Generation and Spectroscopic Profiles of Stable Multiarylaminium Radical Cations Bridged by Fluorenes
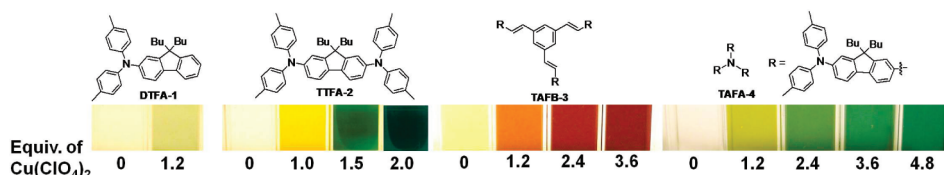
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ABSTRACT

A series of arylaminofluorene derivatives (DTFA-1, TTFA-2, TAFB-3, and TAFA-4) were synthesized, and the generation of their corresponding arylaminium cation radicals was readily achieved by $Cu(ClO_4)_2$ in CH_3CN. Moreover, the cation radicals were stable at ambient temperature with substantially long life times and exhibited distinct colors. The oxidation mechanism and spectroscopic features of the resulting cation radicals were probed by UV−vis−NIR spectroscopy and electron spin resonance experiments.

Triarylamine-based compounds have been found in many applications such as organic optoelectronics,[1] electrochromism,[2] organic magnets,[3] intervalence charge-transfer (IVCT),[4] metal ion sensors,[5] and synthetic utilities.[6] Most of these applications stem from the unshared lone pair of electrons at the nitrogen, which can be readily converted to cation radicals at a moderate oxidizing potential. Organic magnets and organic mixed-valence (MV) compounds all possess two or more triarylamino centers connected by extended π-conjugated molecular bridges.[4a,c,g,h] Arylaminium cation radicals warrant a significant spin concentration for spin-mediated organic molecular spintronics as well as an intense and well-separated IVCT band to allow accurate estimation of electronic coupling and valence delocalization. The bridging structures have a strong influence on the chemical stability and spin alignment of cation radicals as well as the efficiency of intersite electron coupling.

The generation of arylaminium cation radicals can be achieved either by electrochemical oxidation or chemical oxidants such as certain metal ions,[7] zeolite,[8] and protic acids.[9] Although electrochemical anodic oxidation[12] warrants

(1) (a) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953. (b) Chi, C.-C.; Chiang, C.-L.; Liu, S.-W.; Yueh, H.; Chen, C.-T.; Chen, C.-T. *J. Mater. Chem.* **2009**, *19*, 5561.

(2) Lim, B.; Nah, Y.-C.; Hwang, J.-T.; Ghim, J.; Vak, D.; Yun, J.-M.; Kim, D.-Y. *J. Mater. Chem.* **2009**, *19*, 2380.

(3) (a) Yan, X. Z.; Pawlas, J.; Goodson, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 9105. (b) Fukuzaki, E.; Nishide, H. *J. Am. Chem. Soc.* **2006**, *128*, 996 and references therein. (c) Kulszewicz-Bajer, I.; Gosk, J.; Pawłowski, M.; Gambarelli, S.; Djurado, D.; Twardowski, A. *J. Phys. Chem. B* **2007**, *111*, 9421. (d) Ito, A.; Sakamaki, D.; Ino, H.; Taniguchi, A.; Hirao, Y.; Tanaka, K.; Kanemoto, K.; Kato, T. *Eur. J. Org. Chem.* **2009**, 4441.

(4) (a) Lambert, C.; Noll, G. *J. Am. Chem. Soc.* **1999**, *121*, 8434. (b) Lambert, C.; Noll, G.; Schelter, J. *Nat. Mater.* **2002**, *1*, 69. (c) Lambert, C.; Risko, C.; Coropceanu, V.; Schelter, J.; Amthor, S.; Gruhn, N. E.; Durivage, J. C.; Brédas, J.-L. *J. Am. Chem. Soc.* **2005**, *127*, 8508. (d) Seibt, J.; Schaumlöffel, A.; Lambert, C.; Engel, V. *J. Phys. Chem. A* **2008**, *112*, 10178. (e) Nelsen, S. F.; Ismagilov, R. F.; Trieber, D. A. *Science* **1997**, *278*, 846. (f) Jones, S. C.; Coropceanu, V.; Barlow, S.; Kinnibrugh, T.; Timofeeva, T.; Brédas, J.-L.; Marder, S. R. *J. Am. Chem. Soc.* **2004**, *126*, 11782. (g) Barlow, S.; Risko, C.; Chung, S.-J.; Tucker, N. M.; Coropceanu, V.; Jones, S. C.; Levi, Z.; Brédas, J.-L.; Marder, S. R. *J. Am. Chem. Soc.* **2005**, *127*, 16900. (h) Coropceanu, V.; Gruhn, N. E.; Barlow, S.; Lambert, C.; Durivage, J. C.; Bill, T. G.; Nöll, G.; Marder, S. R.; Brédas, J.-L. *J. Am. Chem. Soc.* **2004**, *126*, 2727. (i) Lancaster, K.; Odom, S. A.; Jones, S. C.; Thayumanavan, S.; Marder, S. R.; Brédas, J.-L.; Coropceanu, V.; Barlow, S. *J. Am. Chem. Soc.* **2009**, *131*, 1717 and references therein. (j) Odom, S. A.; Lancaster, K.; Beverina, L.; Lefler, K. M.; Thompson, N. J.; Coropceanu, V.; Brédas, J.-L.; Marder, S. R.; Barlow, S. *Chem.—Eur. J.* **2007**, *13*, 9637.

(5) Sanna, E.; Martinez, L.; Rotger, C.; Blasco, S.; González, J.; Garcia-España, E.; Costa, A. *Org. Lett.* **2010**, *12*, 3840.

(6) (a) Sumalekshmy, S.; Gopidas, K. R. *Chem. Phys. Lett.* **2005**, *413*, 294. (b) Sreenath, K.; Suneesh, C. V.; Ratheesh Kumar, V. K.; Gopidas, K. R. *J. Org. Chem.* **2008**, *73*, 3245.

(7) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(8) Garcia, H.; Marti, V.; Casades, I.; Fornes, V.; Roth, H. D. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2955.

(9) Davies, A. G. *J. Chem. Res., Synop.* **2001**, 253.

complete oxidation, transient-oxidized species are difficult to isolate and structurally elucidate. Moreover, the cation radicals are formed in very high concentrations at the electrode surface, possibly leading to dimerization. Several concerns also arise when using chemical oxidants, which are rather expensive, environmentally unfriendly, and give low oxidization yields depending on the substance. Recently, $Cu(ClO_4)_2$, an inexpensive and mild chemical oxidant, was reported to effectively generate stable monoarylaminium cation radicals and tris(4-anisyl)amine dications.[6,10] The general applicability of this oxidant in generating multiple arylaminium cation radicals remains to be explored.

A wide variety of bridge structures such as phenylene, biphenyl, phenylene-ethynylene, vinylene, and various lengths of phenylene-vinylene have been extensively investigated for their roles in mediating electron coupling and valence delocalization.[4a,g,h] Fluorene, which possesses two benzene rings coplanar with the central carbon and is much investigated for use as a luminophore in organic light-emitting diodes,[1b] is surprisingly absent among these mixed valence systems. To decipher and understand how
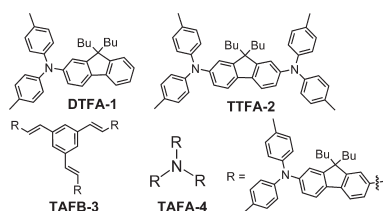

Figure 1. Chemical structures of tolylaminofluorenes **DTFA-1**, **TTFA-2**, **TAFB-3**, and **TAFA-4**.

fluorene-bridged redox centers interact, a new series of tolylaminofluorene derivatives, denoted as **DTFA-1**, **TTFA-2**, **TAFB-3**, and **TAFA-4** (Figure 1) are designed and synthesized. These derivatives consist of one to four tritolylamino centers bridged by fluorenes; the 9-position of fluorene is alkylated with two *n*-butyl groups to prevent it from being oxidized or deprotonated and to increase solubility in organic solvents. In addition, a convenient and cheap chemical oxidant capable of generating polycation radicals is also addressed.

Syntheses of tolylaminofluorenes are depicted in Schemes 1 and 2. Details of the procedures and structural characterization can be found in the Supporting Information. Compounds **3**,[11] **6**,[12] and **7**[13] were synthesized as described in the literature. Starting from 2-bromo-9*H*-

fluorene (**1**), dialkylation proceeded smoothly in the presence of excess KOH to afford **2** in 92% yield. The subsequent Buchwald−Hartwig cross-coupling reaction[14] of **2** with di-*p*-tolylamine yielded 83% of the desired

Scheme 1. Synthesis of **DTFA-1**, **TTFA-2**, and **TAFB-3**
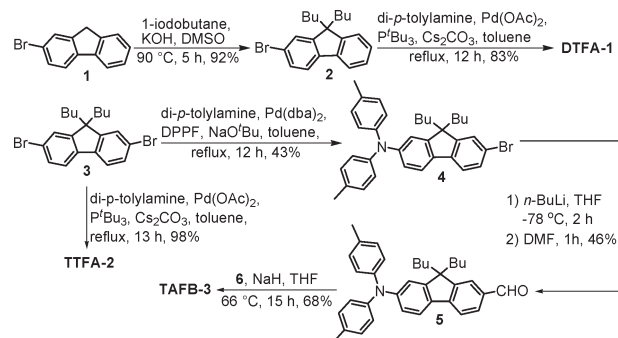
DTFA-1. Both **TTFA-2** and **TAFB-3** started with 2,7-dibromo-9,9-dibutyl-9*H*-fluorene (**3**) but produced either di- or mono-cross-coupling products depending on the amination conditions. Using $Pd(OAc)_2$ and P^tBu_3 as the catalyst and 3 equiv of di-*p*-tolylamine to react with **3**, the di-cross-coupling product-**TTFA-2** was afforded in almost quantitative yield. The mono-cross-coupling product **4** was obtained in a reasonable yield when only 1 equiv each of di-*p*-tolylamine, Pd(dba)₂, and DPPF were used. Addition of *n*-BuLi to **4** and quenching with DMF yielded the Vilsmeier formylation product **5** in 46% yield. Treatment of **5** with {3,5-bis[(diethoxyphosphoryl)methyl]phenyl}methyl diethyl phosphonate (**6**) via the Horner−Wadsworth−Emmons reaction gave **TAFB-3** in 68% yield. **TAFA-4** was obtained by a combination of dialkylation of **7** with 1-iodobutane followed subsequently by coupling with di-*p*-tolylamine via palladium catalysis, hydrogenation, and repeated Buchwald−Hartwig cross-coupling of **4**.

Scheme 2. Synthesis of **TAFA-4**
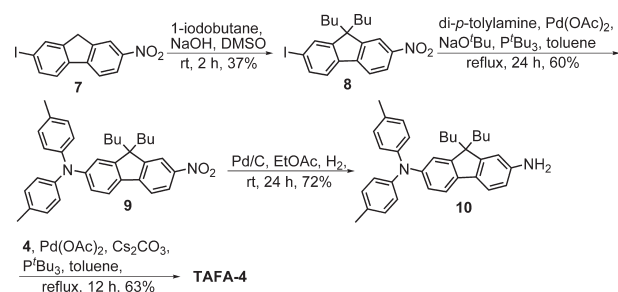
DTFA-1, **TTFA-2**, **TAFB-3**, and **TAFA-4** were subjected to cyclic voltammetry (CV) and differential pulse

(10) Sreenath, K.; Thomas, T. G.; Gopidas, K. R. *Org. Lett.* **2011**, *13*, 1134.

(11) Low, P. J.; Paterson, M. A. J.; Yufit, D. S.; Howard, J. A. K.; Cherryman, J. C.; Tackley, D. R.; Brook, R.; Brown, B. *J. Mater. Chem.* **2005**, *15*, 2304.

(12) Mizoshita, N.; Ikai, M.; Tani, T.; Inagaki, S. *J. Am. Chem. Soc.* **2009**, *131*, 14225.

(13) Rotzler, J.; Vonlanthen, D.; Barsella, A.; Boeglin, A.; Fort, A.; Mayor, M. *Eur. J. Org. Chem.* **2010**, 1096.

(14) (a) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609. (b) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1995**, *34*, 1348.

voltammetry (DPV) analyses. Cyclic voltammograms showed that four arylaminofluorene derivatives underwent reversible oxidizations without any subsequent chemical side reactions such as dimerization or disproportionation, indicating that the tolyl group is electrochemically inert after the formation of tolylaminium cation radicals (Figure 2).[11] Furthermore, the first oxidation voltages of four compounds were all shifted to lower values. In the case of **DTFA-1**, the oxidation potential is shifted to 0.37 V (vs Fc/Fc$^+$) relative to tritolylamine (0.47 V vs Fc/Fc$^+$). This decrease in redox potential[11] can be attributed to charge delocalization of the cation radical to the extended π-system of fluorene.[11] Although **TAFB-3** contains three redox centers, its redox feature is very similar to that of **DTFA** in that only one oxidation process at 0.36 V is observed. This reflects the fact that there is no charge delocalization among the three redox centers via the trivinylbenzene core. **TTFA-2** exhibited two chemically reversible waves at 0.14 and 0.36 V ascribed to one- and two-electron processes, respectively. It is worth noting that the first redox potential is shifted to a much lower voltage, strongly suggesting the delocalization of the first radical cation between two nitrogen atoms. **TAFA-4**, which can be regarded as a three-interconnected **TTFA-2** compound sharing the same nitrogen atom, displayed only three (instead of four) redox potentials at 0.30, 0.44, and 0.60 V, respectively. It was speculated that the lowest oxidation wave was buried in the Fc/Fc$^+$ wave. In fact, when the solvent was THF in lieu of CH$_3$CN, four oxidation waves were clearly observed (Figure S1 in the Supporting Information).

To search suitable oxidants for generating the cation radicals of tritolylaminofluorenes, several chemical oxidants including (4-BrC$_6$H$_4$)$_3$NSbCl$_6$, Pb(OAc)$_4$ and Cu-(ClO$_4$)$_2$ in CH$_3$CN were evaluated. Among them, Cu(ClO$_4$)$_2$ and (4-BrC$_6$H$_4$)$_3$NSbCl$_6$ gave complete conversion of the cation radical with dosimetric quantities, whereas a large excess amount of Pb(OAc)$_4$ failed to give satisfactory cation radicals (Figure S2 in the Supporting
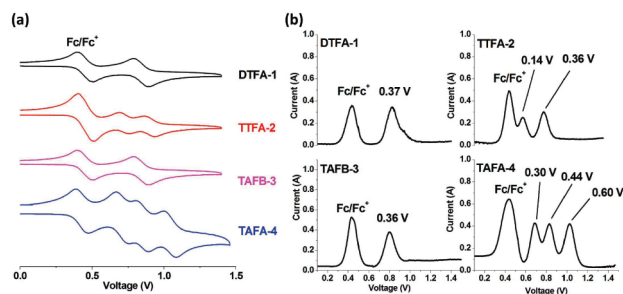
Figure 2. (a) CV and (b) DPV of tolylaminofluorene derivatives (10^{-3} M) in CH$_3$CN solution: working electrode, platinum wire; supporting electrolyte, tetrabutylammonium hexafluorophosphate (0.1 M); scan rate, 0.1 V/s; reference against ferrocene with ferrocene coupling at 0 V.

Information). One advantage of using Cu(ClO$_4$)$_2$ over (4-BrC$_6$H$_4$)$_3$NSbCl$_6$ as the oxidant is that the former shows
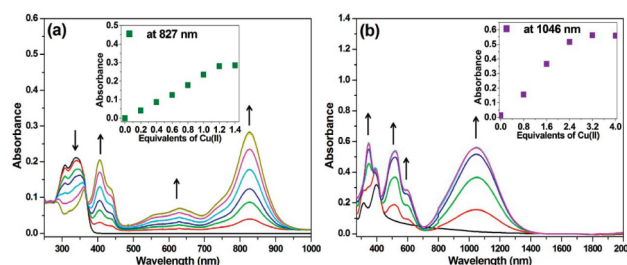
Figure 3. Overlaid UV−vis−NIR absorption spectra of (a) **DTFA-1** (1.25 × 10^{-5} M) and (b) **TAFB-3** (10^{-5} M) in CH$_3$CN with different equivalents of Cu(ClO$_4$)$_2$. Insets show the correlation of the absorbance with the amount of Cu(ClO$_4$)$_2$.

no absorption in UV−vis−NIR spectra. Moreover, the reduction potential of Cu(ClO$_4$)$_2$ in CH$_3$CN is 0.7 V vs Fc/Fc$^+$ (Figure S6 in the Supporting Information), which is sufficiently high to readily oxidize all four tolylaminofluorene derivatives to form the corresponding polycation radicals. Other metal-ion perchlorate or chloride salts in different organic solvents were also examined for the feasibility of generating tolylaminium radical cations of **TTFA-2** and **DTFA-1** (Figures S3−S5 in the Supporting Information). Fluorescence intensity changes were used for the quick assessment of cation radical formation since the presence of the unpaired electrons quenched the fluorescence. The results indicated that the oxidizing power of copper salts can be modulated by counterions as well as solvents, and that Cu(ClO$_4$)$_2$ in CH$_3$CN is the best combination for effectively generating arylaminium cation radicals.

The cation radicals of the tolylaminofluorene derivatives are thus generated using Cu(ClO$_4$)$_2$ in CH$_3$CN solution and characterized by UV−vis−NIR spectroscopy. **DTFA-1** exhibits one absorption band at 338 nm (ε = 17000 M^{-1} cm^{-1}). Upon titration with Cu(ClO$_4$)$_2$, three new absorption peaks gradually appear at 405, 640, 827, and a shoulder emerges at 450 nm, with a concomitant decrease of primordial absorption at 338 nm (Figure 3a). The new absorption peaks are ascribed to the formation of the tolylaminium radical cation. Monitoring the absorbance increment at 827 nm as a function of the amount of Cu(ClO$_4$)$_2$ reveals that saturation is reached when a stoichiometric amount of Cu(ClO$_4$)$_2$ is added (inset in Figure 3a). In the case of **TAFB-3**, with an increasing amount of Cu(ClO$_4$)$_2$, four new absorption peaks appear in the visible and near-IR regions at 348, 520, 602, and 1046 nm, corresponding to the tolylaminium cation radicals (Figure 3b). These absorption signals are saturated when 3 equiv of Cu(ClO$_4$)$_2$ is added (inset in Figure 3b), indicating that three neutral tritolylamines are converted to three monocation radicals. Moreover, no IVCT band is observed, strongly suggesting that there is no interaction among these monocation radicals, consistent with the observation of only one oxidation wave in the cyclic voltammogram.

The overlaid UV−vis−NIR absorption spectra of **TTFA-2** titrated with $Cu(ClO_4)_2$ in CH_3CN are shown in Figure 4a. Two new bands appearing at 482 and 1305 nm,[4a] characteristic of the tolylaminium monocation radicals, linearly increase with the amount of $Cu(ClO_4)_2$ before the addition of one equivalent. When further $Cu(ClO_4)_2$ is added, the IVCT band at 1305 nm starts to diminish and a new band at 739 nm, assigned to dication radicals where each tritolylamine is converted to a tritolylaminium radical, gradually forms. After addition of 2.4 equiv, saturation is reached and two isosbestic points are observed in the spectra obtained from 1.2 to 2.4 equiv, indicating where the cation and dication radicals are in equilibrium during the period. The inset in Figure 4a clearly depicts the correlation of changes in the cation radical and dication radical concentrations during the oxidation process. The symmetric bell-shaped curve with an inversion point around 1.2 equiv of $Cu(ClO_4)_2$ is observed by monitoring the absorbance change at 1305 nm, whereas a sigmoidal curve with a midpoint at 2.0 equiv and an end point at 2.4 equiv is observed for the dication radical. As a result, the solution changed from colorless to yellow, then to green, and finally to dark blue during the titration process.

In the case of **TAFA-4**, the titration profile is very similar to that of **TTFA-2**, except that more oxidant is consumed to oxidize the four redox centers (Figure 4b). Three absorption bands at 442, 700, and 1712 nm steadily increase before the addition of 3 equiv of $Cu(ClO_4)_2$, indicating that three peripheral tritolylaminofluorenes are oxidized to the monocation radical. The absorption band in the near-IR region is
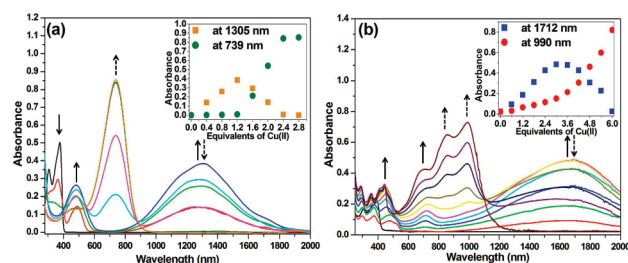

Figure 4. Overlaid UV−vis−NIR absorption spectra of (a) **TTFA-2** (1.25×10^{-5} M) and (b) **TAFB-4** (10^{-5} M) in CH_3CN with different equivalents of $Cu(ClO_4)_2$. Insets show the correlation of the absorbance with the amount of $Cu(ClO_4)_2$.

believed to be the IVCT band as **TAFA-4** is oxidized to trication radicals. When more than 3 equiv are added, the IVCT band decreases and two new bands at 857 and 990 nm emerge from the formation of tetracation radicals. Moreover, isosbestic points start to appear in the spectra taken from 3 equiv or more. Collectively, these observations provide solid and convincing evidence that the oxidation processes occur in a stepwise fashion, starting with the oxidation of peripheral redox centers first, followed by that of the central one later.
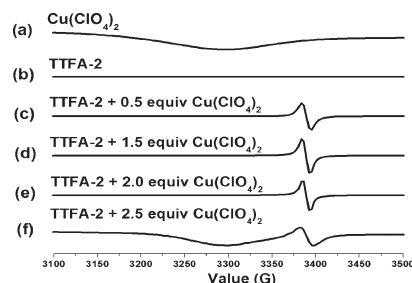

Figure 5. ESR spectra of **TTFA-2** (10^{-3} M) in CH_3CN solution with different equivalents of $Cu(ClO_4)_2$ at 77 K.

The formation of cation radicals and the oxidation states of copper ions during the oxidation processes are further confirmed by electron spin resonance (ESR) spectroscopy. The titration of **TTFA-2** with $Cu(ClO_4)_2$ is used for purposes of illustration. A broad band is observed for Cu^{2+}, whereas **TTFA-2** shows no ESR signal (Figure 5). However, in the presence of 0.5−2.0 equiv of $Cu(ClO_4)_2$, a unique ESR signal centered at $g = 2.0028$ appears. This g value and the lack of hyperfine splitting features are characteristic of arylaminium cation radicals with extensive electron delocalization.[4j] Therefore, the signal can be attributed to the one-electron oxidation product of **TTFA-2** in concomitance with a reduction of Cu^{2+} to Cu^+. When 2.5 equiv of $Cu(ClO_4)_2$ is used for the oxidation, a broad signal at $g = 2.0028$ is observed for **TTFA-2$^{2+\cdot}$** and another broad signal due to excess Cu^{2+} reappears.

In conclusion, four tritolylaminofluorene derivatives are successfully synthesized, and the corresponding arylaminium cation radicals are dosimetrically generated by $Cu(ClO_4)_2$. Their structural features and oxidation processes are characterized and deciphered by UV−vis−NIR spectroscopy in combination with ESR spectroscopy. Studies utilizing these compounds to further investigate mixed-valence charge transfer (MVCT) in detail and to characterize spin states are underway and will be reported in due course.

Supporting Information Available. Synthetic procedures, structural characterization, photospectroscopic, and electrochemical data of **DTFA-1**, **TTFA-2**, **TAFB-3**, and **TAFA-4**. This material is available free of charge via the Internet at http://pubs.acs.org.