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Synthesis and spectroscopic study of diphenylamino-substituted phenylene-(poly)ethynylenes: remarkable effect of acetylenic conjugation modes

Jing-Kun Fang [a,c], De-Lie An [a,*], Kan Wakamatsu [b], Takeharu Ishikawa [b], Tetsuo Iwanaga [b], Shinji Toyota [b], Daisuke Matsuo [c], Akihiro Orita [c,*], Junzo Otera [c,*]

[a] Department of Chemistry, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China
[b] Department of Chemistry, Okayama University of Science, Ridai-cho, Okayama 700-0005, Japan
[c] Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700-0005, Japan

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ABSTRACT

A series of diphenylamino-substituted phenylene-(poly)ethynylenes were successfully synthesized by a combination of Sonogashira coupling and double elimination protocol of β-substituted sulfones. When UV-light was irradiated, the amino-substituted phenylene-(poly)ethynylene emitted strong luminescence. The emission underwent a large bathochromic shift in polar solvent because of stabilization of their charge-separated excited states. Analyses of fluorescence life times of aminoacetylenes revealed that radiationless process was suppressed in the polar solvent CH_2Cl_2, resulting in high quantum yields.

Acetylenes have attracted extensive attention in material sciences[1] such as acetylenic macrocycles[2] and polyynes[3] because they possess abundant π electrons and rigid arrays. We established a double elimination protocol of β-substituted sulfones for access to acetylenes,[4] and disclosed the usefulness of this protocol for the preparation of phenylene-ethynylene fluorophores.[5] It was revealed that amino-substituted fluorophores emit fluorescence from their twisted intramolecular charge-transfer (TICT) states, when UV-light is irradiated.[6] Since the charge-separated excited state is more stabilized in polar solvents than in less polar ones, fluorescence undergoes bathochromic shift in polar solvents. Hirata has already reported that aminoacetylenes **1**[7] and **2**[8] emit fluorescence from *intramolecular* charge-separated states, but little is known about emission of higher analogues. Herein we have prepared various diphenylamino-substituted acetylenes in order to evaluate the effect of acetylenic π systems on optical properties of amino-substituted phenylene-(poly)ethynylenes **3–10** (Fig. 1). We have established a general route for the synthesis of amino-substituted acetylenes,[9] in which ethyne moiety and diyne and triyne moieties are produced by the Sonogashira coupling[10] and the double elimination protocol of β-substituted sulfones,[4] respectively (Fig. 1). For instance, propargyl aldehyde **11** was prepared by repeating the Sonogashira coupling and MnO_2 oxidation, and the addition of a THF solution of LiHMDS (lithium hexamethyldisilazide) to a THF solution of propargyl sulfone **12**, aldehyde **11,** and diethyl chlorophosphate afforded **yne-triyne 10** (Scheme 1). **Triyne-yne 8** was obtained as well in the same procedure. Triyne derivatives **8** and **10** were pale yellow powdery compounds which are stable in air and showed narrow melting points at 168–170 °C and 198–200 °C, respectively. We name herein all these compounds as follows: an acetylenic bond attached to the diphenylaminophenyl group precedes the remaining acetylenic bond.

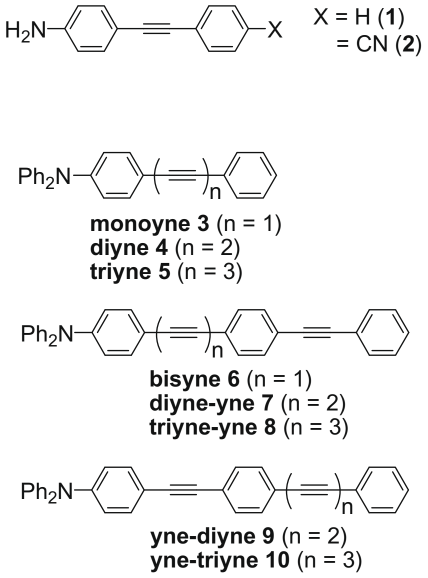

Figure 1. Structures of amino-substituted phenylene-(poly)ethynylenes.

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[*] Corresponding authors. Tel.: +86 731 8827 944; fax: +86 731 8827 944 (D.-L.A.); tel.: +81 86 256 9533; fax: +81 86 256 4292 (A.O.).
E-mail addresses: deliean@sina.com (D.-L. An), orita@high.ous.ac.jp (A. Orita).

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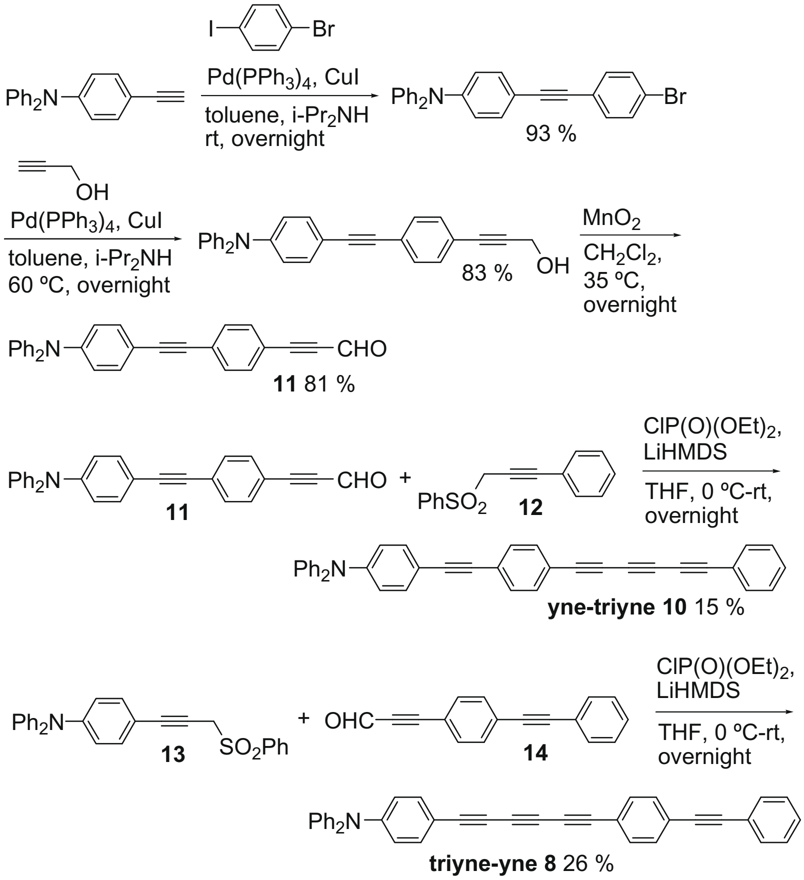

Scheme 1. Syntheses of **yne-triyne 10** and **triyne-yne 8**.

Photochemical data such as UV–vis absorption and fluorescence properties of these compounds are summarized in Table 1. UV absorption spectra of **monoyne 3**, **diyne 4**, and **triyne 5** in cyclohexane (1.0×10^{-5} mol/L) exhibited their longest λ_{max} at 345 nm, 372 nm, and 402 nm, respectively, and this bathochromic shift could be explained by an expansion of acetylenic π-conjugated systems. A similar bathochromic shift was observed in **6–10** as well: **bisyne 6** (363 nm) ⇒ **diyne-yne 7** (395 nm) ⇒ **triyne-yne 8** (418 nm); **bisyne 6** (363 nm) ⇒ **yne-diyne 9** (391 nm) ⇒ **yne-triyne 10** (405 nm). When UV–vis spectra of **3–10** were recorded in CH_2Cl_2 instead of cyclohexane, a little difference was observed. These results show that there is no solvent effect on UV–vis absorption of amino-substituted acetylenes 3–10.

Table 1
UV-vis absorption and fluorescence properties of diphenylaminoacetylenes

			monoyne 3	diyne 4	triyne 5	bisyne 6	diyne-yne 7	triyne-yne 8	yne-diyne 9	yne-triyne 10
UV[a]	c-C_6H_{12}	λ_{max} [nm]	345	372	402	363	395	418	391	405
		(ε [L/mol cm])	(37,008)	(25,528)	(34,353)	(53,865)	(36,187)	(57,514)	(18,190)	(24,092)
	CH_2Cl_2	λ_{max} [nm]	351	372	401	373	392	418	385	401
		(ε [L/mol cm])	(33,307)	(36,958)	(40,170)	(46,465)	(51,691)	(45,248)	(52,648)	(61,020)
PL[b]	c-C_6H_{12}	E_{max}[c] [nm]	376	394	413	397	409	427	408	422
		(Φ_F)[d]	(0.43)	(0.18)	(<0.01)	(0.74)	(0.34)	(0.01)	(0.70)	(0.04)
		τ[e] [ns]	0.5	0.4		0.9	1.1		0.7	
		k_r, k_{nr} [10^8/s]	8.6, 11.4	4.5, 20.5		8.2, 2.9	3.1, 6.0		10.0, 4.3	
		k_r/k_{nr}	0.75	0.22		2.8	0.52		2.3	
	CH_2Cl_2	E_{max}[c] [nm]	419	447	471	467	478	496	491	523
		(Φ_F)[d]	(0.78)	(0.32)	(0.01)	(0.89)	(0.40)	(0.01)	(0.86)	(0.68)
		τ[e] [ns]	1.6	3.0		1.6	0.7		1.7	1.7
		k_r, k_{nr} [10^8/s]	4.9, 1.4	1.1, 2.3		5.6, 0.69	5.7, 8.6		5.1, 0.82	4.0, 1.9
		k_r/k_{nr}	3.5	0.48		8.1	0.66		6.2	2.1
		Δ[f] [nm]	43	53	58	70	69	69	83	101

[a] UV–vis absorption in c-C_6H_{12} and CH_2Cl_2 (1.0×10^{-5} M).
[b] Fluorescence in c-C_6H_{12} and CH_2Cl_2 (1.0×10^{-7} M).
[c] Emission maximum.
[d] Fluorescence quantum yield measured by integrated sphere system (Hamamatsu photonics C9920-02).
[e] Fluorescence life time, solutions degassed by freeze-pump-thaw cycles, 5.0×10^{-6} M.
[f] Difference of emission maxima in c-C_6H_{12} and CH_2Cl_2.

Photoluminescence data of phenylene-(poly)ethynylenes **3–10** such as wavelength and quantum yield are also summarized in Table 1. **Monoyne 3**, **diyne 4,** and **triyne 5** gave strong emission at 376 nm, 394 nm, and 413 nm in cyclohexane (1.0×10^{-7} mol/L), respectively, and the emission maxima underwent bathochromic shift by expansion of acetylenic π-conjugated system (Fig. 2). Quantum yields of these acetylenes decreased remarkably according to the expansion of acetylenic π-conjugated systems: **monoyne 3** (Φ_{F} 0.43), **diyne 4** (Φ_{F} 0.18), **triyne 5** (Φ_{F} <0.01) (Table 1). In CH_2Cl_2, these aminoacethylenes exhibited emission at longer wavelengths than observed in cyclohexane (419 nm for **monoyne 3**, 447 nm for **diyne 4,** and 471 nm for **triyne 5** (Fig. 2), and highly expanded π-system **diyne 4** and **triyne 5** underwent larger solvent effect on wavelengths of emission maxima: differences of emission maxima in cyclohexane and CH_2Cl_2 were 43 nm for **3**, 53 nm for **4,** and 58 nm for **5**. These bathochromic shifts observed by changing solvent polarities can be explained in terms of stabilization of the charge-separated excited states of aminoacetylenes which are generated by irradiation of UV-light. In the excited state, amino-substituted acetylenes undergo *intramolecular* charge transfer giving rise to a positive charge on the amino group and a negative charge on phenylene-(poly)ethynylene moieties. The charge-separated excited state can be stabilized more efficiently than the ground state in polar solvent such as CH_2Cl_2 resulting in bathochromic shift of emission maxima. Aminoacetylenes **3** and **4** indicated larger quantum yields in CH_2Cl_2 than in cyclohexane; **monoyne 3** (0.78 vs 0.43) and **diyne 4** (0.32 vs 0.18). In order to investigate the emission mechanism, fluorescence life times (τ) of **3** and **4** were recorded in cyclohexane and in CH_2Cl_2, and rate constants for radiation process k_{r}, and radiationless process k_{nr} were calculated based on the following equations [$k_{\mathrm{r}} = \Phi_{\mathrm{F}}/\tau$, $k_{\mathrm{nr}} = (1 - \Phi_{\mathrm{F}})/\tau$] (Table 1). Comparison of k_{r} and k_{nr} reveals that expansion of acetylenic π-system accelerates a radiationless process with a radiation process suppressed to result in lower quantum yields of **diyne 4** than those of **monoyne 3** both in cyclohexane and CH_2Cl_2. It was found that in polar solvent CH_2Cl_2 ($\varepsilon = 8.9$), although both radiation and radiationless processes were suppressed, radiationless process was further suppressed. In less polar solvent cyclohexane ($\varepsilon = 2.0$), radiationless process was predominant, and ratios of rate constants $k_{\mathrm{r}}/k_{\mathrm{nr}}$ were 0.75 for **monoyne 3** and 0.22 for **diyne 4**. In contrast to this, in more polar solvent CH_2Cl_2 ($\varepsilon = 8.9$), rate constants $k_{\mathrm{r}}/k_{\mathrm{nr}}$ increased to 3.5 (**monoyne 3**) and 0.48 (**diyne 4**) giving rise to higher quantum yields of **3** and **4**, although radiation rate constant k_{r} in CH_2Cl_2 was remarkably smaller than in cyclohexane.

When UV-light was irradiated to solutions of **bisyne 6**, **diyne-yne 7**, **triyne-yne 8**, **yne-diyne 9,** and **yne-triyne 10**, a strong emission was recorded both in cyclohexane and CH_2Cl_2 (Fig. 3, Table 1). In cyclohexane, aminoacetylenes **7–10** underwent bathochromic shift in comparison with **6** because of their larger expanded acetylenic π-systems. When photoluminescence spectra of **7**–**10** were recorded in CH_2Cl_2, it was found that **yne-diyne 9** and **yne-triyne 10** exhibited a larger bathochromic shift than **6–8**: differences of emission maxima in cyclohexane and CH_2Cl_2 (Δ) were 83 nm for **9** and 101 nm for **10**, but Δ values for **6–8** were less

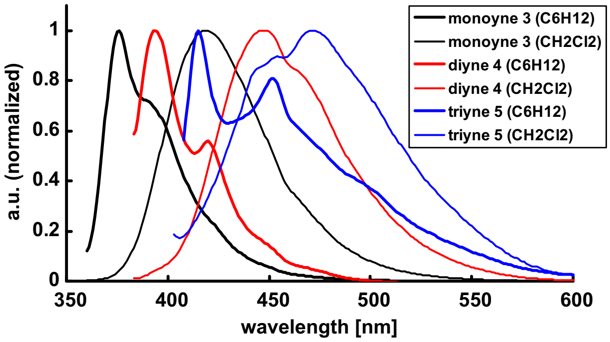

Figure 2. Emission spectra of **3–5** in *c*-hexane and CH_2Cl_2.

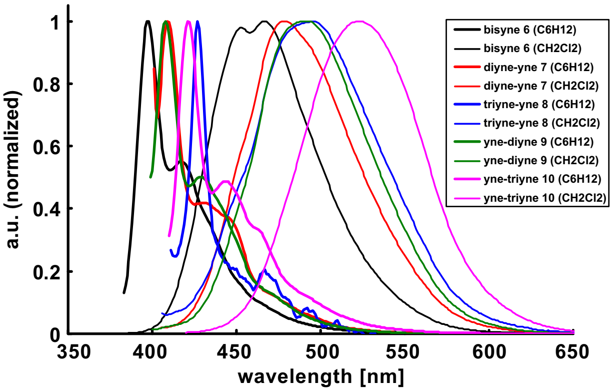

Figure 3. Emission spectra of **6–10** in *c*-hexane and CH_2Cl_2.

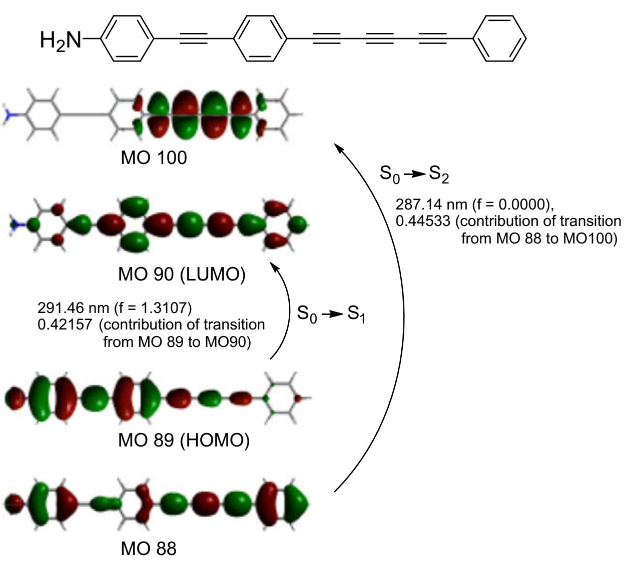

Figure 4. Result of theoretical calculation for NH_2-**yne-triyne** in the excited state.

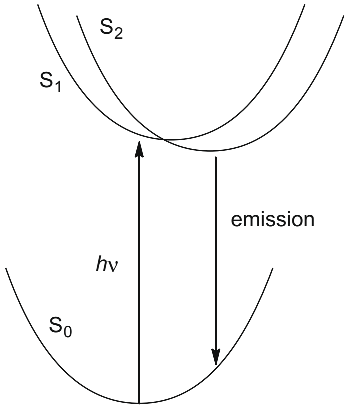

Figure 5. Energy diagram of NH_2-**yne-triyne** in the ground state and the excited state.

than 70 nm. Such larger solvent effects observed in **9** and **10** indicate that diyne and triyne moieties located at the opposite side of amino group could accommodate a negative charge efficiently which was generated in the excited state. Comparison of ratios of rate constants (k_r/k_{nr}) of **6**, **7,** and **9** revealed that radiation process became more predominant in CH_2Cl_2 than in cyclohexane resulting in higher quantum yields (Φ_F). Surprisingly, emission of **yne-triyne 10** was remarkably enhanced in CH_2Cl_2: $\Phi_F(CH_2Cl_2) = 0.68$, $\Phi_F(c\text{-}C_6H_{12}) = 0.04$).

Finally, in order to get better insight into the excited state of **yne-triyne 10**, which exhibited the largest solvent effect of bathochromic shift (Δ) and enhanced quantum yield (Φ_F), theoretical calculations (CIS/6-31+G*) were carried out for a model molecule **NH_2-yne-triyne**.[11] The lowest excited state (S_1) mainly results from electron-transition from HOMO (MO89) to LUMO (MO90) (Fig. 4). The secondary excited state (S_2) resulting from MO88 to MO100 transition, lies close to the S_1 state. Although MO88 is a π molecular orbital expanded over the whole molecule, MO100 is localized on triyne moiety and perpendicular to HOMO and LUMO. The geometry optimization of the excited states revealed that the energy order of the S_1 and S_2 states was inverted at the stationary point (Fig. 5).[12] Therefore, the internal conversion of the excited state ($S_1 \rightarrow S_2$) would easily occur[13] and induce higher polarization of **NH_2-yne-triyne** in the excited state S_2 resulting in great solvent effect of fluorescence.[14]

We succeeded in preparation of a variety of amino-substituted phenylene-(poly)ethynylenes by a combination of Sonogashira coupling and double elimination of β-substituted sulfones. The phenylene-(poly)ethynylenes exhibited strong absorption bands in UV–vis spectroscopy, and emitted strong fluorescence when UV-light was irradiated. In CH_2Cl_2, the phenylene-(poly)ethynylenes showed bathochromic shifts of emission in comparison with emission in cyclohexane. Theoretical calculations suggested that amino-substituted **yne-triyne** undergo high polarization in its excited state resulting in large bathochromic shift through interconversion of excited states. Further study in optical properties of amino-substituted acetylenic π-system and their application for design of organic light-emitting materials are under investigation.

Acknowledgments

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Supplementary data

Supplementary data (full synthetic details and characterization of acetylenic compounds) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.12.023.

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12. Higher level of calculations including electron correlation will be carried out for further quantitative investigation.
13. The energy barrier of rotation for diphenyltriyne moiety of **NH_2-yne-triyne** in ground state is significantly low: free energy difference between its planar and orthogonal forms is calculated as 0.038 kcal mol^{-1} by B3LYP/6-31+G*, and the former is more stable. Although higher level of theoretical calculation is required for further investigation in the excited states S_1 and S_2, the symmetry breaking induced by the rotational vibration would allow the S1→S2 internal conversion. It was reported that, intrinsically perpendicular the π–π^* state underwent internal conversion to n,π^* state: Ismail, N.; Blancafort, L.; Olivucci, M.; Kohler, B.; Robb, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 6818.
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