Synthesis and Chemical Properties of Diacetylenes with Pyridinium and 4,4′-Bipyridinium Groups

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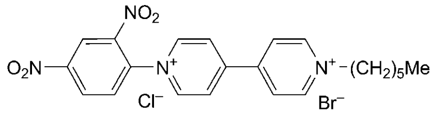
Diacetylenes (DAs) having a dipolar D-π-A structure (D = donor: amino group; $\pi = \pi$-conjugation core; A = acceptor: pyridinium (Py) and bipyridinium (BPy) groups), *i.e.*, **4** (APBPyDA) and **5** (APPyPyDA), or an A-π-A structure, *i.e.*, **7** (DBPyDA) and **8** (PyDA(Cl)), were obtained by 1:1 and 1:2 reactions of 4,4′-(buta-1,3-diyne-1,4-diyl)bis[benzenamine] (APDA; **3**) with 1-(2,4-dinitrophenyl)-1′-hexyl-4,4′-bipyridinium bromide chloride (1:1:1) (**1**), 1-(2,4-dinitrophenyl)-4-(pyridin-4-yl)pyridinium chloride (**2**), or 1-(2,4-dinitrophenyl)pyridinium chloride (**6**) (*Schemes 1* and *2*). The anion-exchange reactions of **8** with NaI and Li(TCNQ) ($TCNQ^-$ = 2,2′-(cyclohexa-2,5-diene-1,4-diylidene)bis[propanedinitrile] radical ion (1−)) yielded the corresponding I^- and $TCNQ^-$ salts **9** (PyDA(I)) and **10** (PyDA(TCNQ)). Compounds **10** and **4** exhibited a UV/VIS absorption due to a charge transfer between the $TCNQ^-$ and the pyridinium groups and a strong solute–solvent interaction of a dipolar solute molecule in the polar environment, respectively. Compounds **8**–**10** exhibited photoluminescence in solution, whereas **4** and **7** did not because of the presence of the 4,4′-bipyridinium quenching groups. Differential-scanning-calorimetry (DSC) measurements suggested that the DAs obtained in this study can be converted into poly(diacetylenes) by thermal polymerization.

Introduction. – Diacetylenes (DAs, *i.e.*, butadiynes) are an important class of compounds that can be converted into functional materials such as polydiacetylenes (PDAs) for third-order nonlinear optical devices [1], thiophene derivatives for organic light-emitting devices [2], and oligoenes/oligoynes for molecular wires [3]. Pyridinium salts have attracted considerable attention because of their applications in cationic surfactants [4], nonlinear optical materials [5], phase-transfer catalysts [6], and also as initiators of cationic polymerization [7]. Similarly, 1,1′-disubstituted 4,4′-bipyridinium salts (viologens) have attracted attention since these species have interesting redox properties and are components of numerous supramolecular systems [8]. Therefore, DAs having pyridinium and 4,4′-bipyridinium moieties are expected to be useful as starting species for the development of new functional materials. Recently, it has been reported that DAs having terminal pyridinium groups exhibit interesting optical properties such as two-photon absorption (TPA); DAs having a dipolar D-π-A structure (D = donor, $\pi = \pi$-conjugation core, A = acceptor) have a large TPA cross-section ($\sigma^{(2)}$) [9]. From these results, DAs having both 4,4′-bipyridinium and electron-donating groups are expected to exhibit interesting optical properties. To the best of our knowledge, however, there have been no reports on DAs having a 4,4′-bipyridinium moiety.

DAs are usually synthesized by the coupling of alk-1-ynes [10]. However, this method is not suitable for the synthesis of D-π-A-type DAs because the cross-coupling reaction of alk-1-ynes with D or A units not only yields the desired D-π-A-type DAs but also homo-coupling D-π-D- and A-π-A-type products.

Recently, we reported two *Zincke* salts, *i.e.*, **1** and **2**, that can react with primary amines to yield various pyridinium and bipyridinium salts [11]. These salts can be useful materials for the synthesis of D-π-A-type DAs. In this work, 4,4′-(buta-1,3-diyne-1,4-diyl)bis[benzenamine] (APDA; **3**) was used as building block for the synthesis of DAs with pyridinium and 4,4′-bipyridinium moieties; the 1:1 and 2:1 reactions of **1** and **2** with **3** yielded D-π-A and A-π-A type DAs ($D = NH_2$, A = pyridinium or bipyridinium), respectively. Herein, we report the synthesis and the optical, electrochemical, and thermal properties of DAs having pyridinium, bipyridinium, and amino groups.



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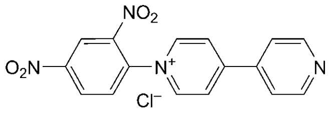

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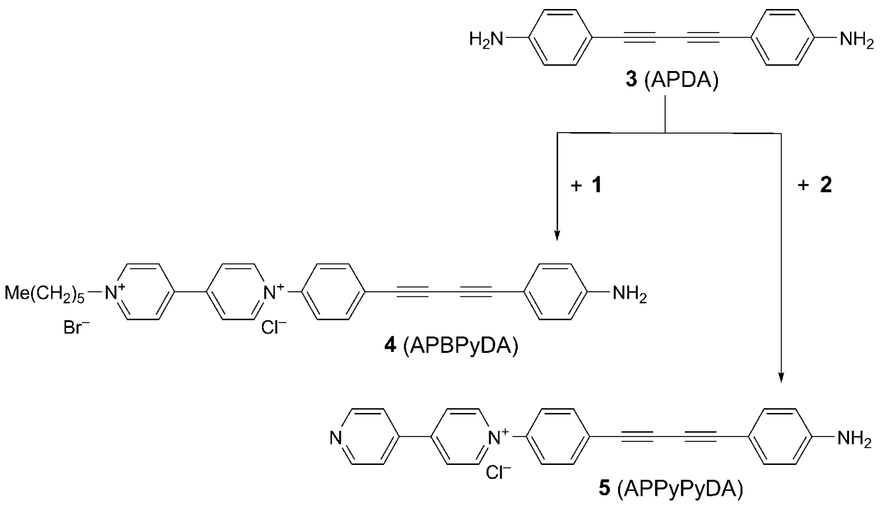
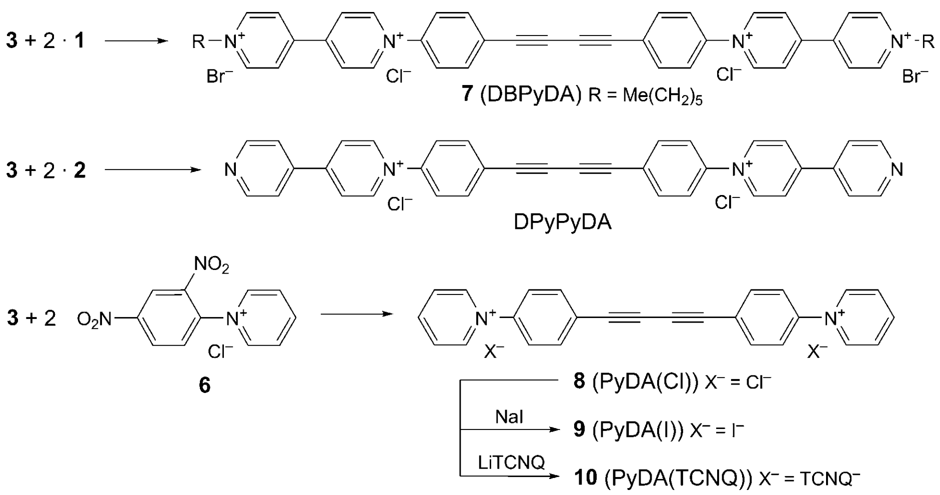
Results and Discussion. – The reactions of bis[benzenamine] **3** with 1-(2,4-dinitrophenyl)-1′-hexyl-4,4′-bipyridinium bromide chloride (1:1:1) (**1**) and 1-(2,4-dinitrophenyl)-4-(pyridin-4-yl)pyridinium chloride (**2**) in a 1:1 molar ratio afforded D-π-A-type **4** (APBPyDA) and **5** (APPyPyDA) in 60% and 66% yield, respectively (*Scheme 1*). The reaction of **3** with **1** or 1-(2,4-dinitrophenyl)pyridinium chloride (**6**) in a 1:2 molar ratio afforded **7** (DBPyDA) or **8** (PyDA(Cl)) in 60% and 42% yield, respectively (*Scheme 2*). It has been reported that the chemical properties and polymerization behavior of DAs with pyridinium rings depend on their counter anions [12]. Among the counter anions, $TCNQ^-$ (radical anion) can form pyridinium salts that exhibit unique optical and electrical properties (TCNQ = 2,2′-(cyclohexa-2,5-diene-1,4-diylidene)bis[propanedinitrile]) [13]. Therefore, anion-exchange reactions were carried out with **8**; its reaction with an excess of NaI and with Li(TCNQ) yielded **9** (PyDA(I)) and **10** (PyDA(TCNQ)) in 54% and 85% yield, respectively (*Scheme 2*). The complete anion exchanges were confirmed by elemental analysis.

The structures of the DAs obtained in this study were determined by ^{1}H- and ^{13}C-NMR spectra and elemental analysis. *Fig. 1* shows the ^{1}H-NMR spectra of **3**, **7**, and **4** in (D_6)DMSO with the signal assignments. The phenylene H-atoms of **7** (DBPyDA) appear as a *s* at δ 8.05. This observation suggests that the bipyridinium and diacetylene groups of **7** have similar electron-withdrawing properties. The signal at δ 5.91 in the ^{1}H-NMR spectrum of **4** (APBPyDA) can be assigned to the H-atoms of NH_2; this assignment is supported by the fact that the signal vanishes on addition of D_2O to the sample. *Fig. 2* shows the ^{1}H-NMR spectra of **8**–**10** in (D_6)DMSO. A signal due to the pyridinium H-atoms H_c in the spectra of **8** (PyDA(Cl)), **9** (PyDA(I)), and **10** (PyDA(TCNQ)) shifts to a higher magnetic field with an increase in the size of the counter anion. However, the chemical shifts of the other signals are independent of the type of counter anions. The presence of a radical anion in $TCNQ^-$ causes the disappearance of its own ^{1}H-NMR signal and the appearance of the low-resolution

Scheme 1. *Synthesis of D-π-A-Type DAs*



Scheme 2. *Synthesis of A-π-A-Type DAs and Their Anion-Exchange Reactions*



^{1}H-NMR signals due to the pyridinium and phenylene H-atoms of **10**. The integrals of the signals support the structures of the above DAs.

The ^{13}C-NMR spectra of the symmetrical compounds **7**–**10** exhibited two signals at δ *ca.* 81 and 75 due to the butadiyne group. In the ^{13}C-NMR spectra of the asymmetrical compounds **4** and **5**, four signals which are assignable to the butadiyne group appeared at δ *ca.* 87, 79, 78, and 71.

Fig. 3 shows the IR spectra of **8** (PyDA(Cl)), **10** (PyDA(TCNQ)), **7** (DBPyDA), and **4** (APBPyDA). The bands due to $\tilde{\nu}(C\equiv C)$ of **8**, **10**, **7**, and **4** depend on the structures of the DAs; **7** and **8** have a symmetrical structure, and they exhibit a weak

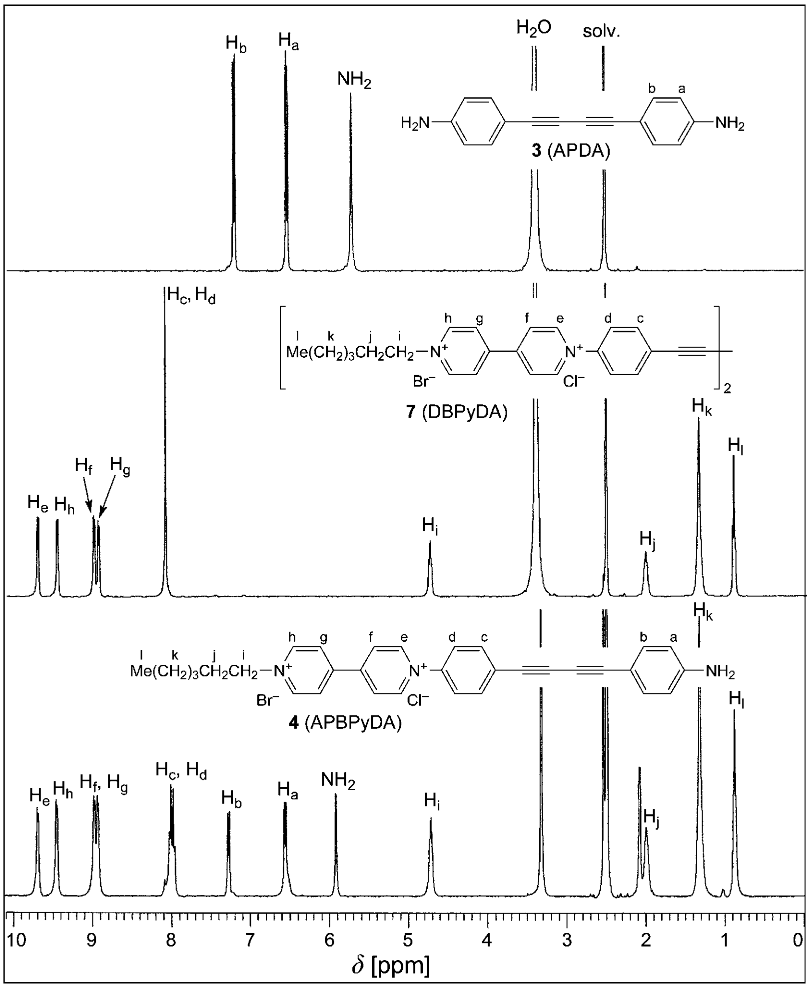


Fig. 1. *^{1}H-NMR Spectra of* **3** (APDA), **7** (DBPyDA), *and* **4** (APBPyDA) *in* (D_6)DMSO

absorption for $\tilde{\nu}(C{\equiv}C)$ at *ca.* 2200 cm^{-1}. This observation corresponds to a small dipole moment in the butadiyne moiety of the DAs having a symmetrical structure. In the IR spectrum of **10**, the absorption for $\tilde{\nu}(C{\equiv}C)$ overlaps with the strong absorption for $\tilde{\nu}(C{\equiv}N)$ of $TCNQ^-$ at 2173 cm^{-1}. In contrast, **4** has an asymmetrical structure, and it exhibits two absorptions at 2160 and 2200 cm^{-1} from the symmetric and asymmetric stretching vibrations of the $C{\equiv}C$ bonds, respectively. This observation is consistent with the fact that the IR spectra of asymmetrical diacetylenes exhibit two absorptions for $\tilde{\nu}(C{\equiv}C)$, as reported previously [14].

The optical data of the DAs obtained in this study are summarized in the *Table*. The UV/VIS spectrum of **8** (PyDA(Cl)) in MeOH exhibits absorptions at *ca.* 250 and 325 nm (*Fig. 4*). In addition to these absorptions, **10** (PyDA(TCNQ)) in MeOH shows

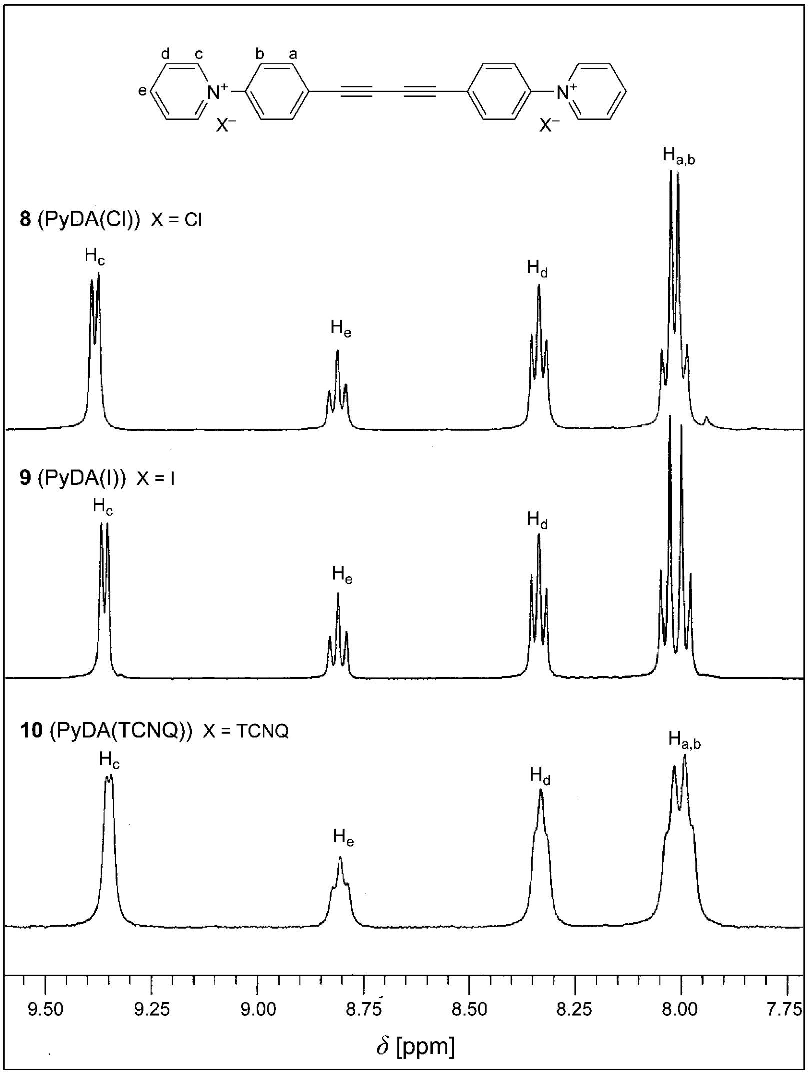


Fig. 2. *^{1}H-NMR Spectra of* **8** (PyDA(Cl)), **9** (PyDA(I)), *and* **10** (PyDA(TCNQ)) *in* (D_6)DMSO

absorptions due to the charge-transfer (CT) bands between TCNQ$^-$ and the pyridinium moiety in the range of 420–838 nm. These wavelengths are similar to those of pyridinium TCNQ$^-$ salts reported previously [13]. The UV/VIS spectrum of **7** (DBPyDA) displays absorptions at longer wavelengths as compared to **8** (PyDA(Cl)) and **4** (APBPyDA) because of the longer π-conjugation system of **7**. However, **4** exhibits a broader band at 328 with an onset position at *ca.* 550 nm. This band is attributed to the strong solute–solvent interaction in the dipolar solute molecule in a polar environment. It has been reported that a dipolar D-π-A-type butadiyne exhibits a broader absorption than a quadrupolar A-π-A-type butadiyne [9].

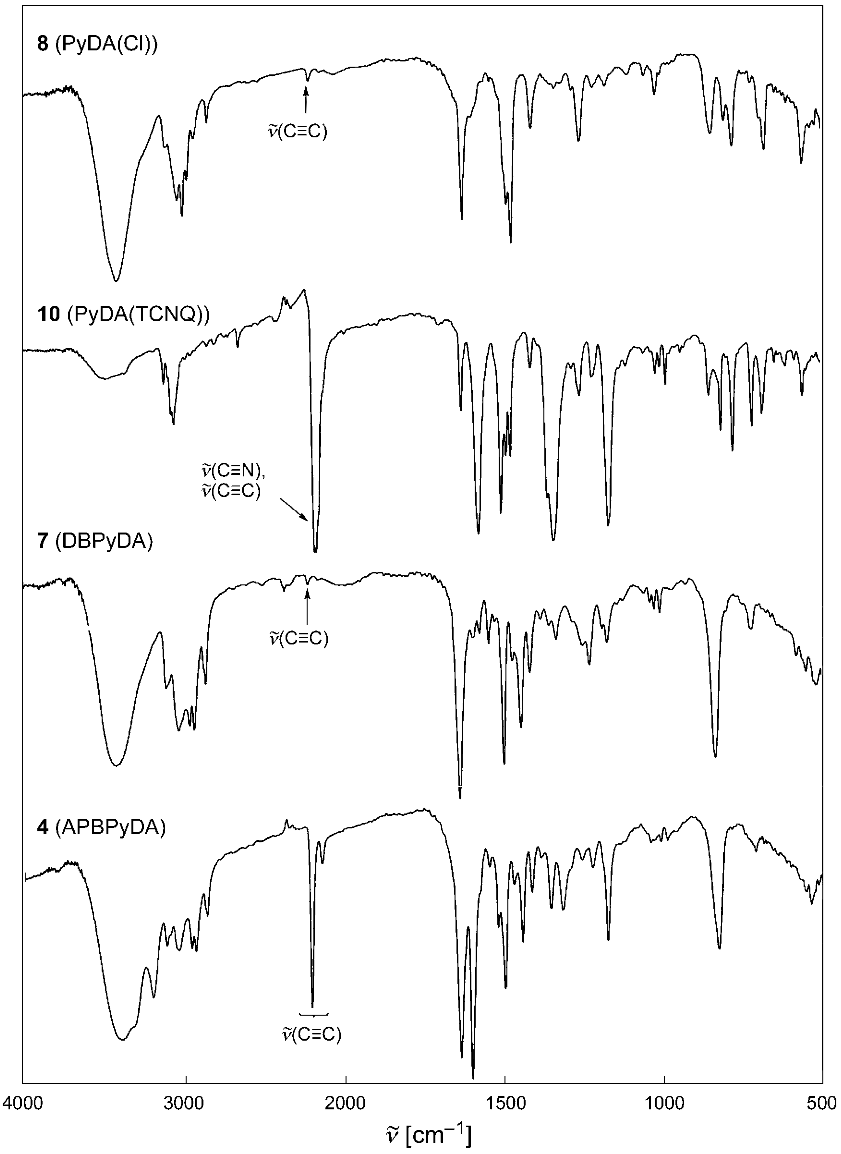


Fig. 3. *IR Spectra of* **8** (PyDA(Cl)), **10** (PyDA(TCNQ)), **7** (DBPyDA), *and* **4** (APBPyDA)

The DAs **8**–**10** were photoluminescent in MeOH, with the wavelengths of the photoluminescence being independent of the counter anions (see *Table*). The DAs **7** and **4** were not photoluminescent, which is consistent with the fact that viologens induce a quenching effect on the photoluminescence of aromatic compounds.

Differential-scanning-calorimetry (DSC) measurements are useful to obtain information on the possibility of thermal polymerization of DAs; the heat (ΔH) of

Table. *Optical and Thermal Properties of DAs*

		Absorption [nm][a])	PL [nm][b])	T_{exo} [°][c])	ΔH [kcal/mol][d])
4	(APBPyDA)	268 (4.38), 328 (4.40)		230	32
5	(APPyPyDA)	255 (4.49), 323 (4.40)		228	29
7	(DBPyDA)	271 (4.56), 355 (4.42)		263	16
8	(PyDA(Cl))	249 (4.79), 324 (4.83)	480	340	23
9	(PyDA(I))	222 (4.72), 325 (4.49)	479	310	15
10	(PyDA(TCNQ))	290 (4.72), 325 (4.46), 422 (4.45), 687 (4.04), 751 (4.55), 768 (4.51), 832 (4.59), 851 (4.73)	481	240	17

a) In MeOH; log ε in parentheses. b) Photoluminescence (PL) in MeOH. c) Temperature at which an exothermic peak was observed. d) Heat of polymerization estimated from the integral of the exothermic peak.

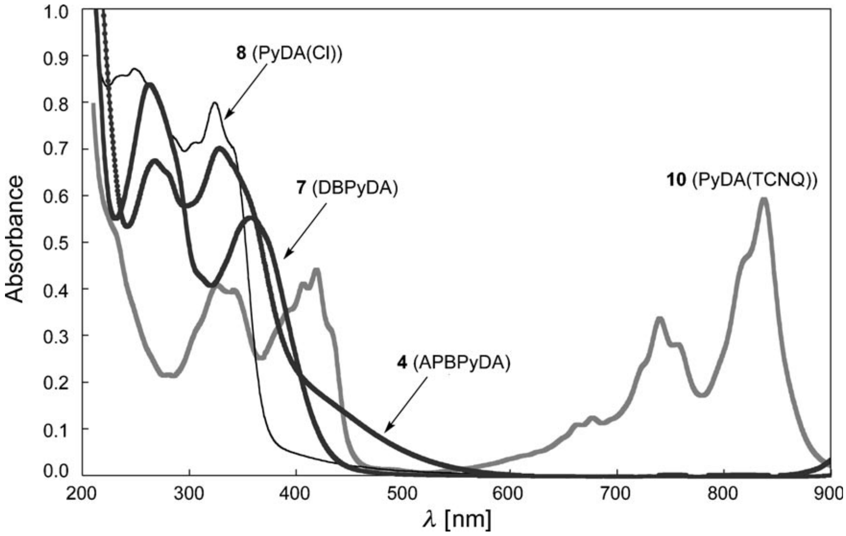


Fig. 4. *UV/VIS Spectra of* **8** (PyDA(Cl)), **10** (PyDA(TCNQ)), **7** (DBPyDA), *and* **4** (APBPyDA) *in MeOH*

1,4-addition polymerization of DAs that can be estimated from the integral of an exothermic peak is in the range of 30–37 kcal/mol [15]. The DSC curves of **8** (PyDA(Cl)) and **7** (DBPyDA) exhibited an exothermic peak at 340° and 263°, respectively; at this point, the heats of polymerization (ΔH) were estimated to be 23 and 16 kcal/mol, respectively (see *Table*). These ΔH values are comparable to those of the conventional 1,4-addition polymerization of DAs [15], suggesting that **7** and **8** can be converted into 1,4-addition poly(diacetylenes) by thermal polymerization. The *Table* summarizes the temperatures at which the exothermic peak of **9** (PyDA(I)), **10** (PyDA(TCNQ)), and **4** (APBPyDA) was observed and the ΔH values estimated from the integral of the exothermic peak. In the series of DAs **8**–**10** with pyridinium rings, the temperature at which the exothermic peak was observed decreased with the size of the counter anion. This behavior is in agreement with the assumption that the bulky counter anions prevent the packing of the DA molecules that can easily cause thermal polymerization.

The results demonstrate that new DAs can be obtained by reaction of *Zincke* salts with 4,4′-(buta-1,3-diyne-1,4-diyl)bis[benzenamine] (**3**), and that the thermal polymerization of DAs may provide new functional materials.

Experimental Part

General. Solvents were dried, distilled, and stored under N_2. The 1-(2,4-dinitrophenyl)pyridinium chloride (1:1) (**6**) [16], 1-(2,4-dinitrophenyl)-1′-hexyl-4,4′-bipyridinium bromide chloride (1:1:1) (**1**) [11a], 1-(2,4-dinitrophenyl)-4-(pyridin-4-yl)pyridinium chloride (=1-(2,4-dinitrophenyl)-4,4′-bipyridinium chloride (1:1); (**2**) [11b], and Li(TCNQ) [17] were prepared according to the literature. Other reagents were purchased and used without further purification. Reactions were carried out with standard *Schlenk* techniques under N_2. DSC Measurements: *Shimadzu-DSC-50* instrument.

UV/VIS Spectra: *Jasco-V-560* spectrometer. Photoluminescence: *Jasco-FP-6200* spectrometer. IR Spectra: *Jasco-FT/IR-660-Plus* spectrophotometer. NMR Spectra: *Jeol-AL-400* spectrometer; δ in ppm, J in Hz. Elemental analyses: *Yanagimoto-MT-5* CHN analyzer.

4,4′-(Buta-1,3-diyne-1,4-diyl)bis[benzenamide] (**3**; APDA). $Cu(OAc)_2$ (0.91 g, 5.0 mmol) was added to a soln. of 4-ethynylbenzenamine (0.23 g, 2.0 mmol) in pyridine/MeOH 1:1 (*v*/*v*; 20 ml). After the soln. was stirred at 20° for 24 h, the solvents were evaporated, and the resulting solid was extracted with acetone. The acetone was evaporated and the resulting solid washed with H_2O and dried *in vacuo*: **3** (0.21 g, 99%). Brown powder. ^{1}H-NMR (400 MHz, (D_6)DMSO; *cf. Fig. 1*): 7.18 (*d*, J = 8.4, 4 H); 6.50 (*d*, J = 8.4, 4 H): 5.69 (br., 4 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 150.1; 133.5; 113.5; 106.4; 82.9; 72.0. Anal. calc. for $C_{16}H_{12}N_2$: C 82.73, H 5.21, N 12.06; found: C 82.60, H 5.41, N 12.29.

1,1″-(Buta-1,3-diyne-1,4-diyldi-4,1-phenylene)bis[1′-hexyl-4,4′-bipyridinium] Bromide Chloride (1:2:2) (**7**; DBPyDA). Bis[benzamine] **3** (0.23 g, 1.0 mmol) and **1** (1.6 g, 3.0 mmol) were dissolved in DMSO (15 ml) at 90°. After the mixture was stirred at 90° for 24 h, the solvent was evaporated and the resulting solid washed with acetone and extracted with hot H_2O (*ca.* 95°). After evaporation of the H_2O, the resulting solid was washed with MeOH (5 ml) and dried *in vacuo*: **7** · H_2O (0.54 g, 60%). Yellow powder. ^{1}H-NMR (400 MHz, (D_6)DMSO; *cf. Fig. 1*): 9.69 (*d*, J = 6.4, 4 H); 9.45 (*d*, J = 6.4, 4 H); 8.99 (*d*, J = 6.8, 4 H); 8.93 (*d*, J = 6.4, 4 H); 8.05 (*s*, 8 H); 4.69 (*t*, J = 7.2, 4 H); 1.96 (*t*, J = 6.4, 4 H); 1.28 (*s*, 12 H); 0.84 (*t*, J = 7.2, 6 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 149.6; 148.0; 145.90; 145.87; 142.7; 134.3; 126.8; 126.5; 125.8; 123.4; 81.4; 75.6; 60.9; 30.8; 30.6; 25.1; 21.9; 13.9. Anal. calc. for $C_{48}H_{50}Br_2Cl_2N_4 \cdot H_2O$: C 61.88, H 5.63, N 6.01; found: C 62.01, H 5.70, N 5.89.

1-{4-[4-(4-Aminophenyl)buta-1,3-diyn-1-yl]phenyl}-1′-hexyl-4,4′-bipyridinium Bromide Chloride (1:1:1) (**4**; APBPyDA). Bis[benzenamine] **3** (0.35 g, 1.5 mmol) and salt **1** (0.39 g, 0.75 mmol) were dissolved in DMSO (22 ml). After the mixture was stirred at 90° for 24 h, the solvent was evaporated and the resulting solid washed with acetone and extracted with hot H_2O (*ca.* 95°). The solvent was evaporated and the resulting solid dried *in vacuo*: **4** · 0.4 H_2O (0.54 g, 60%). Brown powder. ^{1}H-NMR (400 MHz, (D_6)DMSO; *cf. Fig. 1*): 9.69 (*d*, J = 6.4, 2 H); 9.45 (*d*, J = 6.0, 2 H); 8.97 (*d*, J = 6.4, 2 H); 8.93 (*d*, J = 6.4, 2 H); 8.01 (*d*, J = 8.4, 2 H); 7.97 (*d*, J = 8.4, 2 H); 7.27 (*d*, J = 8.8, 2 H); 6.56 (*d*, J = 8.8, 2 H); 5.91 (*s*, 2 H); 4.72 (*t*, J = 7.2, 2 H); 1.99 (br. *s*, 2 H); 1.31 (*s*, 6 H); 0.88 (*t*, J = 6.4, 3 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 151.1; 149.4; 148.0; 145.9; 145.7; 141.9; 134.1; 133.6; 126.8; 126.5; 125.5; 124.6; 113.6; 104.7; 86.5; 79.1; 77.7; 71.0; 60.8; 30.8; 30.6; 25.1; 21.9; 13.8. Anal. calc. for $C_{32}H_{31}BrClN_3 \cdot 0.4\ H_2O$: C 66.25, H 5.52, N 7.24; found: C 66.27, H 5.70, N 7.11.

1-{4-[4-(4-Aminophenyl)buta-1,3-diyn-1-yl]phenyl}-4,4′-bipyridinium Chloride (1:1) (**5**; APPyPyDA). As described for **4**, with **3** and **2**: **5** · 0.5 H_2O (66%). ^{1}H-NMR (400 MHz, (D_6)DMSO): 9.51 (*d*, J = 6.4, 2 H); 8.91 (*d*, J = 5.2, 2 H); 8.81 (*d*, J = 6.4, 2 H); 8.16 (*d*, J = 5.2, 2 H); 7.98 (*d*, J = 8.8, 2 H); 7.94 (*d*, J = 8.4, 2 H); 7.27 (*d*, J = 8.4, 2 H); 6.56 (*d*, J = 8.0, 2 H); 5.91 (*s*, 2 H). ^{13}C-NMR (100 MHz, (D_6)DMSO):

151.0; 149.4; 147.9; 145.9; 145.6; 142.0; 134.1; 133.0; 126.7; 126.5; 124.9; 111.9; 104.0; 86.9; 79.0; 77.5; 70.8. Anal. calc. for $C_{26}H_{18}ClN_3 \cdot 0.5\ H_2O$: C 74.90, H 4.59, N 10.08; found: C 75.05, H 4.70, N 10.37.

1,1′-(Buta-1,3-diyne-1,4-diyldi-4,1-phenylene)bis[pyridinium] Chloride (1:2) (**8**; PyDA(Cl)). Bis[benzenamine] **3** (0.75 g, 3.2 mmol) and **6** (2.7 g, 9.6 mol) were dissolved in DMSO (9 ml) and stirred at 90° for 48 h. The solvent was evaporated and the resulting solid extracted with H_2O. The solvent was evaporated and the resulting solid washed with acetone and dried *in vacuo*: **8** (0.57 g, 42%). Brown powder. ^{1}H-NMR (400 MHz, (D_6)DMSO; *cf. Fig. 2*): 9.38 (*d*, $J = 5.6$, 4 H); 8.81 (*t*, $J = 8.0$, 2 H); 8.34 (*t*, $J = 7.2$, 4 H); 8.03 (*d*, $J = 8.8$, 4 H); 7.98 (*d*, $J = 8.8$, 4 H). ^{13}C-NMR (100 MHz, D_2O): 147.6; 144.9; 143.5; 135.1; 129.0; 125.2; 125.1; 81.3; 76.3. Anal. calc. for $C_{26}H_{18}Cl_2N_2$: C 72.73, H 4.23, N 6.52; found: C 72.59, H 4.11, N 6.37.

1,1′-(Buta-1,3-diyne-1,4-diyldi-4,1-phenylene)bis[pyridinium] Iodide (1:2) (**9**; PyDA(I)). An aq. soln. (5 ml) of NaI (1.8 g, 1.2 mmol) was added dropwise to an aq. soln. (5 ml) of **8** (0.093 g, 0.30 mmol). After 6 h stirring at 20°, the solvent was evaporated and the resulting solid washed with acetone and dried under vacuum: **9** (0.10 g, 54%). Light brown powder. ^{1}H-NMR (400 MHz, (D_6)DMSO; *cf. Fig. 2*): 9.36 (*d*, $J = 5.6$, 4 H); 8.81 (*t*, $J = 8.0$, 2 H); 8.34 (*t*, $J = 7.2$, 4 H); 8.03 (*d*, $J = 8.8$, 4 H); 7.98 (*d*, $J = 8.8$, 4 H). ^{13}C-NMR (100 MHz, D_2O): 147.4; 144.6; 143.3; 135.1; 128.9; 125.0; 125.0; 81.3; 76.3. Anal. calc. for $C_{26}H_{18}I_2N_2$: C 51.01, H 2.96, N 4.58; found: C 50.54, H 2.99, N 3.77.

1,1′-(Buta-1,3-diyne-1,4-diyldi-4,1-phenylene)bis[pyridinium] 2,2′-(Cyclohexa-2,5-diene-1,4-diylidene)bis[propanedinitrile] Radical Ion (1−) (1:1) (**10**; PyDA(TCNQ)). An aq. soln. (5 ml) of Li(TCNQ) (0.52 g, 2.4 mmol) was added dropwise to an aq. soln. (5 ml) of **9** (0.11 g, 0.18 mmol). After the mixture was stirred at 20° for 6 h, the precipitate was collected from the mixture by filtration, washed with acetone, and dried *in vacuo*: **10** · 0.1 H_2O (0.096 g, 85%). Bluish purple powder. ^{1}H-NMR (400 MHz, (D_6)DMSO; *cf. Fig. 2*): 9.35 (*d*, $J = 4.4$, 4 H); 8.81 (2 H); 8.33 (4 H); 8.03 (4 H); 7.98 (4 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 147.1; 145.1; 143.3; 134.4; 128.2; 125.7; 122.9; 81.2; 75.1. Anal. calc. for $C_{50}H_{26}N_{10} \cdot 0.1\ H_2O$: C 78.13, H 3.44, N 18.22; found: C 78.19, H 3.39, N 18.40.

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