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

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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.

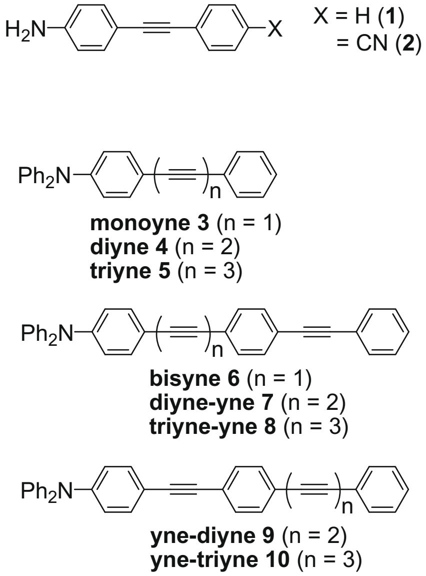

Figure 1. Structures of amino-substituted phenylene-(poly)ethynylenes.

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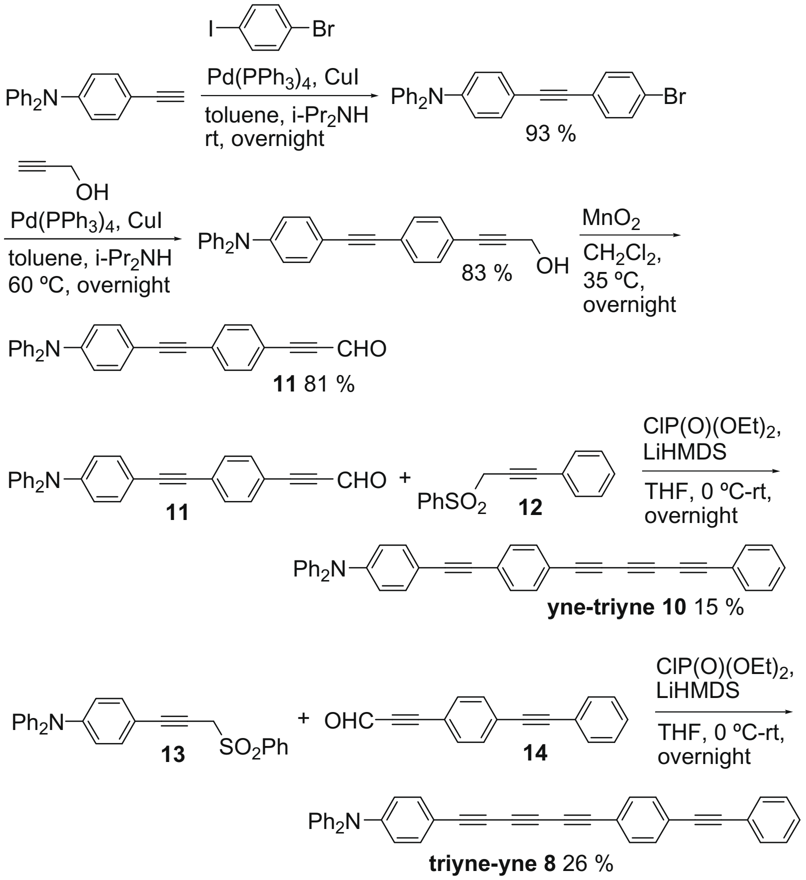

Scheme 1. Syntheses of **yne-triyne 10** and **triyne-yne 8**.

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.