

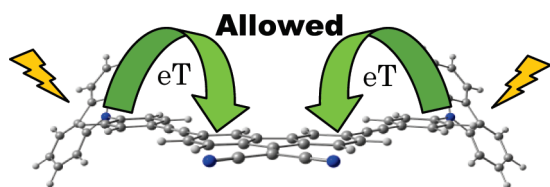
Synthesis and Photophysics of Ambipolar Fluoren-9-ylidene Malononitrile Derivatives[†]

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The efficient synthesis of ambipolar 2,7- and 3,6-disubstituted fluoren-9-ylidene malononitrile derivatives (**4** and **9**) is described. Structure–activity relationships depend on the position of substitution. Population of the S_1 excited state in the 2,7-disubstituted FM derivatives is achieved via higher states, as evidenced from the UV–vis absorption and emission spectra. The results are supported by TDDFT calculations. Charge transfer states were the main deactivation path of the excited states of ambipolar **9b** in polar solvents, as evidenced by fluorescence spectroscopy.

Current efforts leading to new multiphoton-absorbing materials are reflected by the number of organic ambipolar compounds recently reported.¹ Fluorene has become a favorite synthon in this.² 2,7-Derivatives mainly focus on the delocalizing π -electron density via byphenylene, whereas derivatives at C-9 usually improve solubility, processability, and interchain charge and energy transfer in polymer composites. Incorporating electron-withdrawing groups at C-9 stabilizes the LUMO of fluorene, making it remarkably electrophilic. Thus, fluorenone (FO) and fluoren-9-ylidene

malononitrile (FM) derivatives had been integrated as photosensitizers for carbazole-containing conductive polymers.^{3,4} While looking for improvements in the electron affinity of electron-deficient fluorene derivatives, a series of nitro-containing FOs and FMs were mainly developed by Perepichka's and Bryce's research groups.⁵ These efforts recently led to amazingly low band gap materials if covalently attached to electron-rich tetrathiafulvalene (TTF).⁶

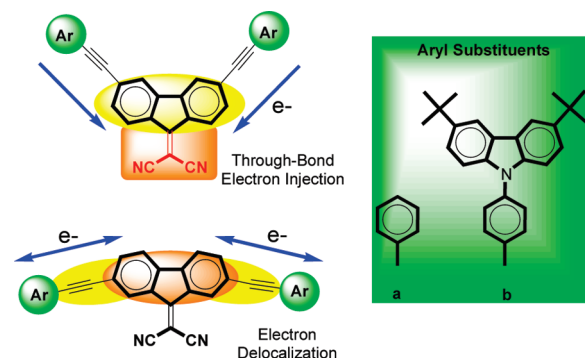


FIGURE 1. Design and purpose of target compounds.

Substitution at positions 3, 6, and 9 offer, in theory, good electronic communication through the fluorene skeleton, making it suitable for antenna-type systems where proper electron donor and acceptor groups incorporated (Figure 1). The rigid fluorene carbon frame should aid in electron and energy transfer processes in a similar fashion as well-studied compounds for this purpose.^{7,8} Though transition-metal-catalyzed C–C coupling⁹ reaction processes have enabled the incorporation of a plethora of substituents in

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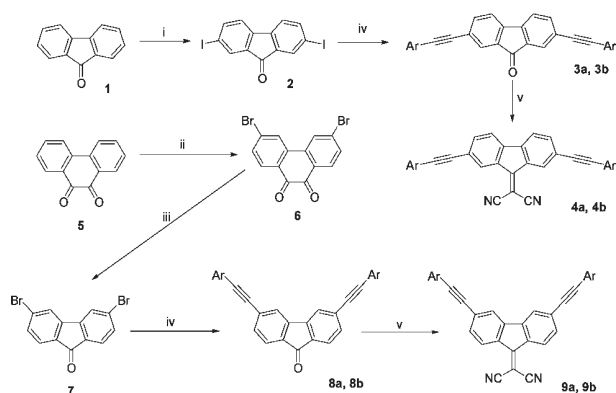
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SCHEME 1. Synthetic Route for the Synthesis of Compounds 4–9^a


^aReagents and conditions: (i) I₂, H₃IO₆, AcOH/H₂SO₄/H₂O, Δ, 98%; (ii) *hν* (λ = 350 nm, P = 100 W), Bz₂O₂, Br₂, PhNO₂, 77%; (iii) KOH/KMnO₄, H₂O, Δ, 69%; (iv) phenylacetylene (a) or 3,6-di-*tert*-butyl-9(4-ethynylphenyl)carbazole (b), PdCl₂(PPh₃)₂, CuI, Et₃N, DMF, 90 °C, 12 h, 80–99%; (v) malononitrile, pyridine (anhyd.), 90 °C, 2 h, 68–91%.

carbons 2 and 7 for further exploration of fluorene electronic properties, there are few reported examples of such substitutions at 3,6-positions.^{10–12}

Herein, the synthesis and characterization of an ambipolar 3,6-disubstituted FM derivative were pursued. Carbazole was selected as the electron donor because of its electronic properties and processability,¹³ while phenylacetylene (PA) was chosen as the electronic bridge.¹⁴ FMs substituted at the 2,7-positions and compounds lacking of carbazole were also synthesized for comparison purposes.

The synthetic route is outlined in Scheme 1. Carbazole-containing PA was synthesized according to Hou's protocol.¹⁵ 2,7-Diiodofluorenone (2) was prepared by iodination of fluorenone with a mixture of I₂/H₃IO₆ under acid conditions.¹⁶ 3,6-Dibromofluorenone (7) was synthesized by a modified Bhatt's protocol starting from phenanthrene-9,10-dione (6).¹⁷

Purification of 7 via Soxhlet extraction with toluene initially reported by Bhatt, and subsequently adapted by others,^{10,11} is likely to leave < 5% of starting material as impurity. This is hard to detect by ¹H NMR. A little amount of 6 proved to be detrimental toward efficient Sonogashira couplings (SCs) since the Pd catalyst loading is usually around the same low mole percentage. Analytically pure 7 was obtained after two sublimation steps and final Soxhlet

TABLE 1. Photophysical Properties Recorded in Toluene

cmpd	λ _{abs} (nm) [ε (M ⁻¹ cm ⁻¹)]	λ _{em} max (nm)	τ _F (ns)	k _{rad} (s ⁻¹)	Φ _F ^c %
4a	320 [120000]	540	9.98 ^a	1.00 × 10 ⁸	0.06
	550 [1700]				
4b	350 [120000]	550	6.89 ^a	1.45 × 10 ⁸	0.7
	560 [2500]				
9a	290 [98000]	615	1.00 ^b	9.96 × 10 ⁸	0.9
	475 [10000]				
9b	346 [96000]	620	3.18 ^b	3.15 × 10 ⁸	2
	470 [32000]				

^aλ_{exc} = 340 nm. ^bλ_{exc} = 370 nm. ^cΦ_F was measured against 0.1 M solution of quinine sulfate in 1 M H₂SO₄ (aq) as fluorescence standard.

extraction in the decarbonylation step under basic conditions, as previously suggested by Ipaktschi et al.¹² The yields of SC dramatically improved (3–4-fold) when sublimed 7 was used as starting material. Apparently, Pd(0) is deactivated by complexation with the *o*-quinone competing with the oxidative C–Br addition step. Although this hypothesis is yet to be proved, it is known that Pd coupling of dihalophenanthrene-9,10-dione (DHPD) gives irreproducible results, and the yields are often low.¹⁸ Tour et al. was the first group to successfully derivatize DHPD after generation of 9,10-diethyleneglycol-etal under acid conditions prior to Pd coupling.¹⁹ Müllen et al. recently reported a similar approach: protection of DHPD with Me₂SO₄ and regeneration of the *o*-quinone with CAN.²⁰

The target compounds were obtained after Knoevenagel condensation (KC) of FO derivatives with malononitrile in anhydrous pyridine.²¹ SC after KC was avoided since functionalization of 2,7-dibromo-FM under SC conditions leads to replacement of one of the nitriles for an acetylidate.²²

Photophysical properties are reported in toluene in Table 1. UV–vis absorption spectra show intense absorption bands in the UV-blue region for each compound (Figure 2). The high energy absorption profile for 4a is similar to the π–π* absorption of 2,7-bis(phenylethynyl)fluorene (BPF).²³ This allows the assignment of these bands to locally excited states of the chromophore since electronic communication between BPF and malononitrile units must be poor in the ground state. The lower energy weak bands are assigned to forbidden intramolecular charge transfer (ICT) transitions between high energy occupied orbitals of the aromatic donor and a low energy unoccupied orbital of the dicyanovinylene (DCV) acceptor. This is similar to the case of FM reported by Rault-Berthelot.²⁴ The 4b absorption band red shifts with respect to 4a given the increased conjugation conferred by the carbazole units; however, 4b displays the same characteristics as compound 4a: allowed π_{Ar}→π_{Ar}* and forbidden π_{Ar}→π*_{DCV} transitions.

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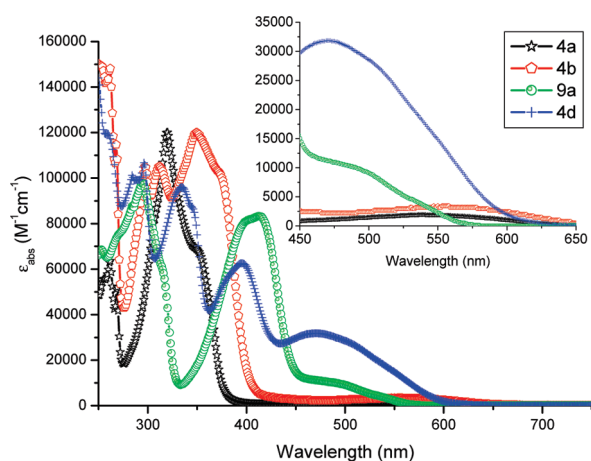


FIGURE 2. Normalized UV–vis absorption spectrum of solutions of the ambipolar compounds in toluene at 25 °C. Inset: 425–650 nm region shows the weak absorption bands for the series compounds.

FM derivatives **9a** and **9b** show strong absorption bands around 400 nm and medium intensity bands centered ca. 475 nm. Interestingly, compounds with similar structures to **9b**, used as sensitizers for photoelectrochemical cells, show comparable molar absorptivities and absorption profiles.²⁵ The highest energy band for compound **9a** centered at ca. 290 nm is similar to that of 1,2-diphenylacetylene.²⁶ Even so, the rest of the bands could not be assigned by comparison with reported absorptions for similar compounds; this indicates effective electronic communication between the 3,6-positions and C-9. Additionally, none of the spectra for any of the compounds shows much solvent dependency (see Figure S2 in the Supporting Information), in accordance with previously reported data for other types of aryl-DCVs.²⁷ However, the absorption band maximum centered at ca. 470 nm of **9b** blue shifts upon increasing solvent polarity. This may indicate higher polarity of the ground state compared to that of the excited state for this compound, yet its red-edge bathochromic shift points toward a different direction.

The normalized fluorescence spectra in toluene are shown in Figure 3. Most compounds show broad and structureless emission bands, with maxima centered at $\lambda > 500$ nm. Excimer formation was ruled out after concentration dependence studies revealed the same appearance at low concentrations (120–1200 nM for **4a**; see Figure S4 in Supporting Information).²⁸ Moreover, vibrational features ($\nu_{\text{IR}} \sim 0.19$ eV) were found in the emission spectra for some of the compounds when measured in cyclohexane at room temperature and in glasses of methyl-THF at 77 K (see Figures S3 and S5 in Supporting Information). Since the intermolecular distance between chromophores is the same before and after radiative relaxation for any excimer, there is no possibility of vibrational modes in the emission spectrum because

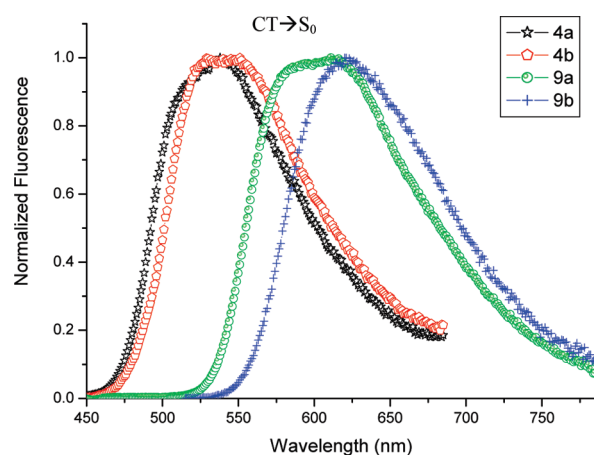


FIGURE 3. Normalized emission spectrum of solutions of the ambipolar compounds in toluene at 25 °C.

excimers become repulsive and separate immediately after photon emission.²⁹

Radiative decay was found to be sensitive to solvent polarity (see Figure S3, Supporting Information). Compounds **4a** and **4b** showed bathochromic shifts with increasing polarity, though in DMF, the emission maxima shifted to shorter wavelengths. In the case of **9a**, such an unusual shift was not apparent. Compound **9b** showed total emission quenching in EtOAc, DCM, and DMF, contrary to the high intensity displayed when dissolved in cyclohexane or toluene. This suggests that charge transfer states are involved as one of the possible nonradiative deactivation pathways. Furthermore, the lack of emission at 300 K in MeTHF compared with high emission intensity at 77 K suggests that rotational modes could also be involved in the nonradiative decay (i.e., dicyanoethylene isomerization). This finding further explains the low fluorescence quantum yields of all the compounds at room temperature. Transient absorption spectroscopic measurements are underway in order to resolve completely the photophysics of these materials.

To gain more insight into such unique excited state behavior, DFT calculations were performed for all carbazole-containing compounds. The B3LYP functional^{30,31} and the 6-31G*³² basis set were used for the present computations. Geometry optimization of **4b** and **9b** showed that PA units were planar to the FM skeleton, whereas carbazole units were quite twisted from such a plane (see abstract graphic). Localization of HOMO was found in the CPA units and LUMO in the FM unit (Figure 4), in line with the experimental behavior exhibited by the lowest energy transitions. Additionally, the calculated ground state dipole moment was higher for **4b** ($\mu_{\text{g}} = 6.33$ D) than for **9b** ($\mu_{\text{g}} = 1.34$ D). From TDDFT calculations, the first vertical transition for **4b** is of lower energy than that of **9b** and involves a smaller oscillator strength ($f = 0.12$, $\lambda \sim 750$ nm for **4b**; $f = 0.30$, $\lambda \sim 664$ nm for **9b**). Although this trend is consistent

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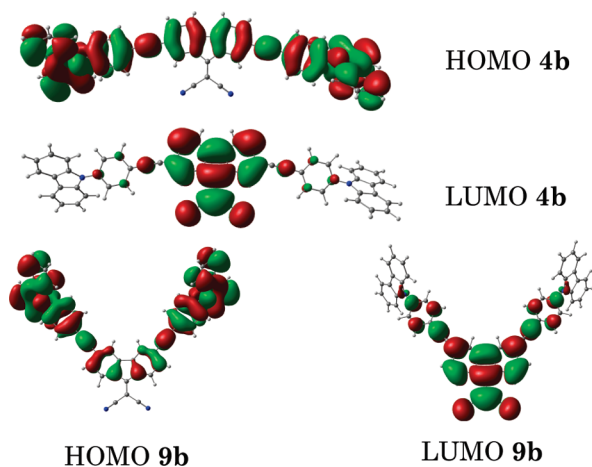


FIGURE 4. DFT calculated HOMO and LUMO orbitals for compounds **4b** and **9b** in vacuum.

with the experimental observations, the calculated oscillator strength for **4b** seems to predict higher photon absorption than what is seen from the UV–vis spectra. This should not be surprising given the limitations of TDDFT when treating long-range CT transitions.³³ The transitions dealing with LUMO+1 and LUMO+2 for **4b**, which involve CPA units, accounted for the biggest oscillator strengths. This also suggests that S_1 in this compound is mainly populated via higher energy excited states (S_n where $n > 1$). Conversely, all of the transitions involving LUMO for compound **9b** showed moderate oscillator strength. Finally, the difference between the first excited state and ground state dipole moments was found to be remarkably different for both compounds ($\Delta\mu = +2.35$ D for **4b**, and $\Delta\mu = +35.1$ D for **9b**). Such numbers anticipate a sensitive bathochromic shift from such transition in compound **9b**, in line with the observed red-edge behavior. Therefore, its unexpected absorption maximum blue shift must be caused by coalescence of two or more absorption bands.

In summary, four novel fluorene-based ambipolar compounds were synthesized in order to evaluate the electronic communication of positions 2,7 and 3,6 with C-9 in the fluorene core. Compound **9b** containing carbazole units displayed efficient charge separation in moderate to high polarity solvents. The structural design of these molecules would aid in the search of novel materials as candidates for electron transfer systems in which good charge separation is required for varied applications in electronic devices.

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Experimental Section

General Procedure for Knoevenagel Condensation. Starting fluorenone (0.50 mmol) and malononitrile (5.0 mmol) were combined under argon atmosphere and suspended in 5 mL of argon-saturated pyridine. After 1 h of vigorous stirring, the system was heated to 70 °C and allowed to further react for 2 h. Upon cooling to room temperature, 10 mL of absolute ethanol was added and then the mixture was cooled at –20 °C overnight. The formed precipitate was collected by vacuum filtration and washed with chilled ethanol. After air drying at 60 °C for 4–5 h, the title compound was obtained.

2,7-Bis(1-(4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl)-2-ethynyl)-fluorene-9-ylidene malononitrile (4b**).** Dark-gray powder. Analytically pure product was obtained after recrystallization from DMF (82 mg, 78% yield): mp > 250 °C; IR (neat, cm^{-1}) 2215, 1603; ^1H NMR (CDCl_3 , 300 MHz) δ (ppm) 8.59 (s, 2H), 8.14–8.17 (d, $J = 1.2$ Hz, 4H), 7.72–7.82 (m, 6H), 7.59–7.64 (d, $J = 8.4$ Hz, 6H), 7.47–7.53 (dd, $J_1 = 1.2$ Hz, $J_2 = 8.7$ Hz, 4H), 7.40–7.45 (d, $J = 8.7$ Hz, 4H), 1.49 (s, 36H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ (ppm) 32.0, 34.8, 77.2, 88.9, 91.6, 109.2, 113.0, 116.3, 120.7, 121.0, 123.6, 123.8, 124.7, 126.4, 129.7, 133.3, 134.6, 137.9, 138.7, 138.8, 141.2, 143.3; MALDI-TOF-MS 982.62 (M^+); HRMS calcd for $[\text{C}_{72}\text{H}_{62}\text{N}_4]$ 982.4977, found m/z 982.4974.

3,6-Bis(1-(4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl)-2-ethynyl)-fluorene-9-ylidene malononitrile (9b**).** Maroon colored powder. Analytically pure product was obtained as a deep red solid after reprecipitation from pyridine/ethanol (89 mg, 73% yield): mp 240 °C (dec.); IR (neat, cm^{-1}) 2202, 1598; ^1H NMR (CDCl_3 , 300 MHz) δ (ppm) 8.40–8.45 (d, $J = 8.1$ Hz, 2H), 8.15 (s, 4H), 7.76–7.84 (m, 6H), 7.60–7.67 (d, $J = 8.1$ Hz, 4H), 7.52–7.58 (d, $J = 8.4$ Hz, 2H), 7.44–7.51 (d, $J = 8.7$ Hz, 4H), 7.38–7.44 (s, $J = 8.7$ Hz, 4H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ (ppm) 32.0, 34.8, 76.0, 77.2, 89.6, 94.2, 109.2, 113.4, 116.4, 120.5, 123.6, 123.75, 123.78, 126.4, 126.9, 129.8, 132.5, 133.4, 133.8, 138.8, 139.1, 141.7, 143.5; MALDI-TOF-MS 982.66 (M^+); HRMS calcd for $[\text{C}_{72}\text{H}_{62}\text{N}_4 + \text{H}^+]$ 983.5053, found m/z 983.5056.

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Supporting Information Available: Experimental procedures and characterization data. UV–vis absorption and fluorescence spectra in various solvents. Fluorescence spectra in MeTHF at 298 and 77 K. ^1H and ^{13}C NMR spectra of final compounds. DFT calculation data in the gas phase. This material is available free of charge via the Internet at <http://pubs.acs.org>.