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Synthesis and spectroscopic study of phenylene–(poly)ethynylenes substituted by amino or amino/cyano groups at terminal(s): electronic effect of cyano group on charge-transfer excitation of acetylenic π-systems

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ABSTRACT

To gain insight into substituent electronic effect on charge-transfer excitation of acetylenic π-systems, phenylene–(poly)ethynylenes substituted by Ph_2N or Ph_2N/cyano groups were synthesized by combination of Sonogashira coupling and double elimination protocol of β-substituted sulfones. These substituted phenyleneethynylenes showed large molar absorption coefficients ε, and emitted strong fluorescence upon UV light irradiation. Phenylene–(poly)ethynylenes, which involve butadiyne or hexatriyne motifs, emitted fluorescence in remarkably lower fluorescence quantum yields Φ_F as their polyethynylene motifs $-(C{\equiv}C)_n-$ expanded. The drastic decrease of fluorescence quantum yields Φ_F were explained in terms of increasing nonradiative reaction rate constants k_{nr}, which had been determined by the corresponding fluorescence quantum yields Φ_F and lifetime values τ. The emission underwent a large bathochromic shift in polar solvents because the charge-separated excited state is more stabilized than the ground state. Comparison of slope values ρ in Lippert/Mataga plot for the Ph_2N and Ph_2N/cyano-substituted phenylene–(poly)ethynylenes revealed that the latter underwent large change of dipole moments upon photo-excitation although highly expanded acetylenic π-systems with cyano group did little.

1. Introduction

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 double elimination protocol of β-substituted sulfones for access to acetylenes,[4] and disclosed usefulness of this protocol for preparation of phenyleneethynylene fluorophores.[5] It was revealed that amino-substituted fluorophores emit fluorescence from their twisted intramolecular charge-transfer states (TICT), when UV light is irradiated.[6] Since the charge-separated excited state is more stabilized in polar solvents than the less polar ground state, fluorescence undergoes bathochromic shift depending on the solvent polarities. Hirata already reported that aminoacetylenes $H_2N{-}C_6H_4{-}C{\equiv}C{-}C_6H_5$ and $H_2N{-}C_6H_4{-}C{\equiv}C{-}C_6H_4CN$ emit fluorescence from intramolecular charge-separated states,[7,8] and we disclosed that amino-substituted phenylene-(poly)ethynylenes undergo solvent effect in photoluminescence depending on the inherent natures of acetylenic modes, which capture negative charge in the excited states.[9] By taking advantage of the intramolecular charge-transfer excitation, Yamaguchi and Yoshida succeeded to tune emission maxima of phenyleneethynylenes without loss of their high fluorescence quantum yields, which were constructed by connecting donor blocks, methoxy-substituted phenyleneethynylenes with acceptor blocks, cyano-substituted homologs.[10] Because these phenyleneethynylenes emit strong fluorescence in the powdery state, they are promising candidates as emitting material for organic light-emitting diode (OLED). Recently, a number of organic sensitizers for photovoltaics have been developed, the structures of which are depicted as donor-(π-system)/acceptor.[11] These dyes are designed for the electron density of HOMO to be wholly located on the donor group and for LUMO electron density to be on the acceptor, and, upon photo-excitation, an intramolecular electron transfer occurs through the π-system bridge to attain a discrete charge-transferred excited state. Because

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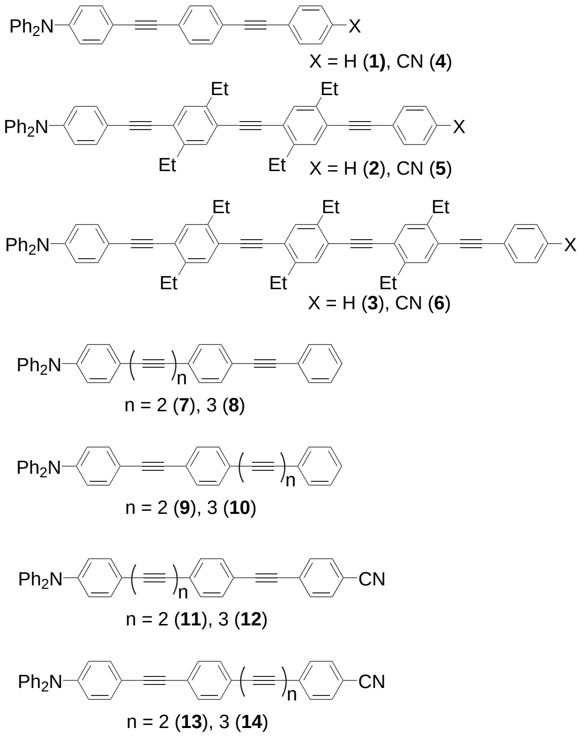


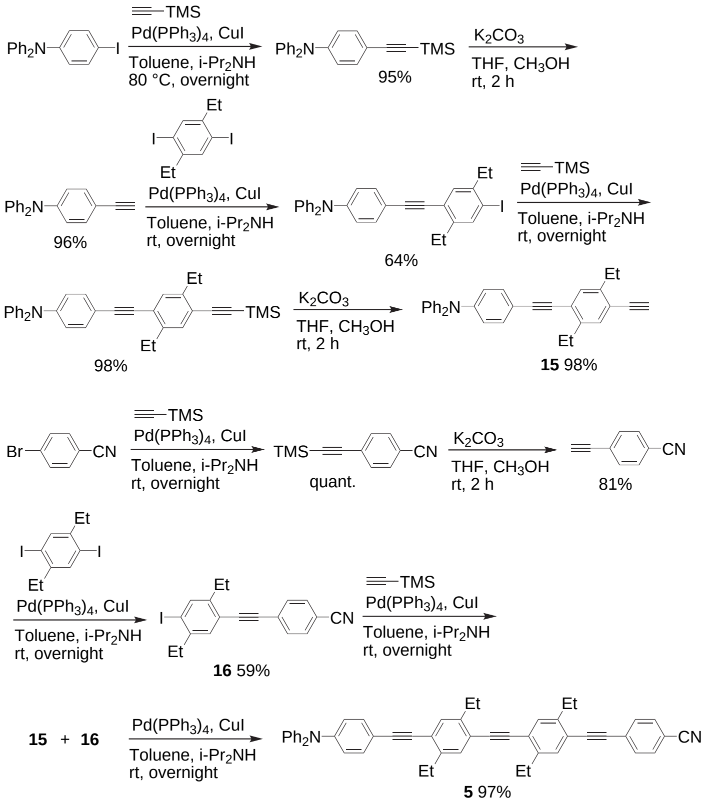
Figure 1. Structures of **1**–**14**.

this charge-transfer excitation of the organic dye plays a pivotal role to achieve high solar-to-electric power conversion, we have been intrigued by the effect of acetylenic π-system and electron-accepting group on nature of donor-(π-system)/acceptor dye in the charge-transferred excited state. Herein we report syntheses of several phenylene–(poly)ethynylenes, which have Ph_2N or Ph_2N/CN groups at their terminal(s) and their photophysical properties such as UV/vis absorption, photoluminescence, and change of dipole moments $\Delta\mu$ between excited and ground states, which are estimated by Lippert/Mataga plot.[12]

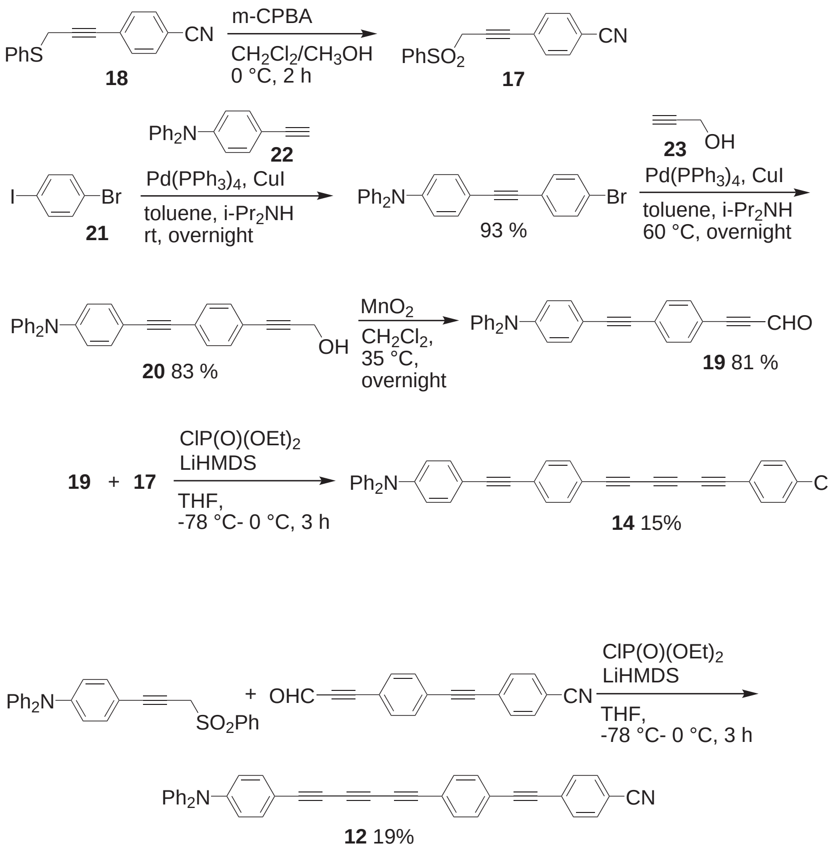
2. Results and discussion

We firstly prepared Ph_2N or Ph_2N/cyano-substituted phenyleneethynylenes **1**–**14** (Fig. 1). Syntheses of **1**–**6** were attained by repeating Sonogashira coupling between the corresponding terminal acetylene and halobenzene. Representative synthetic process for **5** is shown in Scheme 1, and **5** was obtained as yellow powdery compound, and ^{13}C NMR analysis featured six acetylenic carbons (δ 87.4, 92.3, 92.4, 92.8, 93.6, 94.7), and cyano carbon (δ 118.5). All the acetylenes **1**–**6** are white to yellow powdery compounds, which are stable in air. Substitution of ethyl groups on central benzenes of the higher homologs improved their poor solubilities to enable **5** and **6** to be miscible with common organic solvents.

For synthesis of Ph_2N-**7**–**10** and Ph_2N/cyano-substituted phenylene–(poly)ethynylenes **11**–**14**, we established a general procedure: diphenylethyne and polyethyne moieties were constructed by Sonogashira coupling and double elimination protocol, respectively. Representative synthetic processes for **14** and **12** are shown in Scheme 2. Cyano-substituted propargyl sulfone **17** was obtained by *m*-CPBA-oxidation of the corresponding propargyl sulfide **18**, that had been prepared by Sonogashira coupling of 4-bromobenzonitrile with propargyl sulfide. Amino-substituted propargylaldehyde **19** was obtained by MnO_2-oxidation of propargyl alcohol **20**, that had been prepared by stepwise Sonogashira coupling of 1-bromo-4-iodobenzene **21** with aminophenylethyne **22** and propynol **23**. Although Sonogashira coupling using

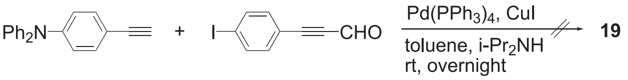


Scheme 1. Synthesis of **5**.

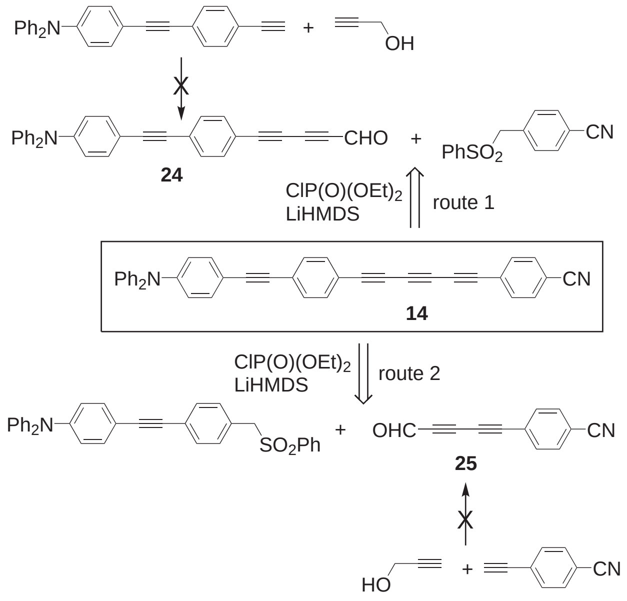


Scheme 2. Syntheses of **14** and **12**.

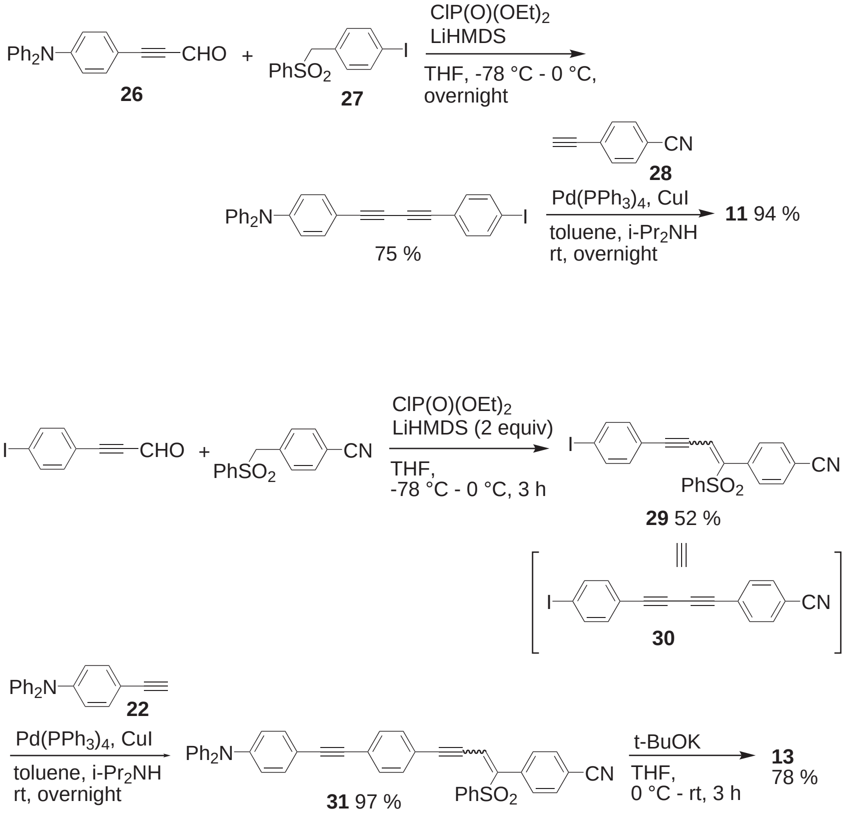
a propargylaldehyde derivative is indeed straightforward for synthesis of **19**, this coupling reaction afforded an inseparable mixture of a number of products (Eq. 1). Subjection of the propargyl sulfone **17** and aldehyde **19** to one-shot double elimination reaction gave the desired product **14**: when a THF solution of LiHMDS (lithium hexamethyldisilazide) was added to a THF solution of **17**, **19**, and diethyl chlorophosphate, **14** was obtained in 15% yield in a pure form after column chromatography on silica gel. TLC analysis of crude products of this double elimination indicated remarkable formation of unidentified polar compounds resulting in the low yield of the desired product. Ph_2N/cyano-acetylene **14** thus obtained is yellow powdery compound, which is stable at room temperature in air but decomposed over 200 °C. When ^{13}C NMR of **14** was recorded in $CDCl_3$, eight acetylenic carbons (δ 66.4, 68.6, 75.6, 76.6, 78.4, 79.6, 88.1, 93.4) and cyano carbon (δ 118.1) were observed. Hexatriyne derivative **12** was successfully synthesized as well by taking advantage of the double elimination as a key reaction (Scheme 2). Although, in these syntheses, propargyl sulfone and propargylaldehyde were used for construction of the hexatriyne motif, double elimination reaction between benzyl sulfone and penta-1,3-diynal were supposed to be an alternative synthetic route (Scheme 3). We attempted to prepare penta-1,3-diynals **24** and **25** by $Cu(OAc)_2$-catalyzed oxidative coupling between terminal acetylenes followed by MnO_2 oxidation, but complicated mixtures of products were obtained in both cases.

 (1)

Combination of Sonogashira coupling and double elimination protocol were applied for syntheses of diphenylbutadiyne derivarives **11** and **13** (Scheme 4). Subjection of propargylaldehyde **26** and benzyl sulfone **27** to double elimination followed by Sonogashira coupling with **28** furnished **11**. For synthesis of **13**, vinylsulfone **29** was exploited as a masked diyne **30** because its polarity enabled a facile purification of Sonogashira coupling product **31**. The vinylsulfone **29** could be obtained by treatment of the corresponding aldehyde, sulfone, and diethyl chlorophosphate with 2 equiv of LiHMDS. When **31** was treated with *t*-BuOK in THF, elimination of sulfinic acid proceeded smoothly to give **13** in 78% yield.



Scheme 3. Attempted synthetic route for **14**.



Scheme 4. Syntheses of **11** and **13**.

Photophysical properties of the Ph_2N- and Ph_2N/cyano-substituted acetylenes **1**–**14** were summarized in Table 1. All the spectral data were recorded in CH_2Cl_2, and absolute quantum yields (Φ_F) were determined by the Hamamatsu C9920–02 integrated sphere system. Fluorescence decays were measured using an apparatus including a femtosecond laser system and a streak camera.

Several consistent trends are seen in UV/vis absorption spectra of **1**–**14**. Substitution of Ph_2N–phenylene–(poly)ethynylene with cyano group induces bathochromic shift of λ_{abs} by several nanometers compared to the parent Ph_2N-acetylenes, and largely expanded π-systems exhibit smaller bathochromic shifts: **1**→**4** ($\Delta\lambda_{abs}$=8 nm), **3**→**6** (1 nm); **7**→**11** (4 nm), **8**→**12** (2 nm); **9**→**13** (7 nm), **10**→**14** (ca. 0 nm).[13] Seven figures of UV/vis absorption spectra of **1** and **4**, **2** and **5**, **3** and **6**, **7** and **11**, **8** and **12**, **9** and **13**, **10** and **14** are added in Supplementary data in order to make clear an electronic effect of cyano group on wavelengths of λ_{abs}. Expansion of π-system by insertion of a phenyleneethynylene unit ($-C_6H_4C{\equiv}C-$) results in a bathochromic shift, while insertion of an ethynylene unit ($-C{\equiv}C-$) caused larger shifts: for phenyleneethynylene insertion, **1** (λ_{abs} 373 nm)→**2** (374 nm)→**3** (382 nm); for ethynylene insertion, **1** (λ_{abs} 373 nm)→**9** (385 nm)→

Table 1
Photophysical properties of Ph_2N- and Ph_2N/CN-substituted phenylene–(poly)ethynylenes **1**–**14** in CH_2Cl_2

	λ_{abs}[a] [nm]	ε[a] [L/mol cm]	ΔE[b] [eV]	λ_{em}[c] [nm]	Stokes shift [cm^{-1}]	Φ_F[d]	τ[e] [ns]	k_r, k_{nr}[f] [10^8/s]	k_r/k_{nr}	ρ [10^2]
1	373	4.6×10^4	3.26	467	5396	0.89	1.6	5.6, 0.69	8.1	145
2	374	6.7×10^4	3.02	470	5461	0.91	1.2	7.6, 0.75	10.1	138
3	382	8.5×10^4	2.88	472	4992	0.91	1.4	6.5, 0.64	10.1	136
4	381	4.7×10^4	2.89	514	6791	0.84	2.2	3.8, 0.73	5.2	177
5	380	7.2×10^4	2.71	501	6356	0.67	2.0	3.4, 1.7	2.0	173
6	383	9.9×10^4	2.62	477	5145	0.62	1.8	3.4, 2.1	1.6	106
7	392	5.2×10^4	3.11	478	4590	0.40	0.7	5.7, 8.6	0.66	147
8	392	4.5×10^4	2.95	496	5349	0.01				135
9	385	5.3×10^4	3.07	491	5607	0.86	1.7	5.1, 0.82	6.2	154
10	401	6.1×10^4	2.88	523	5817	0.68	1.7	4.0, 1.9	2.1	167
11	396	5.0×10^4	2.79	514	5797	0.45	1.5	3.0, 3.7	0.82	177
12	394	4.1×10^4	2.70	522	4224	0.02				134
13	392	4.8×10^4	2.72	539	6957	0.65	2.7	2.4, 1.3	1.9	170
14	399	5.1×10^4	2.55	554	7012	0.22	1.2	1.8, 6.5	0.28	143

[a] UV/vis absorption in CH_2Cl_2 (1.0×10^{-5} M).
[b] Energy difference between HOMO and LUMO calculated at the B3LYP/6-31G* level.
[c] Fluorescence maximum in CH_2Cl_2 (1.0×10^{-7} M).
[d] Fluorescence quantum yield measured by integrated sphere system (Hamamatsu photonics C9920–02).
[e] Fluorescence lifetime, solutions degassed by freeze-pump-thraw cycles, 5.0×10^{-6} M.
[f] $k_r=\Phi_F/\tau$, $k_{nr}=(1-\Phi_F)/\tau$.

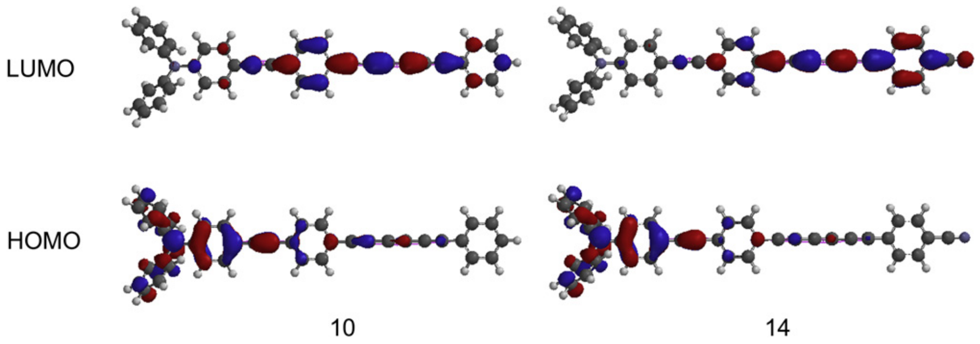


Figure 2. Molecular orbitals of **10** and **14** calculated by DFT method.

10 (401 nm). The degree of bathochromic shift shows fine agreement to ΔE values, which are HOMO/LUMO gaps calculated at the B3LYP/6-31G* level.[14] In Figure 2 are shown molecular orbitals of **10** and **14**, which have been calculated by the DFT method. The HOMOs are located mainly on the electron-donating triphenylamine moieties with a small participation of phenylene–(poly)ethynylene moieties, while the LUMOs mainly on phenylene–(poly)ethynylene moieties with a great participation of the accepting cyano group in **14**. Such remarkable localization of HOMO and LUMO in different areas strongly suggests an intramolecular charge-transfer excitation to occur in **1**–**14** resulting in polarization of excited state S_1. In cyano-substituted compounds, a further polarization is expected because of the strong electron-withdrawing feature of cyano group as shown in Figure 2. In order to elucidate polarization of **1**–**14** in S_1 states, photoluminescence spectra were recorded in several polarity-varying solvents. Emission profiles of **14** in five different solvents are shown in Figure 3 together with UV/vis absorption spectra.[15] Obviously, the emission maxima λ_{em} of **14** are shifted to longer wavelengths as solvent polarity increases,[16] while the absorption maxima λ_{abs} displays virtually no change in any solvents. These results unambiguously support that highly polarized excited state of **14** is stabilized depending on the solvent polarity, while **14** in the ground state undergoes little solvent polarity effect because of its less dipole moment (vide infra). In Table 1 are summarized photoluminescence properties of **1**–**14** such as emission maximum λ_{em}, Stokes shift, and fluorescence quantum yield observed in CH_2Cl_2. The emission maxima λ_{em} show the similar trends as observed in absorption maxima λ_{abs} of UV/vis absorption spectra: substitution by cyano group provides a bathochromic shift, and insertion of –C≡C– unit more efficiently expands acetylenic π-system than $-C_6H_4C{\equiv}C-$ unit: for C≡C insertion, **1** (λ_{em} 467 nm)→**9** (491 nm)→**10** (523 nm); for $C_6H_4C{\equiv}C$ insertion, **1** (λ_{em} 467 nm)→**2** (470 nm)→**3** (472 nm). Interestingly, in Ph_2N/cyano-phenyleneethynylene series **4**–**6**, π-system expansion by insertion of $C_6H_4C{\equiv}C$ leads a blue-shift; the homolog with the shortest π-system **4** emits fluorescence at the longest wavelength among this series. This result can be explained in terms of intramolecular donor/acceptor interaction in the excited state, which is enhanced by proximately locating Ph_2N and CN groups resulting in a narrow S_1–S_0 gap.[10b] All the acetylenes **1**–**14** exhibit considerably large Stokes shift (>4200 cm^{-1}), and Stokes shifts of Ph_2N/cyano derivatives generally exceed those of the corresponding Ph_2N derivatives. Comparison of fluorescence quantum yields Φ_F displays that the quantum yields of diynes and triynes remarkably decrease as the polyyne π-system $-(C{\equiv}C)_n-$ expands; **4** (Φ_F 0.84)→**13** (0.65)→**14** (0.22). In order to get further insight into a mechanism for low emission quantum yields of diyne and triyne derivatives, fluorescence lifetimes τ were recorded for **1**–**14**. Reaction rates for radiative k_r and nonradiative processes k_{nr} are obtained by the following equations ($k_r=\Phi_F/\tau$, $k_{nr}=(1-\Phi_F)/\tau$), and the rate constants k_r, k_{nr}, and the constant ratio k_r/k_{nr} are summarized in Table 1. Notably, as polyyne π-system expands, nonradiative reaction rate constant k_{nr} drastically increases and consequently a ratio of reaction rate constants k_r/k_{nr} decreases resulting in low fluorescence quantum yields of diynes and triynes: **4** (k_{nr}=0.73, k_r/k_{nr}=5.2)→**13** (1.3, 1.9)→**14** (6.5, 0.28); **1** (k_{nr}=0.69, k_r/k_{nr}=8.1)→**9** (0.82, 6.2)→**10** (1.9, 2.1). The solvent polarity effect on λ_{em} and large Stokes shifts observed in **1**–**14** suggest increase of their dipole moments in the excited states S_1 (μ_e) compared to those in the ground state S_0 (μ_g). In order to rationalize the effect of solvent polarity on the dipole moment change $\Delta\mu$, which corresponds to $\mu_e-\mu_g$, we took advantage of the Lippert/Mataga plot,[12] which provides quantitative relationship between the solvent orientation polarizability Δf and Stokes shift $\Delta\nu$ by the following Eqs. 2 and 3:

$$\Delta V = \frac{2}{hc}\frac{\left(\mu_e-\mu_g\right)^2}{a^3}\Delta f + \text{Constant} \\ = \rho\Delta f + C \tag{2}$$

$$\Delta f = \frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1} \tag{3}$$

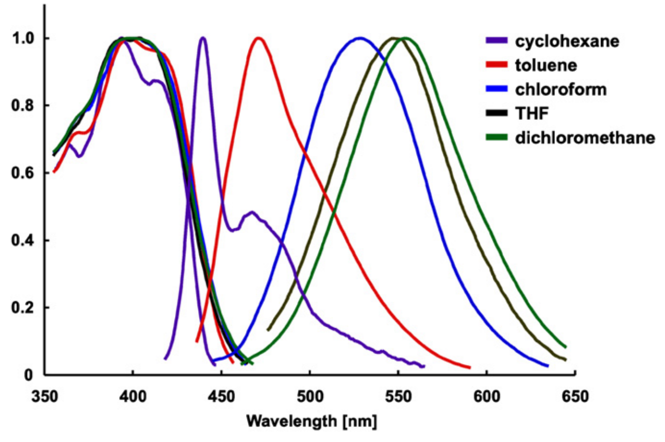


Figure 3. Normalized UV/vis absorption and emission spectra of **14** in cyclohexane (ε 2.0), toluene (ε 2.4), $CHCl_3$ (ε 4.8), THF (ε 7.6), and CH_2Cl_2 (ε 8.9).

where $\Delta\nu$ denotes Stokes shift, μ_e the excited state dipole moment, μ_g the ground state dipole moment, h the Planck constant, c the light velocity, and a the Onsager radius of the solute. The solvent orientation polarizability Δf, which is related to the solvent dielectric constant ε and refractive index n, is calculated by using Eq. 3.[17] Plotting of $\Delta\nu$ versus Δf affords $2(\Delta\mu)^2/hca^3$ as the slope ρ of linear fit, and in Table 1 are represented the slope values ρ thus obtained for **1**–**14**.[13] All the acetylenes exhibit remarkably large slope values ρ (>10,000) indicating charge-transfer excitation occurs with large change of dipole moments $\Delta\mu$.[10] Provided that Onsagar radii of **4**–**6** are identical to those of the corresponding analogs **1**–**3**, respectively, by disregarding bulkiness of cyano group, comparison of ρ values enables to estimate electronic effect of cyano group on $\Delta\mu(=\mu_e-\mu_g)$ of these acetylenes. Ph_2N/cyano acetylenes **4** (17,700) and **5** (17,300) represents large ρ values compared to those of the corresponding Ph_2N acetylenes **1** (14,500) and **2** (13,800) indicating that the changes of dipole moments $\Delta\mu$ are magnified by substitution with electron-withdrawing cyano group. For Ph_2N/cyano higher homolog **6**, the ρ value is provided to be 10,600, which is smaller than that of **3** (13,600), representing that substitution of highly conjugated π-system with cyano group results in a smaller change of dipole moment $\Delta\mu$ than that of the parent Ph_2N π-system. Because the Onsager radii a can be considered to be identical in regioisomeric pairs, Ph_2N-butadiynes **7**, **9**, and Ph_2N/cyano-butadiynes **11**, **13**, respectively, comparison of their ρ values enables to evaluate explicitly effects of regioisomeric acetylene mode and cyano group on the change of dipole moments $\Delta\mu$. Both pairs of Ph_2N-butadiynes **7**, **9**, and Ph_2N/cyano-butadiynes **11**, **13** represent comparable ρ values, respectively, indicating no effect of location of butadiyne moiety on change of dipole moments $\Delta\mu$. It is notable that the ρ value of Ph_2N-hexatriyne **10** is significantly larger than that of the regioisomer **8**, and the remarkably large ρ value of **10** is in good agreement with our previous report describing that hexatriyne moiety captures a negative charge in the excited state providing high polarization.[9] Ph_2N/cyano-hexatriynes **12** and **14** show similar ρ values, indicating no effect of regiomeric acetylene modes on change of dipole moments $\Delta\mu$ in them. The ρ value of **14** is rather smaller than that of **10** suggesting, under assumption of the identical Onsager radius a in **14** and **10**, a smaller change of dipole moment $\Delta\mu$ in **14** despite the substitution of hexatriyne moiety by electron-withdrawing cyano group.[18] These results exemplify that substitution by electron-withdrawing cyano group does not always promote larger change of ρ dipole moments in the charge-transfer excitation as observed in highly conjugated acetylene π-systems such as **14** and **6**, and the origin of this intriguing effect of cyano group on change of dipole moment remains to be investigated.

3. Conclusion

In conclusion, we established a synthetic process for Ph_2N or Ph_2N/cyano-substituted acetylenic π-systems by invoking Sonogashira coupling and double elimination of β-substituted sulfone for construction of diphenylethyne and diphenylpolyethyne moieties, respectively. Thorough investigation of photophysical properties of these acetylenes disclosed that they underwent charge-separated excitation to emit fluorescence with significant bathochromic shifts. Substitution of acetylenic π-systems with cyano group provided large changes of dipole moments upon their excitation resulting in the large bathochromic shift of emission although substitution of highly expanded acetylenic π-systems did small changes. Further investigation of the mechanism and application of these results for design of organic photosensitizer are in progress in our laboratories.[19]

4. Experimental

4.1. Synthesis of 11

To a round-bottom flask were added 4-iodophenylmethyl phenyl sulfone (645 mg, 1.8 mmol), **26** (446 mg, 1.5 mmol), diethyl chlorophosphate (259 mg, 1.5 mmol), and THF (20 mL) under nitrogen. A THF solution of LiHMDS (7.5 mL, 1.0 M, 7.5 mmol) was added at 0 °C, and the mixture was stirred at room temperature overnight. After usual workup with CH_2Cl_2/NH_4Claq, the combined organic layer was dried over $MgSO_4$, and evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH_2Cl_2, 4:1) to give 556 mg of 4-iodo-4′-(dipheynylamino) diphenylbutadiyne (75% yield) as a pale yellow powder.

4-Iodo-4′-(dipheynylamino)diphenylbutadiyne: Mp 163–165 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (d, 8.5 Hz, 2H), 7.08 (t, 7.5 Hz, 2H), 7.11 (d, 8.0 Hz, 4H), 7.21 (d, 8.0 Hz, 2H), 7.28 (t, 8.0 Hz, 4H), 7.34 (d, 8.5 Hz, 2H), 7.66 (d, 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.88, 75.75, 80.22, 83.06, 95.15, 113.33, 121.25, 121.53, 124.04, 125.39, 129.48, 133.51, 133.70, 137.57, 146.71, 148.83.

To a flask were added **28** (19 mg, 0.15 mmol), 4-iodo-4′-(dipheynylamino)diphenylbutadiyne (82 mg, 0.17 mmol), Pd $(PPh_3)_4$ (11 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol), diisopropylamine (5 mL), and toluene (5 mL), and the mixture was stirred under nitrogen at room temperature overnight. After usual workup with CH_2Cl_2/NH_4Claq, the combined organic layer was dried over $MgSO_4$ and evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) to give 70 mg of **11** (94% yield) as a pale yellow powder.

Compound **11**: Mp 248–250 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, 9.0 Hz, 2H), 7.10 (t, 7.5 Hz, 2H), 7.12 (d, 7.5 Hz, 4H), 7.29 (t, 8.0 Hz, 4H), 7.36 (d, 9.0 Hz, 2H), 7.48–7.52 (m, 4H), 7.60 (d, 8.5 Hz, 2H), 7.65 (d, 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.88, 76.72, 80.56, 83.68, 90.00, 93.16, 111.69, 113.25, 118.46, 121.21, 122.58, 122.79, 124.08, 125.42, 127.80, 129.49, 131.71, 132.08, 132.37, 133.54, 146.70, 148.90; HRMS m/z $[M]^+$ calcd for $C_{37}H_{22}N_2$ 494.1783, found 494.1793.

4.2. Synthesis of 12

To a flask were added 4-(4-cyanophenylethynyl)phenylpropynal (128 mg, 0.50 mmol), phenyl 1-(4-diphenylaminophenyl)propyn-3-yl sulfone (254 mg, 0.60 mmol), diethyl chlorophosphate (172 mg, 0.50 mmol), and THF (10 mL) under nitrogen. A THF solution of LiHMDS (1.5 mL, 1.0 M, 1.5 mmol) was added at −78 °C, and the mixture was stirred at 0 °C for 3 h. After usual workup with CH_2Cl_2/NH_4Claq, the combined organic layer was dried over $MgSO_4$ and evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) to give 50 mg of **12** (19% yield) as a yellow powder.

Compound **12**: Mp>250 °C decomp.; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, 9.0 Hz, 2H), 7.11 (t, 8.0 Hz, 2H), 7.12 (d, 8.5 Hz, 4H), 7.30 (t, 8.0 Hz, 4H), 7.36 (d, 9.0 Hz, 2H), 7.49 (d, 8.5 Hz, 2H), 7.52 (d, 8.5 Hz, 2H), 7.60 (d, 8.5 Hz, 2H), 7.65 (d, 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 66.06, 68.38, 73.71, 76.85, 77.73, 80.34, 90.41, 93.03, 111.88, 112.24, 118.41, 120.96, 121.96, 123.24, 124.32, 125.62, 127.75, 129.56, 131.77, 132.10, 132.13, 132.91, 134.11, 146.61, 149.35; HRMS m/z $[M]^+$ calcd for $C_{39}H_{22}N_2$ 518.1783, found 518.1788.

4.3. Synthesis of 13

To a round-bottom flask were added 4-cyanophenylmethyl phenyl sulfone (154 mg, 0.6 mmol), 4-iodopheynylpropynal (128 mg, 0.5 mmol), diethyl chlorophosphate (86 mg, 0.5 mmol), and THF (20 mL) under nitrogen. A THF solution of LiHMDS (1.0 mL, 1.0 M, 1.0 mmol) was added at −78 °C, and the mixture was stirred at room temperature for 3 h. After usual workup with CH_2Cl_2/NH_4Claq, the combined organic layer was dried over $MgSO_4$ and evaporated. The crude product was subjected to column chromatography on silica gel (hexane/EtOAc, 4:1) to give 128 mg of **29** (52% yield) as a pale yellow foam. The product **29** was obtained as a pure geometric isomer, but the geometry E or Z was not determined.

Compound **29**: Mp 136–138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (d, 8.0 Hz, 2H), 7.32 (s, 1H), 7.45 (t, 7.5 Hz, 2H), 7.50 (d, 8.0 Hz, 2H), 7.58 (t, 7.0 Hz, 1H), 7.63–7.66 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ 84.79, 96.57, 102.16, 113.25, 118.11, 120.52, 121.09, 128.23, 129.16, 130.78, 131.81, 133.18, 133.89, 135.37, 137.71, 137.97, 149.03.

To a flask were added 4-ethynyl-*N*,*N*-diphenylbenzenamine (43 mg, 0.16 mmol), **29** (84 mg, 0.17 mmol), Pd$(PPh_3)_4$ (11 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol), diisopropylamine (5 mL), and toluene (5 mL), and the mixture was stirred under nitrogen at room temperature overnight. After usual workup with CH_2Cl_2/NH_4Claq, the combined organic layer was dried over $MgSO_4$ and evaporated. The crude product was subjected to column chromatography on silica gel (hexane/EtOAc, 4:1) to give 99 mg of **31** (97% yield) as an orange foam.

Compound **31**: Mp 91–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, 8.0 Hz, 2H), 7.07 (t, 7.0 Hz, 2H), 7.11 (d, 7.5 Hz, 4H), 7.16 (d, 7.5 Hz, 2H), 7.27 (d, 7.5 Hz, 4H), 7.34 (d, 8.5 Hz, 2H), 7.36 (s, 1H), 7.40 (d, 8.0 Hz, 2H), 7.45 (t, 7.5 Hz, 2H), 7.52 (d, 7.5 Hz, 2H), 7.58 (t, 7.0 Hz, 1H), 7.65 (t, 7.0 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 85.21, 87.97, 93.11, 103.20, 113.25, 114.99, 118.22, 120.22, 121.36, 121.83, 123.71, 125.08, 125.49, 128.26, 129.19, 129.39, 130.89, 131.38, 131.86, 131.92, 132.58, 133.88, 135.51, 138.17, 146.92, 148.28, 148.61.

To a round-bottom flask were added **31** (83 mg, 0.13 mmol), potassium *tert*-butoxide (16 mg, 0.14 mmol), and THF (5 mL) under nitrogen at 0 °C. The mixture was stirred at room temperature for 3 h. After usual workup with CH_2Cl_2/NH_4Claq, the combined organic layer was dried over $MgSO_4$ and evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) to give 50 mg of **13** (78% yield) as a yellow powder.

Compound **13**: Mp 245–247 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, 8.5 Hz, 2H), 7.08 (t, 7.5 Hz, 2H), 7.12 (d, 8.0 Hz, 4H), 7.28 (t, 8.0 Hz, 4H), 7.36 (d, 9.0 Hz, 2H), 7.47 (d, 8.5 Hz, 2H), 7.50 (d, 8.5 Hz, 2H), 7.60 (d, 8.5 Hz, 2H), 7.63 (d, 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 74.77, 78.05, 80.12, 83.64, 88.08, 93.00, 112.35, 115.17, 118.24, 120.23, 121.92, 123.71, 125.10, 126.69, 129.41, 131.41, 132.09, 132.48, 132.60, 132.89, 146.99, 148.28; HRMS *m*/*z* $[M]^+$ calcd for $C_{37}H_{22}N_2$ 494.1783, found 494.1779.

4.4. Synthesis of 14

To a flask were added **19** (100 mg, 0.25 mmol), **17** (85 mg, 0.30 mmol), diethyl chlorophosphate (86 mg, 0.25 mmol), and THF (10 mL) under nitrogen. A THF solution of LiHMDS (0.75 mL, 1.0 M, 0.75 mmol) was added at −78 °C, and the mixture was stirred at 0 °C for 3 h. After the usual workup with CH_2Cl_2/NH_4Claq, the combined organic layer was dried over $MgSO_4$ and evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH_2Cl_2, 1:1) to give 20 mg of **14** (15% yield) as a pale yellow powder.

Compound **14**: Mp>250 °C decomp.; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (d, 8.5 Hz, 2H), 7.08 (t, 7.5 Hz, 2H), 7.12 (d, 8.0 Hz, 4H), 7.29 (t, 7.5 Hz, 4H), 7.36 (d, 8.5 Hz, 2H), 7.46 (d, 8.0 Hz, 2H), 7.50 (d, 8.0 Hz, 2H), 7.61 (d, 8.0 Hz, 2H), 7.64 (d, 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 66.37, 68.61, 75.60, 76.60, 78.40, 79.62, 88.08, 93.39, 112.81, 115.11, 118.11, 119.59, 121.90, 123.75, 125.14, 125.49, 125.98, 129.43, 131.43, 132.12, 132.62, 132.94, 133.35, 147.00, 148.34; HRMS *m*/*z* $[M]^+$ calcd for $C_{39}H_{22}N_2$ 518.1783, found 518.1791.

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Supplementary data

Experimental procedure, characterization details are fully provided. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.05.016.

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13. See Supplementary data for details.
14. Theoretical calculations were carried out on **1**–**14** with benzene rings of phenylene–(poly)ethynylenes fixed in the same plane by using Spartan '08 (Wavefunction, Inc.). Schematic HOMOs and LUMOs of **1**–**14** were shown in Supplementary data together with their energy levels.
15. When emission spectra of Ph_2N/cyano-substituted acetylene **14** were recorded, some decomposition was observed in polar solvents such as DMF and MeCN.
16. This bathochromic shift can be attributed not to excimer formation but to solvent polarity effect because emission spectra of **2** were identical in 10^{-4} M to 10^{-7} M of CH_2Cl_2 solution indicating no sign of excimer formation. See Supplementary data.
17. Solvent dielectric constants ε and refractive indices n were taken from the following: Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd ed.; Taylor & Francis: New York, NY, 2006.
18. This smaller change of dipole moments $\Delta\mu$ could be explained in terms of larger polarization of **14** in the ground state than in the excited state attributed to electron-withdrawing effect of cyano group, but this explanation is unambiguously excluded because of little solvent effect observed in UV/vis absorption spectra.
19. Herein we would like to limit description of syntheses of phenylene(poly)ethynylenes **1**–**14** and their UV/vis absorption and photoluminescence spectral data together with discussion of change of dipole moments $\Delta\mu$ between their excited and ground states because the main issue of this paper is evaluation of electronic effect of acetylenic modes on charge-transferred excited states in donor-π-system/acceptor dyes. As one of reviewers suggested, we are planning to investigate other optoelectronic properties such as two photon absorption and two photon fluorescence of **1**–**14** in the near future.