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Quinoline-Containing, Conjugated Poly(aryleneethynylene)s: Novel Metal and H^+-Responsive Materials

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ABSTRACT: We describe the synthesis of novel copolymers containing quinoline, benzene, and alkyne groups by a Pd-catalyzed Heck−Cassar−Sonogashira−Hagihara reaction. Direct iodination of quinoline by a mixture of iodine, potassium periodate, and sulfuric acid in chloroform gives 3,6-diiodoquinoline. 3,6-Diiodoquinoline was coupled to 1,4-diethynyl-2,5-bis(2-ethylhexyl)benzene, and 3,6-diethynylquinoline was coupled to 1,4-diiodo-2,5-bis(2-ethylhexyloxy)benzene. The polymers formed in good-to-excellent yields with a degree of polymerization (P_n) ranging from 11 to 95 and polydispersities (M_w/M_n) from 1.8 to 3.3. Their optical properties (i.e., absorption and emission) were shown to be dramatically dependent upon the presence of protons and to a lesser extent metal cations. The change in fluorescence upon protonation is different for the alkyl- and alkoxy-substituted polymer. In the alkyl case bright yellow fluorescence is observed upon protonation, while for the alkoxy case the polymer's fluorescence is quenched upon addition of acid at polymer concentrations > 0.1 mg L^{-1}.

Introduction

In this contribution, we describe the synthesis of the unknown 3,6-diiodoquinoline and novel conjugated copolymers of the aryleneethynylene type[1] consisting of alternating benzene, acetylene, and 3,6-quinoline units (**8**, **10**, **12**). When protonated, dialkyl-substituted polymer **8** exhibits bathochromically shifted, brilliantly yellow fluorescence.

Conjugated polymers (CP) are organic semiconductors and as such important in applications that include light-emitting diodes, thin film transistors, and plastic lasers.[1−5] They likewise have received ample attention as active components in sensors.[6] The sensing ability of conjugated polymers can be enhanced either by the appendage of a recognition element as described by Bäuerle, Swager, and others[6,7] or alternatively by the substitution of a C−H group by heteroatoms, preferably nitrogen, into the main chain of the conjugated polymer under consideration. Jenekhe, Schanze, Wasielewski, Eichen, Tour, Klemm, Meijer, and others have amply demonstrated this principle by introducing quinoline, pyridine, bipyridine, or phenanthroline moieties into conjugated polymers.[8−16] Interesting results were obtained by Wasielewski,[10] who demonstrated that bipyridine−poly(*p*-phenylenevinylene) hybrids show sensory properties for transition metal salts in both absorption and emission. He discovered that Pd^{2+} and some lanthanides had a great effect upon λ_{max} in absorption. Intrigued by these results, we have prepared a series of unknown quinoline-containing poly(aryleneethynylene)s **8**, **10**, and **12**, and studied their optical properties with respect to protonation and metal cation coordination.

Results

Syntheses. The direct iodination of quinoline has been reported to give 5,8-diiodoquinoline (**4**),[16b] electrophilic iodination commences in the two most active positions of this interesting heterocycle (Scheme 1). We could not obtain **4**. Under the iodination conditions (I_2/KIO_4/H_2SO_4/$CHCl_3$) utilized, an isomer of **4** formed according to NMR and analytical data. To obtain structural proof of the substitution pattern, we coupled the isolated diiodide with trimethylsilylacetylene under standard Pd catalysis, deprotected, and reacted in a second Pd-catalyzed coupling step with *o*-iodoanisole (Scheme 1). The substitution product was highly crystalline and gave a suitable specimen for single-crystal structure analysis from dichloromethane.[17] The iodination had occurred in the 3,6-position leading to the unknown 3,6-diiodoquinoline and subsequently to **6** (Figure 1). We had started our project under the premise to obtain 5,8-diiodoquionline (**4**) and examine its oligomeric models and its polymers. The facile access to **2** however was of great interest when exploring the synthesis of novel poly(heteroaryl eneethynylene)s.

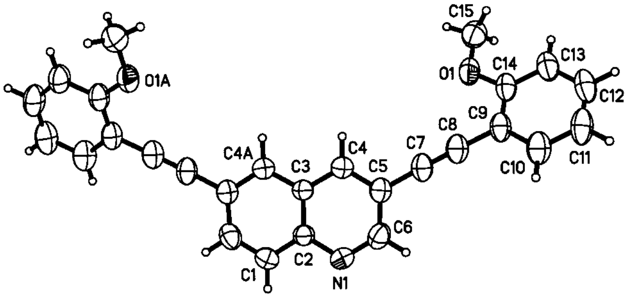

Figure 1. ORTEP plot of **6**. The anisotropic displacement parameters are shown at the 50% probability level. Bond length and bond angles are in excellent agreement with the expected values.

Reaction of **2** with 1,4-diethynyl-2,5-bis(2-ethylhexyl)benzene (**7**)[18] under Pd catalysis in piperidine furnished polymer **8** in a 93% yield with a degree of polymerization (P_n) of 37 and a polydispersity (M_w/M_n, PDI) of 3.3. Polymer **10** was obtained by reaction of 3,6-diethynylquinoline (**3**) with 1,4-diiodo-2,5-bis(2-ethylhexyloxy)benzene **9**[1b] under identical conditions in an 88% yield with a P_n of 95 (PDI = 3.1). In both polymers, **8** and **10**, the

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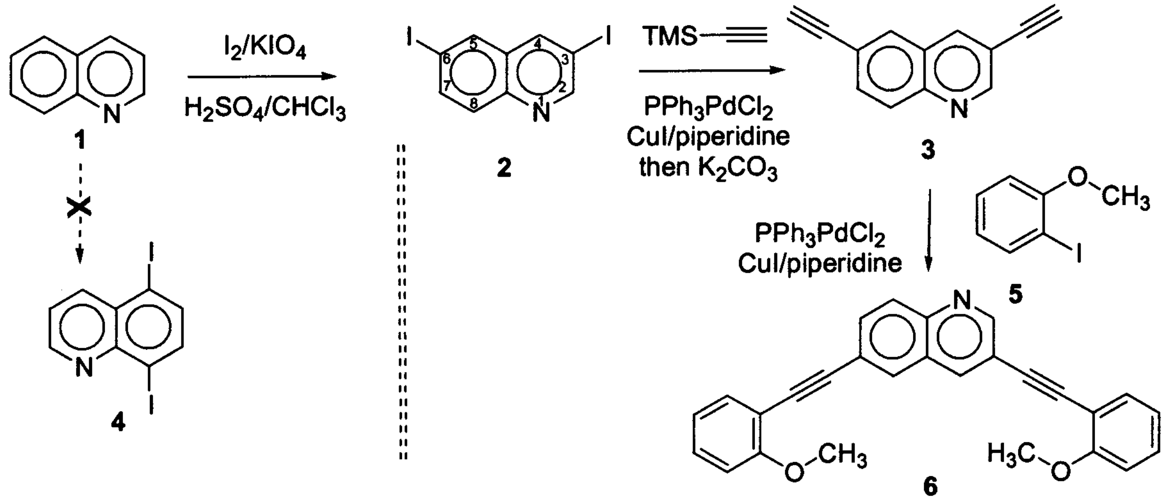
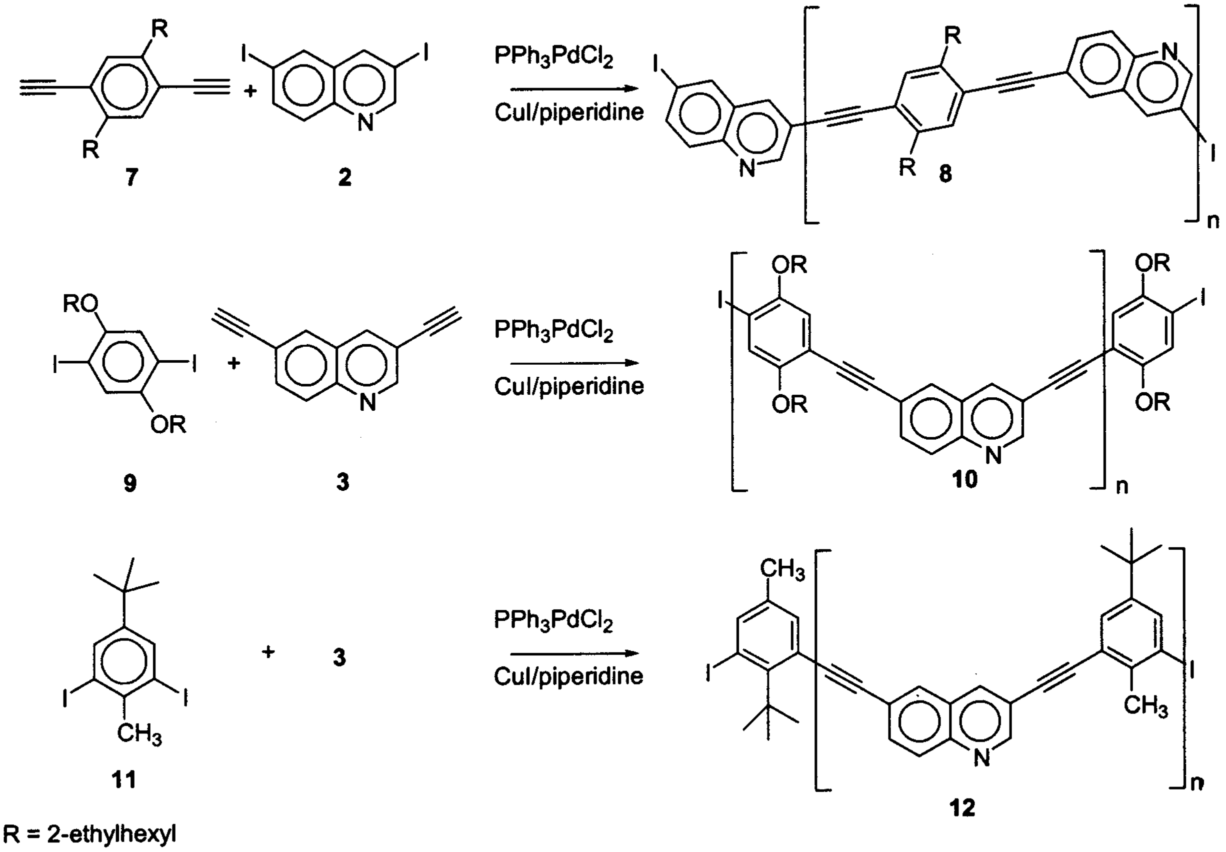
Scheme 1



Scheme 2



orientation of the quinoline units in the chain with respect to each other is random, as can be extracted from their ^{1}H and ^{13}C NMR spectra. The third, effectively nonconjugated, polymer **12** (86%; $P_n = 11$, $M_w/M_n = 1.8$) could be synthesized when **3** and **11** were coupled under Pd catalysis. Similarly, the orientation of the quinoline units in **12** is random according to NMR spectroscopy.

The quinoline-containing polymers were isolated by precipitation into methanol after careful washing with dilute ammonia solution. They are light-yellow or orange powders soluble in chloroform, dichloromethane, and organic acids such as trifluoroacetic acid (TFA) or acetic acid. Polymer **10** had to be heated for several hours in chloroform before it dissolved completely. All of the polymers are air, water, and light stable but decompose above 150 °C under darkening (polarizing microscopy). Samples of **8**, **10**, and **12** produce thin films and show shear-induced birefringence.

Optical and Ion Responsive Properties in Absorption. Dilute solution of **8** in chloroform are light yellow, with a λ_{max} of 380 nm. Addition of methanol induces aggregation and the development of a shoulder at 405 nm (Figure 2a). The aggregation behavior resembles that of the poly(fluorenyleneethynylene)s[19] and dialkyl(poly-*p*-phenyleneethynylene)s.[20] In mixtures of acetic acid and chloroform, **8** displays UV–vis spectra which are superimposable to those obtained by methanol addition.

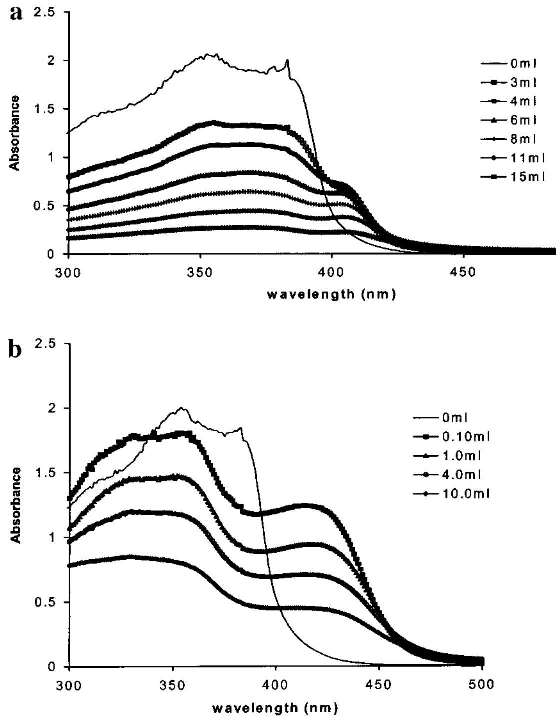


Figure 2. (a) Absorption spectrum of **8** in $CHCl_3$ when acetic acid is added. The same set of spectra is recorded if methanol is added to a solution of **8** in $CHCl_3$. (b) Absorption spectrum of **8** in $CHCl_3$ with addition of trifluoroacetic acid.

Table 1. Absorption Spectra (λ in nm) for Polymers 8, 10, and 12 at 298 K in Chloroform or Dichloromethane in Their Pristine Form and in the Presence and Absence of Metal Ions and Proton

		λ_{max}		
run	metal ion	polymer **8**	polymer **10**	polymer **12**
1	ion free	380 in $CHCl_3$ 406 in MeOH	401 in $CHCl_3$	310, 368
2	protonation H^+	408 with acetic acid 418 with TFA	347, 447	297, 333, 400
3	Pd^{2+}	350, 402	442	327
4	Ag^+	361, 400	441	310, 370
5	Fe^{2+}	347, 381	331, 400	330
6	Fe^{2+}		404	327
7	Ni^{2+}	350, 380	399	310, 369
8	Mn^{2+}	349, 381	399	303, 370
9	La^{2+}	350, 380	400, 452	308, 370
10	Cu^{2+}	352, 381	399	326, 371
11	Al^{2+}	352, 382	nd	308, 369
13	Zn^{2+}	350, 389	399	308, 369

Trifluoroacetic acid is more acidic than acetic acid, and its addition to a solution of **8** in chloroform leads to a substantial change in λ_{max} from 380 to 418 nm ($\Delta\lambda_{max}$ = 38 nm (protonated form Figure 2b). Addition of metal cations (see Table 1) to solutions of **8** leave its absorption spectrum mostly unchanged. The nonconjugated polymer **12** resembles **8** in many respects and also shows a bathochromic shift of 32 nm in its UV-vis spectrum upon protonation with TFA, while addition of metal salts leaves the absorption spectra of **12** (see Table 1) unaltered.

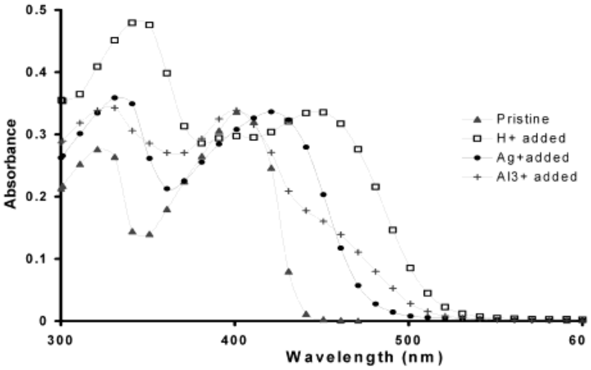


Figure 3. Absorption spectrum of polymer **10** pristine, after addition of trifluoroacetic acid, $AgBF_4$, and $Al_2(SO_4)_3$.

Solutions of **10** display a light orange color and show a larger change in λ_{max} (from 401 to 447 nm, $\Delta E = 0.32$ eV; Figure 3) upon protonation with TFA. A second absorption at higher energy experiences a smaller bathochromic shift (from 331 to 344 nm; 0.14 eV) upon protonation. Similar bathochromic shifts are observed when chloroform solutions of **10** are treated with solutions of Pd^{2+} or La^{3+} salts dissolved in a small amount of methanol (Table 1). However, if Ag^+ is added to a solution of **10**, an ionochromic effect is visible but less pronounced, and a λ_{max} of 422 nm results (Figure 3). The cations Ni^{2+}, Mn^{2+}, Cu^{2+}, and Zn^{2+} do not change the absorption spectrum of **10**, similar to the observations made for **8** and for **12**. The UV−vis spectrum of polymer **10** is most of all affected investigated polymers upon protonation or coordination of Pd^{2+}, La^{3+}, and Ag^+ cations.

Fluorescence Behavior of 8, 10, and 12. Polymer **8** is blue fluorescent in chloroform solution and emitted at 399 nm. If **8** was treated with TFA in a moderately dilute solution (**8**: 5 mg L^{-1}) the original fluorescence disappeared, and a broad emission at 509 nm emerged (Figure 4a). Addition of more TFA led to a slight intensity decrease and shift to 524 nm. Upon addition of very small amounts of TFA no intermediate states could be detected. If the much weaker acetic acid is used to titrate **8**, a decrease of the two bands at 399 and 413 nm is observed, while a new maximum appeared at 515 nm. Only after the addition of a substantial amount of acetic acid, the original emission features disappeared (Figure 4b).

Most metal ions (Table 2) weaken or quench the fluorescence of **8**, but Fe^{3+} and Al^{3+} show an effect upon the fluorescence (weak emission at 505 nm), which is similar to that observed upon protonation. We attribute this behavior to the acidity of the hexaquo ions of iron(III) and aluminum(III) according to $M(H_2O)_6^{3+} + H_2O \rightarrow M(H_2O)_5(OH)^{2+} + H_3O^+$. The emission behavior of **12** resembles that of **8** with respect to both protonation and metal salt complexation (Table 2).

To our surprise, the dialkoxy polymer **10** shows complete quenching of its fluorescence upon addition of TFA at a concentration of 5 mg L^{-1} (Figure 5a), and we did not see the appearance of a bathochromically shifted emission. In this concentration range, self-absorption is not significant.[20] If the polymer solution of **10** was diluted to 0.025 mg L^{-1}, fluorescence persisted upon addition of TFA and was slightly red-shifted with respect to the original emission. Metal salts likewise generally quenched the emission of **10** or left it unchanged. Particularly interesting is that Al^{3+} and Fe^{3+} quench the emission of **10** in a protic environment pointing to the hydrolysis of their hexaquo ions.

Discussion

The alkyl-chain-substituted polymers **8** and **12** resemble each other in absorption and emission. We will

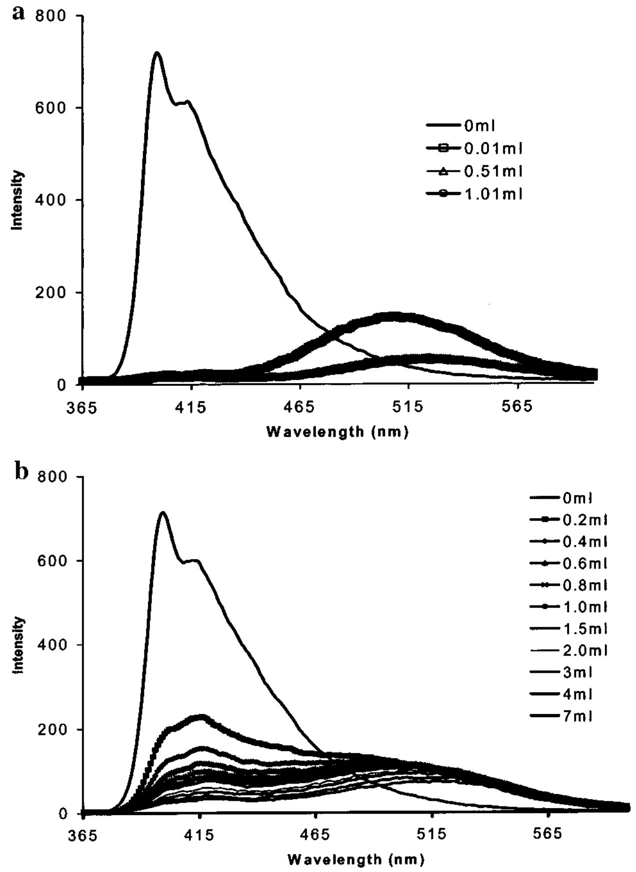


Figure 4. (a) Bathochromic shift of the fluorescence of **8** observed upon addition of TFA. (b) Decrease in fluorescence of **8** is observed upon continuous addition of acetic acid.

Table 2. Emission Spectra for Polymers 8, 10, and 12 at 298 K in Chloroform or Dichloromethane in Their Pristine Form and in the Presence and Absence of Metal Ions and Proton

		λ (nm)		
run	metal ion	polymer **8**	polymer **10**	polymer **12**
1	ion free	399, 417	437	381
2	protonation H^+	505–524, broad	quenched	496
3	Pd^{2+}	422	quenched	quenched
4	Ag^+	quenched, 422 (weak int)	quenched	383
5	Fe^{2+}	417	437	383
6	Fe^{2+}	504 (weak int)	quenched	384
7	Ni^{2+}	411	437	383
8	Mn^{2+}	417	437	383
9	La^{2+}	417	437	383
10	Cu^{2+}	417	437	383
11	Al^{2+}	520 (weak int)	quenched	383
12	Pb^{2+}	417	437	383, 589
13	Zn^{2+}	417	437	383

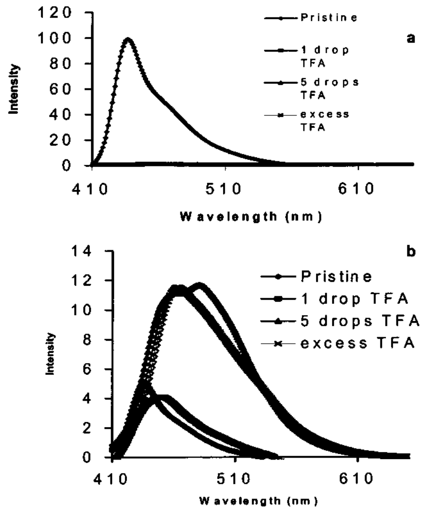


Figure 5. Emission spectrum of **10** in the presence of TFA at two different concentrations: (a) 5 mg/L, (b) 0.025 mg/L.

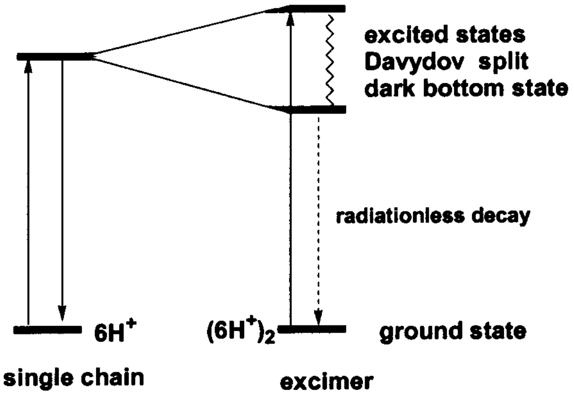


Figure 6. Emission behavior of protonated chains of **10**, with and without excimer formation.

discuss the optical properties of **8**, which are almost superimposable to the optical properties of **12**, while the dialkoxy polymer **10** shows a distinctly different behavior. Polymer **12** is formally cross-conjugated due to the presence of the meta-benzene linkages, but **8** shows similar conjugation to most poly(aryleneethynylene)s leading to a 12 nm bathochromic shift in its solution UV–vis spectrum if compared to **12**. Polymer **8** shows a distinct aggregation behavior (Figure 2a) upon addition of either methanol or acetic acid (!).[19,20] Acetic acid is not acidic enough to protonate **8** in the ground state; however, it induces aggregation. The UV–vis spectroscopic signature of the aggregates looks similar to those observed in other PPE types[19,20], and is suggestive of planarization of the backbone under maximization of conjugation. The shift of 26 nm is small compared to the one recorded for the PPEs (380–439 nm) under similar conditions. If TFA is added to solutions of **8** in chloroform (Figure 2b), protonation leads to a distinctly red-shifted, intense broad band at 420 nm. As a consequence, aggregation and protonation are decoupled in the electronic ground state of **8**. Polymer **12** behaves similarly. Pd^{2+} and Ag^+ lead to a significant bathochromic shift in the absorption spectrum of **8**, similarly as to observed upon the addition of methanol. However, the UV–vis spectrum of **12** is virtually unchanged by the addition of those metal salts (Table 1).

The change in the *emission* spectrum of **8** upon protonation with TFA is remarkable (Figure 4a), because it features a brilliantly yellow emission band at 504 nm in acid that shifts to 524 nm after addition of a large excess of TFA. The large half-width of the emission suggests an intramolecular charge-transfer band. The lifetimes of polymer **8**'s emission in its protonated and unprotonated forms were below 1 ns, excluding excimer formation. The emission at 504 nm is due to the polymer, in which only every second quinoline unit is protonated, while the feature at 524 nm would represent fluorescence of the fully protonated species **8H**$^+$. Small amounts of TFA (10–100 μL) are sufficient to switch the emission of **8**, but the presence of acetic acid leads to a gradual change in emission from 417 to 504 nm, suggesting that partially protonated **8** is in equilibrium with its basic nonprotonated form. Acetic acid leads to aggregation of polymer **8** in its ground state but not to protonation. However, in the excited state, protonation occurs according to the fluorescence data, suggesting that **8** is considerably more basic in its excited than in its ground state, similarly to the related dipyridophenazines, for which the LUMO is centered mainly at the phenazine nitrogens.[21,22] The emission spectra of **8** in the presence of metal cations display a weak feature at $>$500 nm for Fe^{3+} and Al^{3+} both which are hydrolyzed to provide protons. We interpret the behavior of **8** as being primarily due to protonation and not metal complexation.

The alkoxy-substituted polymer **10** (Figure 3) features large bathochromic shifts upon protonation as well as metal salt coordination. An explanation for this behavior is not clear, but may involve a substantial intramolecular charge-transfer character in these donor−acceptor substituted polymers.

Emission of **10** in its protonated form is critically dependent upon its concentration.[20] Upon addition of TFA to solutions of **10** (5 mg L^{-1}); the fluorescence disappears, while at 0.025 mg L^{-1}, a red-shifted emission is observed in strongly acidic solution. This behavior was somewhat surprising, but the formation of an excimer complex with a nonemissive lowest lying excited state is known to occur in aggregates, and explains the behavior if the dimerization of partially protonated chains of **10** into excimers is assumed.[22] At very low concentration such excimers would not form, and thus emission from single polymer chains would be expected and is observed. The emission is shifted from 437 to 462 nm due to formation of **10H$^+$**.

In conclusion, quinoline-containing poly(aryleneethynylene)s can be prepared by conventional Pd-catalyzed couplings. Depending upon their solubilizing groups, these polymers display a remarkable variation in their optical behavior with respect to emission and absorption. Protonation of these heterocyclic and basic polymers has a large effect upon their optical properties, leading in the case of **10** to a bathochromically shifted absorption and in the case of **8** to brilliant yellow and strong fluorescence. In the future we will report upon the synthesis and properties of the corresponding poly(aryleneethynylene)s that incorporate quinolines featuring a 5,8-substitution pattern.

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Note added in proof: Very recently Jenekhe[24] published the synthesis of quinoline-containing poly(aryleneethynylene)s of similar structure.

Supporting Information Available: Experimental and spectroscopic details for synthesis of and spectroscopic examination of **2**, **3**, **6**, **8, 10**, and **12** as well as details of the solution of the X-ray crystal structure of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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