Functionalization of 9-(Dicyanomethylene)fluorene Derivatives with Substituted Acetylenes

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Treatment of (2,7-dibromo-9H-fluoren-9-ylidene)malononitrile (**1**) with excesses of substituted acetylenes RC≡CH [R = Ph, MeC$_6$H$_4$, (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$)] under Sonogashira coupling catalytic conditions afforded novel 9-[cyano(ethynyl)methylene]fluorene derivatives **2–4**, respectively, in moderate yields. In these reactions, facile functionalization occurs at the 9-methylene position in the fluorene, one of the cyano groups being substituted by an acetylide moiety. In order to prepare the 2,7-diethynyl-substituted 9-(dicyanomethylene)-fluorene compounds **8–10**, palladium-catalyzed coupling reactions between 2,7-dibromofluoren-9-one and RC≡CH in a

1:2 molar ratio first have to be carried out, initially resulting in the formation of compounds **5–7** in good yields. Upon subsequent thermal treatment of **5–7** with malononitrile in DMSO, compounds **8–10** can be isolated in high purity. All attempts to obtain **8–10** from direct coupling of **1** and RC≡CH failed. Single-crystal X-ray structural analyses and density functional calculations have been performed on **3**, **4**, **7**, and **8**.

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Introduction

There is continuing research interest in the development of carbon-rich organic and organometallic compounds containing rigid, π-conjugated chains, due to their widespread applications in the field of materials science.[1−3] In this context, the use of fluorenyl chromophores and their derivatives offers exciting perspectives for the design of new molecular and polymeric materials for various optoelectronic applications.[4] It has been demonstrated that poly(2,7-fluorenediyl) derivatives are attractive as active components of organic light-emitting diodes, thanks to their thermal and chemical stability and their high emission quantum yields.[5] Substituent derivatization at the C-9 position of the monomeric fluorenes offers the prospect of controlling polymer properties such as solubility, emission wavelengths, processability, and potential interchain interactions in films.[6] A number of elegant synthetic means have been employed to generate novel fluorene-containing materials with enhanced device performance.[7]

On the other hand, electron acceptors of the fluorene series have also aroused considerable attention in the study of charge-transfer complexes with semiconducting and photoconducting properties and as electron-transport materials.[8] Electron-deficient fluorene derivatives substituted

with a donor moiety can efficiently sensitize the photoconductivity of carbazole-containing polymers in the intramolecular charge-transfer spectral region of the acceptors.[8a,8b] A large number of polynitro-substituted fluoren-9-ones and 9-(dicyanomethylene)fluorenes have been synthesized and studied, particularly by Perepichka's group.[8] Very recently, a comprehensive program investigating some organometallic polyyne polymers incorporating fluorene-based auxiliaries was initiated in our laboratory.[9] In the course of our studies, the first example of a soluble, low-bandgap platinum(II) polyyne with a 9-(dicyanomethylene)fluorene spacer has been reported.[9b] It has a bandgap located at 1.58 eV, the lowest of any of the metal polyynes known in the literature. Modification of the polymer backbone with electron-deficient dicyano-substituted electron acceptors in the side chain was found to be effective for tuning the bandgaps of this class of materials or of similar compounds while maintaining their solubility and processability. In a further step we have studied the coupling reactions between (2,7-dibromo-9H-fluoren-9-ylidene)malononitrile (**1**) and some terminal acetylenes. Although palladium-catalyzed Sonogashira coupling between aryl halides and terminal acetylenes has been shown to be a versatile method for introduction of ethynyl groups into organic structures,[10] no direct coupling products were obtained in these particular cases. Instead, some unexpected molecules were formed, one of the cyano groups being expelled by the incoming acetylide moiety to afford unsymmetrical monocyano-substituted fluorene compounds. Attempts to produce the symmetrical coupling products require the utilization of the corresponding fluoren-9-one derivatives in the first step in

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such a way that coupling reactions must take place before the condensation reaction with malononitrile.

Results and Discussion

Synthesis

Scheme 1 summarizes the reaction steps affording the new compounds in this study. Compound **1** was readily accessible in high yield by condensation between 2,7-dibromofluoren-9-one and malononitrile in DMSO at 110 °C.[8a,8d,8e,8g,9b] Treatment of **1** with slight excesses of substituted acetylenes RC≡CH [R = Ph, MeC$_6$H$_4$, (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$)] in a Pd(OAc)$_2$/PPh$_3$/CuI/iPr$_2$NH mixture resulted in the production of new unsymmetrical acetylide-functionalized compounds **2−4**, respectively, in moderate yields, accompanied by the elimination of HCN. No substitution at the methylene position took place under identical experimental conditions in the absence of the catalysts, and only the hydrolyzed product 2,7-dibromofluoren-9-one was isolated. However, the mechanistic pathway for this reaction has not yet been established.[11] There was also no sign of the formation of the expected direct coupling products in each case. Compounds **2−4** were purified by preparative TLC on silica with a mixture of hexane and CH$_2$Cl$_2$ as eluent and obtained as solids in high purity. Attempted substitution of the remaining cyano group with acetylenes by treatment of **2−4** with more RC≡CH was unsuccessful[12] and again only hydrolysis took place to give 2,7-dibromofluoren-9-one as the sole product. In place of the use of **1** as the starting precursor, Sonogashira coupling reactions between 2,7-dibromofluoren-9-one and 1-alkynes with a feed ratio of 1:2 provided, as anticipated, a high-yield synthesis of bis(acetylene)-functionalized compounds **5−7** after TLC purification.[9,10] Subsequent treatment of **5−7** with malononitrile in DMSO was able to furnish the desired dicyano-substituted products **8−10**. All the new compounds are generally soluble in common chlorinated solvents such as CH$_2$Cl$_2$ and CHCl$_3$, but we note that the solubility is significantly lower for **8−10**. Satisfactory analytical and spectroscopic (FTIR, NMR, and MS) data readily establish the exact identity of each compound, and the molecular structures of **3**, **4**, and **8** have been determined unequivocally by single-crystal X-ray analyses.

Spectroscopic and Structural Characterization

The solution IR spectra in each case reveal the characteristic ν(C≡C) vibrational bands, and the values at the side chain for **2−4** span the narrow 2186−2192 cm^{-1} range. For the rigid-rod bis(acetylene) species, the C≡C stretching frequencies along the main chain are higher for the ferrocenyl derivatives **7** and **10** (2210 cm^{-1}) than for the analogous phenyl and tolyl congeners (ca. 2123−2144 cm^{-1}). In addition, strong absorptions due to ν(C≡N) and ν(C=O) stretching modes are apparent for the 9-(cyanomethylene)-substituted fluorene and fluoren-9-one species, respectively. The ^{1}H NMR spectra are entirely consistent with the struc-
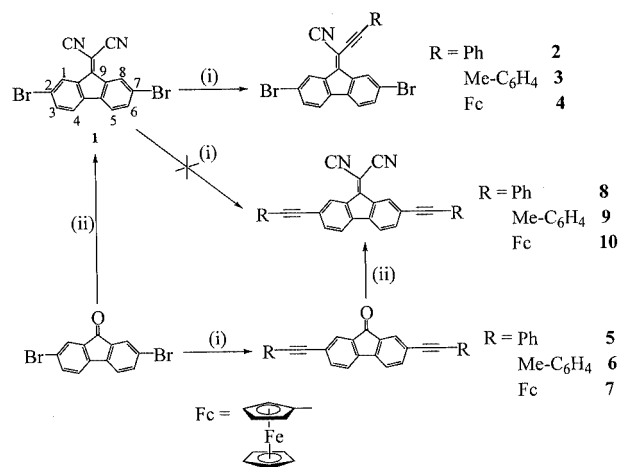
Scheme 1. (i) RC≡CH, Pd(OAc)$_2$, PPh$_3$, CuI, iPr$_2$NH; (ii) CH$_2$(CN)$_2$, DMSO, 110 °C

tures, by comparison with data for previous 2,7-disubstituted fluorenes.[8,9] The proton signals due to the aromatic and methyl groups are clearly evident from the ^{1}H NMR spectra. For **4** and **10**, the expected ferrocenyl spectral pattern can be observed, the unsubstituted C$_5$H$_5$ ring resonating as a strong singlet and the monosubstituted C$_5$H$_4$ ring giving an unsymmetrical pair of "pseudo" triplets corresponding to the A$_2$B$_2$ spectrum with J(adjacent) ≈ J(cross). The spectral features of **5−10** confirm the symmetrical arrangements of these molecules. In most cases the formulae of new compounds were also established by the appearance of intense molecular ion peaks in the respective positive FAB mass spectra.

The molecular structures of **3**, **4**, and **8** were successfully determined by X-ray crystallography and are illustrated in Figures 1, 2, and 3, respectively. Pertinent bond lengths and angles are collected in Tables 1 and 2. The crystal structure of **7** was reported in our earlier paper.[13] The structure of **3** shows one of the cyano groups of the original precursor replaced by a tolylacetylene fragment. This, together with the remaining cyano unit, is bonded to C(14) at the 9-methylene position of the fluorene nucleus.[12] Compound **4** is structurally similar to **3**, except that a ferrocenylacetylene group is bound to the methylene carbon atom at C(14) instead. To the best of our knowledge, compounds **3** and **4** represent the first structurally characterized examples of fluorene derivatives possessing σ-acetylene groups at their 9-methylene positions. The two structures do not show significant differences in the structural parameters of their cyanofluorene moieties. The central fluorene ring is nearly planar in each case (mean deviation ca. 0.0223 Å in **3** and 0.0067 Å in **4**) and makes a dihedral angle of 9.2° with the C$_6$H$_4$ ring in **3**. The *exo* double bond C(13)−C(14) is distorted from planarity by 6° [defined by C(1)−C(13)−C(14)−C(15)] in **3**, but the distortion is less pronounced in **4**. The C(13)−C(14) double bond length is typical at 1.361(8) (**3**) and 1.363(7) Å (**4**), which compares well with those in [(η^5-C$_5$H$_5$)Fe{η^5-C$_5$H$_4$CH=(Ar)}] [Ar = 2-formyl-9-fluorenyl: 1.354(6),[14] 2,7-diformyl-9-fluorenyl:

1.340(3),[14] 2,7-diethynyl-9-fluorenyl: 1.348(3) Å],[9c] *trans*-[Ph(Et₃P)₂PtC≡CArC≡CPt(PEt₃)₂Ph] [Ar = 9-(ferrocenyl-methylene)fluorene-2,7-diyl: 1.37(2),[9c] 9-(dicyanomethy-lene)fluorene-2,7-diyl: 1.348(9) Å],[9b] 9-[cyano(dimethylam-ino)methylene]-2,4,5,7-tetranitrofluorene [1.388(4) Å][8e] and other polynitro-substituted 9-(dicyanomethylene)fluor-enes.[8d][8g] The exocyclic double bond is partially conjug-ated with the acetylenic fragment, resulting in notable π-bond delocalization along the C(13)−C(14)−C(16) frag-ment, with the C(14)−C(16) bond lengths being 1.444(8) Å (**3**) and 1.432(8) Å (**4**). The C(16)−C(17) bond lengths [**3**: 1.189(8); **4**: 1.187(8) Å] are characteristic of acetylene σ-bonding and the C(16)−C(17)−C(18) fragment does not deviate significantly from linearity. For **4**, the two cyclo-pentadienyl rings are almost parallel, with a ring tilt angle of 1.2°, and the ferrocenyl group is nearly eclipsed in the solid state. The Fe−C(cyclopentadienyl) distances vary from 2.019(6) to 2.051(6) Å and Fe(1) is at an average dis-tance of 1.6489 Å from the centroids of the rings. In neither case was any sign of formation of well-defined stacks in the crystals detected.
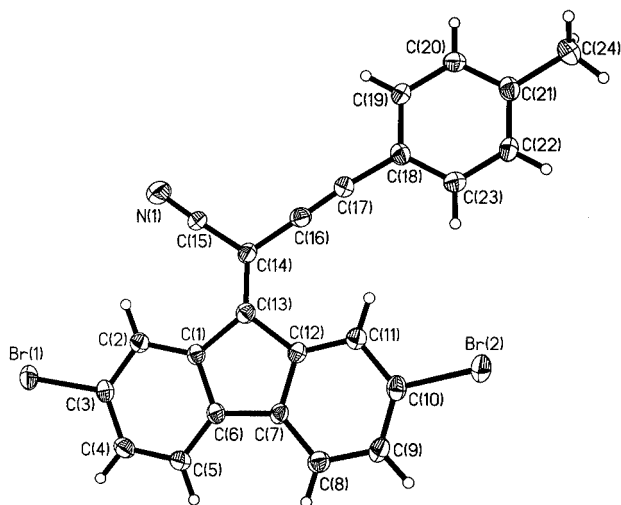

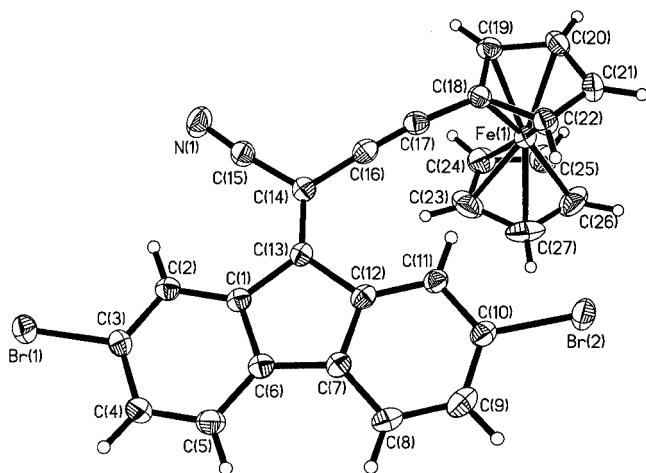Figure 1. A perspective drawing of compound **3**

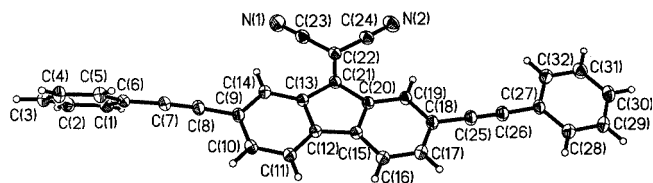Figure 2. A perspective drawing of compound **4**

Figure 3. A perspective drawing of compound **8**

Structurally, the molecule of **8** consists of two phenylacet-ylene end groups covalently appended to the central 9-(di-cyanomethylene)fluorene moiety at the 2,7-positions through C(8)−C(9) and C(18)−C(25) bonds. The 9-substi-tuted fluorenediyl ring system is planar, with a mean devi-ation from the best plane of 0.0206 Å, and almost coplanar with the C(27) phenyl plane (dihedral angle 4.7°). The two phenyl planes are significantly twisted with respect to each other (dihedral angle 66.8°). The C(21)−C(22) bond is 1.360(3) Å long, while the C≡C bond lengths are 1.198(2) and 1.194(3) Å. We anticipate that conjugation through the molecule in the ground-state configuration should produce a shortening of the C(6)−C(7), C(8)−C(9), C(18)−C(25), and C(26)−C(27) bonds [1.425(2)−1.434(2) Å] and a lengthening of the C(7)−C(8) and C(25)−C(26) bonds.[14] Again, no plane-to-plane stacking between adjacent molec-ules occurs in the crystal lattice of **8**.

Absorption Properties

The solution electronic absorption spectra of all new compounds were measured, and the data are collected in Table 3. In general, the absorption spectra of the non-ferro-cenyl compounds show intense, relatively high-energy bands in the near UV and visible region, arising from the π → π* transitions of the aromatic fragments. The electronic spectra of the ferrocenyl species **4**, **7**, and **10** are essentially charac-terized by the structureless π → π* transition bands of the corresponding fluorene π skeleton together with metal-to-ligand charge-transfer (MLCT) transitions in the low-en-ergy region of the spectra, which was supported by molecu-lar orbital calculations (vide infra). Within each particular fluorene spacer, replacement of the R groups in the purely organic compound with the ferrocenyl unit tends to red-shift the positions of λ_max. We note a bathochromic shift of ca. 186 nm on going from **2** to **4** and of 135 nm on going from **9** to **10**. Comparison of the data for **5−10** shows that the presence of the two π*-accepting cyano groups lowers the optical gap values significantly, by as much as 0.50 eV, since these groups can stabilize the LUMO to a greater ex-tent than the carbonyl group in the fluoren-9-one counter-parts. Moreover, the introduction of two terminal ethynyl bridges at the 2,7-positions in **8−10** causes a narrowing of the optical gaps relative to **1**. One remarkable feature in this study is the observation of a solvatochromic phenomenon for the lowest-energy MLCT band in **4** (hexane → CH₂Cl₂, red shift of 30 nm), consistent with a dipolar excited state due to intramolecular charge-transfer (ICT) transition from the electron-donating ferrocenyl group to the electron-with-drawing cyano group through the conjugated system.[14]

Table 1. Selected bond lengths [Å] and angles [°] for compounds **3** and **4**

	3	**4**		**3**	**4**
Br(1)−C(3)	1.920(6)	1.894(6)	Br(2)−C(10)	1.891(6)	1.894(6)
C(13)−C(14)	1.361(8)	1.363(7)	C(14)−C(15)	1.427(8)	1.451(8)
C(15)−N(1)	1.155(8)	1.134(7)	C(14)−C(16)	1.444(8)	1.432(8)
C(16)−C(17)	1.189(8)	1.187(8)	C(17)−C(18)	1.443(8)	1.429(8)
Fe(1)−C(18)		2.019(6)	Fe(1)−C(19)		2.039(6)
Fe(1)−C(20)		2.051(6)	Fe(1)−C(21)		2.051(6)
Fe(1)−C(22)		2.030(6)	Fe(1)−C(23)		2.046(8)
Fe(1)−C(24)		2.034(7)	Fe(1)−C(25)		2.034(7)
Fe(1)−C(26)		2.045(8)	Fe(1)−C(27)		2.025(7)
C(13)−C(14)−C(15)	122.4(5)	121.9(5)	C(14)−C(15)−N(1)	176.8(7)	174.6(7)
C(14)−C(16)−C(17)	176.9(6)	176.4(7)	C(16)−C(17)−C(18)	175.0(6)	173.9(7)

Table 2. Selected bond lengths [Å] and angles [°] for compound **8**

C(7)−C(8)	1.198(2)	C(21)−C(22)	1.360(3)
C(22)−C(23)	1.429(3)	C(23)−N(1)	1.139(3)
C(22)−C(24)	1.436(3)	C(24)−N(2)	1.143(3)
C(25)−C(26)	1.194(3)		
C(7)−C(8)−C(9)	175.6(2)	C(21)−C(22)−C(23)	123.01(17)
C(22)−C(23)−N(1)	178.6(2)	C(21)−C(22)−C(24)	123.29(17)
C(22)−C(24)−N(2)	177.4(2)	C(18)−C(25)−C(26)	179.2(2)

The presence of such an MLCT band in **4** accounts for the deep blue color of its solution in CH_2Cl_2. In contrast, the higher-energy absorptions of **4** are relatively insensitive to variation in solvent polarities (Table 3). Electron acceptors of the fluorene series exhibiting strong ICT bands have been well documented,[8] although no evidence of significant solvatochromic shifts in the electronic absorptions was obtained for the other compounds.

Electrochemistry

The electrochemical behavior of our compounds was studied by cyclic voltammetry in CH_2Cl_2 at room temperature, and the results for the electroactive compounds are given in Table 3. For the ferrocene-containing species, each cyclic voltammogram is characterized by a single quasi-reversible oxidation wave due to the presence of the ferrocenyl electrophore in the compound. An anodic shift of the ferrocene/ferrocenium couple with respect to the ferrocene standard is consistent with the unsaturation of the ethynyl bridge, which makes the removal of an electron more difficult than in pure ferrocene.[15] Clearly, the $E_{1/2}$ value is more anodic in **4** than in **7** and **10**, owing to the closer attachment of the strongly electronegative cyano group to the ferrocenyl unit in the former. Analogously to **7** and to other, previously reported, related bis(ferrocenyl) complexes, the two ferrocenyl end groups exhibit only sparse electronic communication in **10** and the oxidation wave only corresponds to a single-step, two-electron oxidation involving concomitant oxidation of the two terminal ferrocenyl moieties.[3f,13] A single irreversible reduction wave, attributable to the central 9-(dicyanomethylene)fluorene unit, is detected for each of **8**−**10**, occurring at potentials slightly more cathodic than that of **1**. The more negative value of this reduction peak in **10** agrees with increased electron density in the vicinity of the electron-donating ferrocenyl chromophore. This is in contrast to that found for (2,7-diethynyl-9H-fluoren-9-ylidene)malononitrile and its gold(I) derivative, for which two irreversible waves are observed.[16] However, no reduction is associated with the cyano group in **2**−**4**.

Table 3. Electronic absorption and redox data for **1**−**10**

Compound	λ_{max} [nm] ($\varepsilon \times 10^{-4}$ [$M^{-1}\cdot cm^{-1}$])[a]	Optical gap [eV][b]	E_{ox} (ΔE_p) [V][c]	E_{red} [V]
1	284, 316, 345, 361, 480[d]	2.13		−1.01[e]
2	260 (7.6), 269 (11.8), 283 (3.8), 386 (1.5), 406 (1.6)	2.89		
3	273 (5.6), 283 (7.0), 394 (3.3), 415 (3.6)	2.81		
4	270 (5.0), 284 (4.0), 387 sh (1.6), 404 (1.7), 592 (0.4)[f]	1.74	0.27 (119)	
5	302 (6.7), 341 (4.2), 351 (4.7), 443 (0.4)	2.45		
6	295 (1.4), 313 (1.3), 334 (1.0), 421 (0.05)	2.57		
7	288 (8.7), 349 (4.7), 493 (0.8)[g]	2.13	0.14 (159)	
8	320 (11.1), 352 sh (6.8), 544 (0.3)	1.94		−1.06[h]
9	286 (3.9), 314 (2.3), 345 (2.2), 360 (1.8), 488 (0.04)	2.11		−1.04[h]
10	320 (5.4), 461 sh (0.3), 623 (0.1)	1.62	0.14 (99)	−1.13[h]

[a] All absorption spectra were recorded in CH_2Cl_2 at 293 K. [b] Estimated from the absorption edge. [c] All the potential values are with reference to the external ferrocene standard. $E_{ox} = (E_{pc} + E_{pa})/2$ for reversible oxidation. ΔE_p in mV. Scan rate = 100 mV·s^{-1}. [d] Limited solubility for accurate determination of ε. [e] Reversible wave. [f] Data [nm] (in ethanol): 267, 365, 400, 583; (in hexane): 257, 266, 274, 383, 400, 562. [g] Ref.[13] [h] Irreversible wave.

Theoretical Studies

To study the electronic structures of the unsymmetrical monocyano complexes, we carried out molecular orbital calculations (at the B3LYP level of density functional theory) for **3** and **4**, based on their experimental geometries obtained from the crystallographic studies,[17] and the results were compared to those for **7** and **8**. Examining the characteristics of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals for **3** and **4**, the structures of which differ by only one substituent, we found that the LUMOs of the two systems have almost the same orbital characteristics as the π* antibonding in the common conjugated unit. However, the HOMO in the ferrocenyl system in **4** contains mainly the Fe d_δ metal orbitals while the HOMO in **3** is principally composed of atomic orbitals of the tolyl substituent (Figure 4). The calculated HOMO−LUMO gaps for **3** and **4** are 3.35 and 3.07 eV, respectively. The difference in the orbital characteristics in the HOMO explains why compound **4** has a smaller optical gap than **3**, because the metal orbitals generally have higher orbital energies than the π bonding orbitals of an aromatic C_6H_4 group because of their ionization potentials.
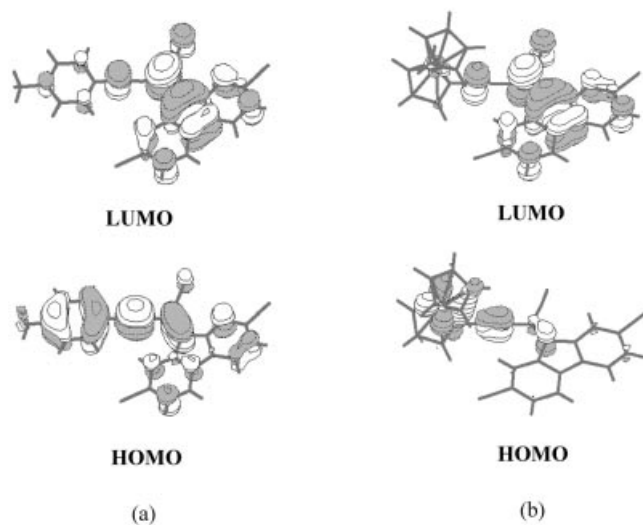

Figure 4. Spatial plots of the highest occupied (HOMO) and the lowest unoccupied molecular orbitals (LUMO) for (a) **3** and (b) **4**

Figure 5 shows contour plots[18] of the frontier molecular orbitals for the bis(ferrocenylethynyl) species **7**. We found that the HOMOs are very close to each other in orbital energies and essentially consist of the four Fe d_δ metal orbitals together with small contributions from the highest π-bonding orbitals of the fluorenone unit.[3f] The reason we have four such d_δ orbitals is because we have two Fe centers in the complex and each Fe metal center would be expected to have two. The δ-type is defined by viewing the orbitals along the Ct−Fe−Ct axes (Ct: the center of each cyclopentadienyl ligand). If the Ct−Fe−Ct axis is defined as the z axis, the two d_δ orbitals correspond to the d_{xy} and $d_{x^2-y^2}$

orbitals. Each iron center in the complex is formally regarded as Fe^{II}. The two d_{z^2} orbitals (of the two Fe centers) are located in the lower energy region. The LUMOs correspond to the π* orbitals of the organic aromatic entity. The calculated HOMO−LUMO gap for **7** (3.20 eV) is larger than that found for **4** since the cyano group in the latter molecule has a stabilizing effect on the LUMOs, resulting in their remarkably low orbital energies. For **8**, the HOMO is π-bonding in nature and extensively delocalized in the three aromatic rings and the two acetylenic units, while the LUMO corresponds to the π*-antibonding of the central fluorenyl unit with the participation of π* from the two CN groups.
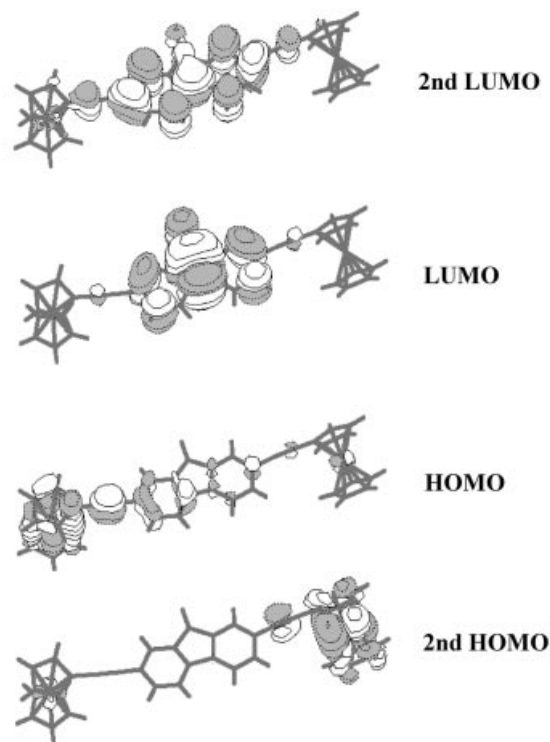

Figure 5. Spatial plots of the frontier molecular orbitals for **7**

Conclusions

In continuation of our recent studies on the chemistry of 9-(dicyanomethylene)-substituted fluorene derivatives, a novel reactivity pattern − by which introduction of a σ-acetylene group at the 9-methylene position of the central fluorene system is feasible − has been demonstrated here and a series of 9-[cyano(ethynyl)methylene]fluorene compounds have been prepared. The electronic absorption and redox properties of these unsymmetrical molecules have been examined as a function of the electronic and geometric natures of the 9-substituents of fluorene and are consistent with the theoretical calculations. Of particular interest is the intramolecular charge-transfer transition encountered in

the donor/acceptor-type compound **4**, for which significant solvatochromism is observed for the lowest-energy MLCT band. The work here provides us with better understanding in the molecular design of new C-9-functionalized fluorene-based conjugated oligomers and copolymers for fine-tuning of various physical properties.

Experimental Section

General Procedures: All reactions were carried out under nitrogen with the use of standard Schlenk techniques, but no special precautions were taken to exclude oxygen during workup. Solvents were predried and distilled from appropriate drying agents. All chemicals were obtained from commercial sources, unless otherwise stated, and used as received. Preparative TLC was performed on 0.7 mm silica plates (Merck Kieselgel 60 GF$_{254}$) prepared in our laboratory. Ethynylferrocene[19] and compound **7**[13] were prepared by literature methods. IR spectra were recorded in CH_2Cl_2 with a Perkin−Elmer Paragon 1000 PC or a Nicolet Magna 550 Series II FTIR spectrometer. Proton NMR spectra were measured in $CDCl_3$ with a JEOL EX270 or a Varian INOVA 400 MHz FT NMR spectrometer, with ^{1}H NMR chemical shifts quoted relative to SiMe$_4$. Fast atom bombardment (FAB) mass spectra were recorded with a Finnigan MAT SSQ710 mass spectrometer. Electronic absorption spectra were obtained with a Hewlett Packard 8453 UV/Vis spectrometer. Cyclic voltammetry experiments were performed with a Princeton Applied Research (PAR) model 273A potentiostat. A conventional three-electrode configuration consisting of a glassy-carbon working electrode, a Pt wire counter-electrode and an Ag/AgNO$_3$ reference electrode (0.1 M in acetonitrile) was used. The solvent in all measurements was deoxygenated CH_2Cl_2 and the supporting electrolyte was 0.1 M [Bu$_4$N]PF$_6$. Ferrocene was added as a calibrant after each set of measurements and all potentials reported are with reference to the ferrocene/ferrocenium couple. The number of electrons transferred for compound **10** was estimated by comparison of the peak height of the respective ferrocene oxidation wave with an equal concentration of the ferrocene standard added in the same system, in which one-electron oxidation was assumed. *CAUTION:* The by-product HCN is extremely toxic, and all experimentation in the preparations of **2**−**4** should be carried out in a well-vented hood!

Computational Details: Density functional calculations at the B3LYP level were carried out to study the electronic structures presented in the text. We were interested in knowing the properties of the molecular orbitals in the frontier region for the molecules, so single-point calculations were performed on the basis of their X-ray crystal structures. The basis set used for C and H atoms was 6-31G[20] while effective core potentials with a LanL2DZ basis set[21] were employed for Br and Fe atoms. Polarization functions were added for Br atoms [ζ_d(Br) = 0.389]. The Gaussian 98 program was used for the calculations.[22] Molden 3.5 was used to generate the contour plots of molecular orbitals.[18]

Compound 1: A mixture of 2,7-dibromofluoren-9-one (203 mg, 0.60 mmol) and malononitrile (43.6 mg, 0.66 mmol) in DMSO (3 mL) was heated at 110 °C for 5 h, during which the starting yellow suspension turned dark red. The red powder was then filtered off and washed with MeCN to give **1** in almost quantitative yield (224 mg, 97%). IR (CH_2Cl_2): ṽ = 2227 [v(C≡N)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.42 (d, $J_{H,H}$ = 8.0 Hz, 2 H, 4-H, 5-H), 7.65 (dd, $J_{H,H}$ = 1.2, 8.0 Hz, 2 H, 3-H, 6-H), 8.49 (d, $J_{H,H}$ = 1.2 Hz, 2 H, 1-H, 8-H) ppm. MS (FAB): m/z = 386 [M$^+$]. C$_{16}$H$_6$Br$_2$N$_2$

(386.05): calcd. C 49.78, H 1.57, N 7.26; found C 49.50, H 1.38, N 7.02.

Compound 2: A mixture of **1** (38.6 mg, 0.10 mmol) and phenylacetylene (24.2 μL, 0.22 mmol) in iPr$_2$NH (5 mL) was combined with CuI (1.0 mg), Pd(OAc)$_2$ (1.0 mg), and PPh$_3$ (2.0 mg). The mixture was heated at reflux for 18 h. After all the volatile components had been removed under reduced pressure, the residue was taken up in CH_2Cl_2 and the extract was filtered through a short silica gel column. The filtrate was concentrated and subjected to silica gel TLC separation with hexane/CH_2Cl_2 (2:1, v/v) as eluent. The yellow band (R_f = 0.29) afforded an orange product, which was subsequently recrystallized from CH_2Cl_2/hexane to give **2** in 22% yield (10.0 mg). IR (CH_2Cl_2): ṽ = 2220 [v(C≡N)], 2192 [v(C≡C)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.45−7.50 (m, 5 H, Ph), 7.55−7.58 (m, 2 H, 4-H, 5-H), 7.69−7.71 (m, 2 H, 3-H, 6-H), 8.57 (d, $J_{H,H}$ = 2.0 Hz, 1 H, 1-H or 8-H), 8.83 (d, $J_{H,H}$ = 2.0 Hz, 1 H, 1-H or 8-H) ppm. MS (FAB): m/z = 461 [M$^+$]. C$_{23}$H$_{11}$Br$_2$N (461.16): calcd. C 59.90, H 2.40, N 3.04; found C 59.59, H 2.26, N 2.95.

Compound 3: Compound **3** was prepared under the conditions described above for **2**, but 4-ethynyltoluene (27.9 μL, 0.22 mmol) was used instead, to afford **3** as a pale orange solid in 35% yield (16.6 mg) after preparative TLC purification on silica (R_f = 0.59) with hexane/CH_2Cl_2 (2:1, v/v). IR (CH_2Cl_2): ṽ = 2219 [v(C≡N)], 2190 [v(C≡C)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.44 (s, 3 H, Me), 7.30 (m, 2 H, C$_6$H$_4$), 7.47−7.50 (m, 2 H, 4-H, 5-H), 7.57−7.61 (m, 4 H, 3-H, 6-H + C$_6$H$_4$), 8.60 (d, $J_{H,H}$ = 2.0 Hz, 1 H, 1-H or 8-H), 8.87 (d, $J_{H,H}$ = 2.0 Hz, 1 H, 1-H or 8-H) ppm. MS (FAB): m/z = 475 [M$^+$]. C$_{24}$H$_{13}$Br$_2$N (475.18): calcd. C 60.66, H 2.76, N 2.95; found C 60.30, H 2.63, N 2.88.

Compound 4: Compound **4** was synthesized similarly, from ethynylferrocene (46.2 mg, 0.22 mmol), and was isolated as a deep blue solid in 39% yield (22.0 mg) by TLC on silica (R_f = 0.76) eluting with hexane/CH_2Cl_2 (4:3, v/v). IR (CH_2Cl_2): ṽ = 2220 [v(C≡N)], 2186 [v(C≡C)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 4.34 (s, 5 H, C$_5$H$_5$), 4.49 (t, $J_{H,H}$ = 2.0 Hz, 2 H, C$_5$H$_4$), 4.76 (t, $J_{H,H}$ = 2.0 Hz, 2 H, C$_5$H$_4$), 7.46−7.50 (m, 2 H, 4-H, 5-H), 7.55−7.60 (m, 2 H, 3-H, 6-H), 8.57 (d, $J_{H,H}$ = 1.6 Hz, 1 H, 1-H or 8-H), 8.82 (d, $J_{H,H}$ = 1.6 Hz, 1 H, 1-H or 8-H) ppm. MS (FAB): m/z = 569 [M$^+$]. C$_{27}$H$_{15}$Br$_2$FeN (569.08): calcd. C 56.99, H 2.66, N 2.46; found C 56.79, H 2.50, N 2.37.

Compound 5: 2,7-Dibromofluoren-9-one (101 mg, 0.30 mmol), phenylacetylene (0.10 mL, 0.90 mmol), and iPr$_2$NH (40 mL) were mixed with catalytic amounts of CuI (2.0 mg), Pd(OAc)$_2$ (2.0 mg), and PPh$_3$ (4.0 mg). The resulting mixture was stirred at 75 °C for 16 h. The volatile components were evaporated in vacuo, the residue was taken up in CH_2Cl_2, and the solution was filtered through a short silica column before being purified by TLC on silica (R_f = 0.61), eluting with hexane/CH_2Cl_2 (3:2, v/v). Compound **5** was obtained as an orange solid in 56% yield (63.5 mg). IR (CH_2Cl_2): ṽ = 2123 [v(C≡C)], 1723 [v(C=O)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.36−7.38 (m, 6 H, Ph), 7.52−7.56 (m, 6 H, 4-H, 5-H + Ph), 7.67 (dd, $J_{H,H}$ = 1.6, 7.6 Hz, 2 H, 3-H, 6-H), 7.82 (d, $J_{H,H}$ = 1.6 Hz, 2 H, 1-H, 8-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 88.53, 91.43 (C≡C), 120.57, 122.71, 124.49, 127.43, 128.44, 128.72, 131.68, 134.42, 137.80, 143.19 (Ar), 192.29 (quat. C) ppm. MS (FAB): m/z = 380 [M$^+$]. C$_{29}$H$_{16}$O (380.45): calcd. C 91.56, H 4.24; found C 91.40, H 4.34.

Compound 6: A procedure similar to that used for **5** was employed, using 4-ethynyltoluene (0.11 mL, 0.90 mmol) to produce an analytically pure sample of **6** as an orange solid in 78% yield (95.6 mg) after purification by TLC on silica (R_f = 0.55), eluting with hexane/

Table 4. Crystal data for compounds **3**, **4**, and **8**

	3	**4**	**8**
Empirical formula	$C_{24}H_{13}Br_2N$	$C_{27}H_{15}Br_2FeN$	$C_{32}H_{16}N_2$
Formula mass	475.17	569.07	428.47
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1$	Pbca	$P\bar{1}$
a [Å]	3.9962(4)	15.1338(12)	7.7804(7)
b [Å]	25.246(3)	10.7557(9)	9.1837(8)
c [Å]	9.3067(10)	26.333(2)	16.2714(14)
α [°]	90	90	93.397(2)
β [°]	94.871(2)	90	100.1110(10)
γ [°]	90	90	102.203(2)
V [Å^3]	935.53(17)	4286.3(6)	1113.10(17)
Z	2	8	2
T [**K**]	293	293	293
μ(Mo-K_α) [mm^{-1}]	4.341	4.448	0.075
Reflections collected	5494	23960	5542
Unique reflections	3409	4856	3839
R_{int}	0.0229	0.0890	0.0306
Observed reflections [$I > 2.0\sigma(I)$]	2820	2050	3066
GOF on F^2	0.989	0.802	1.077
$R1$, $wR2$ [$I > 2\sigma(I)$][a]	0.0389, 0.1001	0.0416, 0.0988	0.0585, 0.1729
$R1$, $wR2$ (all data)[a]	0.0488, 0.1049	0.1353, 0.1517	0.0675, 0.1835

$R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

CH$_2$Cl$_2$ (3:2, v/v). IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2140 [ν(C≡C)], 1728 [ν(C=O)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 2.37 (s, 6 H, Me), 7.14 (d, $J_{H,H}$ = 7.8 Hz, 4 H, C$_6$H$_4$), 7.38−7.43 (m, 6 H, 4-H, 5-H + C$_6$H$_4$), 7.63 (dd, $J_{H,H}$ = 1.8, 8.0 Hz, 2 H, 3-H, 6-H), 7.77 (d, $J_{H,H}$ = 1.8 Hz, 2 H, 1-H, 8-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 21.70 (Me), 73.43, 81.51 (C≡C), 118.69, 121.74, 123.22, 127.74, 129.10, 132.26, 135.16, 137.34, 139.36, 142.13 (Ar), 190.98 (quat. C) ppm. MS (FAB): m/z = 393 [M$^+$ − Me]. C$_{31}$H$_{20}$O (408.50): calcd. C 91.15, H 4.93; found C 91.10, H 4.88.

Compound 8: Compound **5** (30.4 mg, 0.08 mmol) and malononitrile (5.30 mg, 0.08 mmol) were mixed in degassed DMSO (1 mL). The yellow suspension was then heated to about 110 °C and stirred for 5 h. After cooling and filtration, a dark brown precipitate was obtained, and this was washed with a small amount of MeCN to afford **8** in 94% yield (32.3 mg). IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2228 [ν(C≡N)], 2144 [ν(C≡C)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.37−7.39 (m, 6 H, Ph), 7.55−7.58 (m, 6 H, 4-H, 5-H + Ph), 7.68 (dd, $J_{H,H}$ = 1.2, 8.0 Hz, 2 H, 3-H, 6-H), 8.53 (d, $J_{H,H}$ = 1.2 Hz, 2 H, 1-H, 8-H) ppm. MS (FAB): m/z = 428 [M$^+$]. C$_{32}$H$_{16}$N$_2$ (428.49): calcd. C 89.70, H 3.76, N 6.54; found C 89.56, H 3.55, N 6.40.

Compound 9: The reaction between **6** (in place of **5**; 102 mg, 0.25 mmol) and malononitrile (16.5 mg, 0.25 mmol) in degassed DMSO (3 mL) at 110 °C resulted in the precipitation of the desired product **9**, which was worked up as above to give a reddish-orange solid in 47% yield (53.6 mg). IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2227 [ν(C≡N)], 2138 [ν(C≡C)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 2.37 (s, 6 H, Me), 7.14 (d, $J_{H,H}$ = 8.1 Hz, 4 H, C$_6$H$_4$), 7.40−7.44 (m, 6 H, 4-H, 5-H + C$_6$H$_4$), 7.66 (dd, $J_{H,H}$ = 1.2, 8.1 Hz, 2 H, 3-H, 6-H), 8.50 (d, $J_{H,H}$ = 1.2 Hz, 2 H, 1-H, 8-H) ppm. MS (FAB): m/z = 456 [M$^+$]. C$_{34}$H$_{20}$N$_2$ (456.55): calcd. C 89.45, H 4.42, N 6.13; found C 89.20, H 4.38, N 6.02.

Compound 10: This compound was prepared in a manner similar to that used for **8**, with compound **7** (47.7 mg, 0.08 mmol) as starting material, giving the product as a greenish blue powder in 78% yield

(40.2 mg). IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2229 [ν(C≡N)], 2209 [ν(C≡C)] cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 4.28 (s, 10 H, C$_5$H$_5$), 4.30 (t, $J_{H,H}$ = 2.0 Hz, 4 H, C$_5$H$_4$), 4.55 (t, $J_{H,H}$ = 2.0 Hz, 4 H, C$_5$H$_4$), 7.49 (d, $J_{H,H}$ = 7.6 Hz, 2 H, 4-H, 5-H), 7.60 (dd, $J_{H,H}$ = 1.2, 7.6 Hz, 2 H, 3-H, 6-H), 8.46 (d, $J_{H,H}$ = 1.2 Hz, 2 H, 1-H, 8-H) ppm. MS (FAB): m/z = 644 [M$^+$]. C$_{40}$H$_{24}$Fe$_2$N$_2$ (644.34): calcd. C 74.56, H 3.75, N 4.35; found C 74.30, H 3.68, N 4.24.

X-ray Crystallography: Yellow crystals of **3**, **4**, and **8** suitable for X-ray diffraction studies were grown by slow concentration of their solutions in hexane/CH$_2$Cl$_2$ at room temperature. Geometric and intensity data were collected by use of graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) with a Bruker Axs SMART 1000 CCD area-detector. The collected frames were processed with SAINT[23a] software and an absorption correction (SADABS[23b]) was applied to the collected reflections. The structures of these molecules were solved by direct methods (SHELXTL)[24] in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix, least-squares analyses on F^2. All non-hydrogen atoms were assigned with anisotropic displacement parameters and the hydrogen atoms were generated in their idealized positions and allowed to ride on the respective carbon atoms. Crystal data and other experimental details are summarized in Table 4. CCDC-187006 to -187008 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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