABLE 2. Number of Segments A and B in Triazine−Amine Conjugated Oligomers (X = NMe)

Oligomer	number of segments A 	 B	ratio **B/A**
4 (*n* = 1)	3	0	0
5 (*n* = 2)	4	1	0.25
6 (*n* = 3)	5	2	0.4
7 (*n* = 4)	6	3	0.5

conjugated oligomers, the HOMO level of the ICT state in the oligomers is raised to cause the secondary ICT, while the HOMO levels of the oligomers after the pentamer are almost the same. The reductive potentials of the oligomers are out of the window of the electrochemical transparency of CH_2Cl_2, and the oligomers are soluble only in CH_2Cl_2 and $CHCl_3$. Therefore, it is impossible to experimentally determine the LUMO level and the electrochemical HOMO−LUMO gap for the oligomers. It is suggested that π-electron conjugations are practically disrupted at the amine nitrogen atoms in the oligomers, and the number of electrons participating in the ICT electronic transitions increases.

Fluorescence Spectra. Triazine−amine conjugated oligomers are bright blue emitters in $CHCl_3$, and the emission bands are fairly broad with tailing. Similarly to the UV−vis spectra, the difference in the optical properties between trimer **4** and the other oligomers was observed in the fluorescence spectra. As shown in Figure 9, the λ_{max} value was red-shifted as the oligomer structure was enlarged from trimer **4** to pentamer **5**. However, λ_{max} and the spectral features of the oligomers after the pentamer were almost the same. These results are consistent with the absorption spectra. The oligomers after the pentamer have a secondary ICT band in the long-wavelength region, and the positions of this ICT band were not changed with enlarging the oligomer

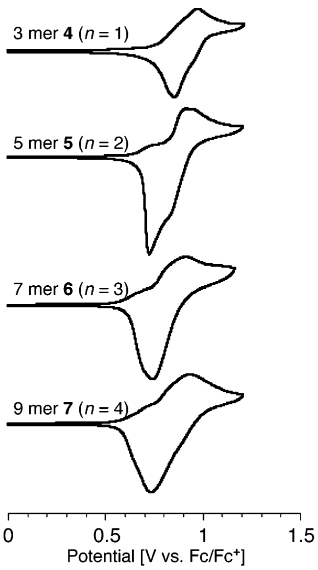


FIGURE 8. Cyclic voltammograms of triazine–amine conjugated oligomers.

TABLE 3. Electrochemical Properties of Triazine–Amine Conjugated Oligomers

oligomer	$E_{1/2}^{ox}$ [V vs Fc/Fc$^+$]^a
4 ($n = 1$)	0.89, 0.96
5 ($n = 2$)	0.75, 0.87
6 ($n = 3$)	0.74, 0.89
7 ($n = 4$)	0.74, 0.91

^{a} CH_2Cl_2, 0.1 M Bu_4NPF_6, 100 mV·s^{-1}. Ferrocence (Fc) was used as an external standard.

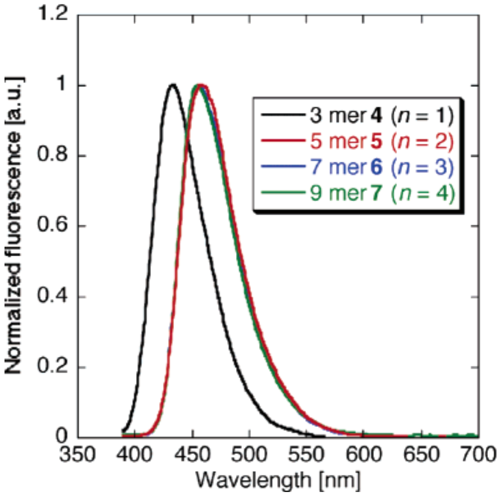


FIGURE 9. Normalized fluorescence spectra of triazine–amine conjugated oligomers **4**–**7** in $CHCl_3$. Excitation wavelength is 385 nm for each oligomer.

structure. Therefore, it is concluded that the λ_{max} values of the fluorescence spectra are related to the ICT bands.

The fluorescence spectra were sensitive to solvent polarity. The fluorescence intensities of trimer **4** and pentamer **5** at the band maxima showed a dramatic decrease, accompanied by a considerable red shift, on successive addition of MeOH (0 to 50% v/v) to $CHCl_3$ solutions of trimer **4** (Figure 10a) and pentamer **5** (Figure 10b). Even 1% v/v TFA strongly quenched the fluorescence of the oligomers, and the fluorescence disappeared in 10% v/v TFA solution. The fluorescence band maxima are collected in Table 4. The solvatochromic shifts of the fluorescence spectra are much larger than those of the absorption spectra, suggesting that the interaction between the oligomers and the solvents affects the deactivation of the ICT excited states of the oligomers. It is known that fluorescence quenching of the initially planar FC excited state involves an intramolecular twist which places the donor D and acceptor A moieties of the molecule out of mutual conjugation.[35–38] This leads to a further enhancement of the electronic charge separation to generate a twisted intramolecular charge transfer (TICT), a biradicaloid zwitterionic excited state, $[D^{+\bullet}–A^{-\bullet}]$.[35] More polar solvents prefer an orthogonality of the donor and acceptor moieties in the emitting species of molecules,[36] and the TICT state itself exhibits a week fluorescence strongly red-shifted with respect to the fluorescence of the precursor ICT state.[38] The above statements apply to our experimental results. Therefore, it is deduced that the rotations of the phenyl carbon–amino nitrogen bonds in the ICT excited states of the oligomers have been promoted with the increasing solvent polarity, resulting in there being TICT states and decreasing fluorescence intensities.

The fluorescence quantum yields (Φ_F) for trimer **4**, pentamer **5**, heptamer **6**, and nonamer **7** in $CHCl_3$ solution were 0.66, 0.82, 0.66, and 0.60, respectively. Triazine–amine conjugated oligomers **4**–**7** have the high Φ_F values, and pentamer **5** was the most efficient emitter among them. While the trimer contains only segment A, the pentamer involves both segments A and B. Presumably, segment B, in which the NMe group is put between two triazines, is responsible for the high Φ_F value. Despite having segment B in the structures, the Φ_F values for the heptamer **6** and nonamer **7** were lower than that for the pentamer **5**. When the structure of the triazine-containing oligomers is enlarged, the conformational freedom increases and the number of cyano groups also increases. The rotations of the bonds and CN stretching vibration are considered to increase radiationless transition to the ground state, resulting in low Φ_F. Thus, the Φ_F value of 0.82 in pentamer **5** was decreased to 0.66 and 0.60 as the structure of the oligomer was enlarged. Therefore, it is concluded that pentamer **5** is the best blue emitter among the triazine–amine conjugated oligomers. The optical properties of **4**–**7** are summarized in Table 5.

The other triazine-containing oligomers (X = CH_2, O) did not show fluorescence at all. Judging from the above results, the conjugation of the triazine and amine moieties is indispensable for the high Φ_F value.

Conclusion

In summary, a series of triazine-containing oligomers were synthesized via trimerization of precursor aromatic dinitriles. The oligomers with the combination of amine

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[35] Cowley, D. J.; Pasha, I. *J. Chem. Soc., Perkin Trans. 2* **1981**, *6*, 918.

[36] Cowley, D. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, *2*, 281.

[37] Retting, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.

[38] Cowley, D. J.; O'Kane, E.; Todd, R. S. J. *J. Chem. Soc., Perkin Trans. 2* **1991**, *10*, 1495.

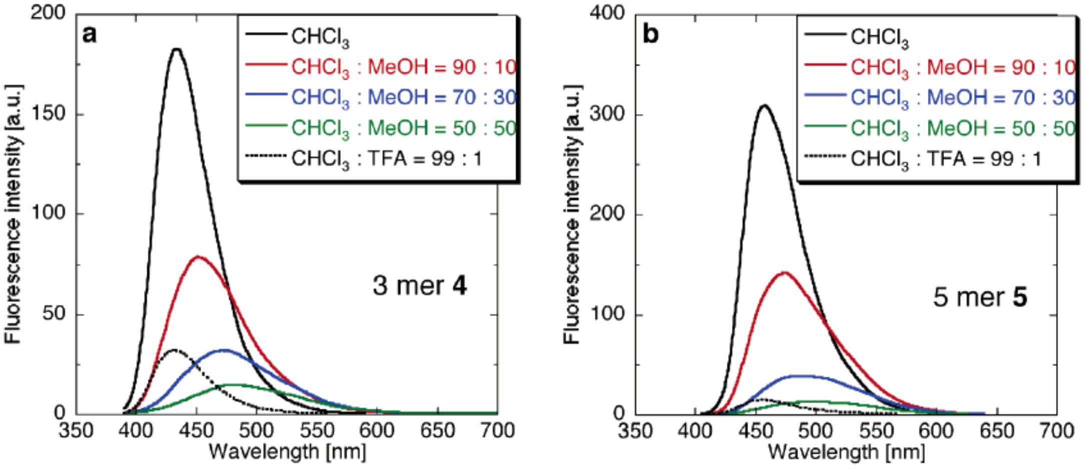

FIGURE 10. Changes in the fluorescence spectra of trimer **4** (a) and pentamer **5** (b) in $CHCl_3$/MeOH (TFA) solvent systems. Concentration of **4** or **5**: 2.5 × 10^{-6} M in $CHCl_3$/MeOH (TFA).

TABLE 4. Variation of the Fluorescence Band Position of Trimer 4 and Pentamer 5 in $CHCl_3$/MeOH (TFA) Solvent Systems

solvent	λ_{em} [nm][a] 4 ($n = 1$)	λ_{em} [nm][a] 5 ($n = 2$)
$CHCl_3$	434	459
$CHCl_3$/MeOH = 90:10	452	475
$CHCl_3$/MeOH = 70:30	472	488
$CHCl_3$/MeOH = 50:50	483	496
$CHCl_3$/TFA = 99:1	433	457
$CHCl_3$/TFA = 90:10[b]	ND	ND

[a] Excitation wavelength is 385 nm. [b] Fluorescence was not detected under these conditions.

TABLE 5. Optical Properties of Triazine−Amine Conjugated Oligomers in $CHCl_3$ at Ambient Temperature

oligomer	λ_{abs} [nm] (ϵ, 10^5 $M^{-1}\cdot cm^{-1}$)	λ_{em} [nm][a]	Φ_F[b]
4 ($n = 1$)	255 (0.407), 291 (0.472), 387 (0.798)	434	0.66
5 ($n = 2$)	255 (0.696), 291 (0.662), 385 (1.20)	459	0.82
6 ($n = 3$)	253 (1.00), 290 (0.872), 387 (1.65)	456	0.66
7 ($n = 4$)	255 (1.24), 290 (1.01), 389 (2.02)	456	0.60

[a] Excitation wavelength is 385 nm. [b] Quinine sulfate was used as a standard in estimation of fluorescent quantum yields (Φ_F = 0.546).

and triazine moieties have a $(D-\pi-A-\pi)_n$ array. Because of this unique electronic array, strong ICT was confirmed by electronic absorption spectra. The ICT band of trimer **4** showed two-step bathochromic shifts by adding TFA to the $CHCl_3$ solution. More interestingly, they were strong blue emitters in $CHCl_3$, and the fluorescence properties largely depended on the structure of the oligomers. Pentamer **5** ($n = 2$) showed the highest Φ_F value ($\Phi_F = 0.82$) among them. Such fluorescence properties are characteristic of triazine−amine conjugated oligomers and responsible for the alternate $(D-\pi-A-\pi)_n$ arrangement of amines (D) and triazines (A) through phenylene groups.

The synthetic strategy also deserves attention. In contrast to the other stepwise methods for synthesizing fluorescent compounds, such as oligofluorene[39] and phenyleneethynylene[40] derivatives, the one-step synthesis of triazine−amine conjugated oligomers via trimerization of aromatic dinitriles is very practical. By simply changing the methyl group to other substituents at the nitrogen position, their fluorescence properties can be modulated. Therefore, we conclude that trimerization of aromatic dinitriles with an amine moiety is a novel and versatile method for preparing highly fluorescent triazine-containing oligomers.

Experimental Section

All reactions with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under an argon atmosphere. All commercially available materials were of reagent grade unless otherwise noted.

4,4′-Dicyanodiphenylamine (2) was prepared as described in the literature[30] and identified by ^1H NMR. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.60 (d, J = 8.8 Hz, 4H), 7.16 (d, J = 8.8 Hz, 4H), 6.32 (br s, 1H).

4,4′-Dicyano-*N*-methyldiphenylamine (3). A mixture of compound **2** (2.40 g, 10.9 mmol), methyl iodide (64.0 g, 450 mmol), and K_2CO_3 (5.71 g, 41.3 mmol) in dry DMF (25 mL) was stirred at 130 °C for 65 h. The reaction mixture was filtered, and the solvent was removed in vacuo. The solid residue was dissolved in $CHCl_3$ (30 mL), washed with water (40 mL × 2), a saturated aqueous solution of sodium thiosulfate (50 mL × 2), and brine (50 mL), and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography ($CHCl_3$/hexane 5:1) to give **3** as a pale yellow powder (2.34 g, 92%): mp 155.5−156.4 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.58 (d, J = 9.0 Hz, 4H), 7.11 (d, J = 9.0 Hz, 4H), 3.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.7 (C), 133.7 (CH), 120.6 (CH), 119.0 (C), 105.1 (C), 40.0 (CH_3). IR (KBr, cm^{-1}): 2917, 2359, 22113, 1900, 1593, 1553, 1503, 1348, 1304, 1275, 1261, 1178, 1143, 1128, 1107, 1065, 872, 828. UV−vis ($CHCl_3$) λ_{max}, nm (ϵ, L·

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(39) (a) Li, B.; Li, J.; Fu, Y.; Bo, Z. *J. Am. Chem. Soc.* **2004**, *126*, 3430. (b) Sandee, A. J.; Williams, C. K.; Evans, N. R.; Davies, J. E.; Boothby, C. E.; Koehler, A.; Friend, R. H.; Holmes, A. B. *J. Am. Chem. Soc.* **2004**, *126*, 7041. (c) Kulkarni, A. P.; Kong, X.; Jenekhe, S. A. *J. Phys. Chem. B* **2004**, *108*, 8689. (d) Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695.

(40) (a) Li, J.; Pang, Y. *Synth. Met.* **2004**, *140*, 43. (b) Li, K.; Wang, Q. *Macromolecules* **2004**, *37*, 1172. (c) Boydston, A. J.; Yin, Y.; Pagenkopf, B. L. *J. Am. Chem. Soc.* **2004**, *126*, 10350. (d) Chen, Z.; Xue, C.; Shi, W.; Luo, F.-T.; Green, S.; Chen, J.; Liu, H. *Anal. Chem.* **2004**, *76*, 6513. (e) Nielsen, K. T.; Spanggaard, H.; Krebs, F. C. *Macromolecules* **2005**, *38*, 1180. (f) Khan, A.; Mueller, S.; Hecht, S. *Chem. Commun.* **2005**, *5*, 584. (g) Fan, Q.-L.; Zhou, Y.; Lu, X.-M.; Hou, X.-Y.; Huang, W. *Macromolecules* **2005**, *38*, 2927.

mol^{-1}·cm^{-1}): 275 (14 700), 345 (27 800). MALDI-TOF MS *m/z* calcd for $[M + H]^+$: 234.10; found 234.07. Anal. Calcd for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01. Found: C, 77.15; H, 5.00; N, 17.96.

Triazine−Amine Conjugated Oligomers (4−7). Compound **3**, NaOH powder, and a reaction vessel were dried at 50 °C in vacuo for 4 days and stored over P_2O_5 prior to use. A mixture of compound **3** (1.00 g, 4.29 mmol) and NaOH powder (173 mg, 4.32 mmol) was heated in a molten state at 200 °C for 36 h. The reaction mixture was chromatographed through a short silica gel column (eluting with $CHCl_3$) to remove byproducts and hydrated species, in which the terminal cyano groups are partly hydrolyzed to amide ones. The eluted products were separated and purified by preparative GPC, eluting with $CHCl_3$, to give **4**−**7** as yellow oily residues, which were recovered as yellow powders by adding a large quantity of methanol to them. The isolated yields of trimer **4**, pentamer **5**, heptamer **6**, and nonamer **7** were 106 mg (11%), 67.1 mg (6.7%), 36.3 mg (3.6%), and 28.4 mg (2.8%), respectively.

Preparation of Compound 4′ and 4″ (Trimer, X = O or CH_2). These compounds were prepared from 4,4′-dicyanodiphenyl ether[41] or 4,4′-dicyanodiphenylmethane[42] in a similar manner as that used for the triazine−amine conjugated oligomers (**4**−**7**) using $ZnCl_2$ instead of NaOH. The isolated yields of trimer **4′** (X = O) and **4″** (X = CH_2) were 12% and 0.9%, respectively.

Supporting Information Available: General experimental procedures and spectral data for the new compounds **3**, **4**, **5**, **6**, **7**, **4′**, and **4″**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[41] Li, F.; Wang, Q.; Ding, Z.; Tao, F. *Org. Lett.* **2003**, *5*, 2169.

[42] Friedman, L.; Shechter, H. *J. Org. Chem.* **1961**, *26*, 2522.