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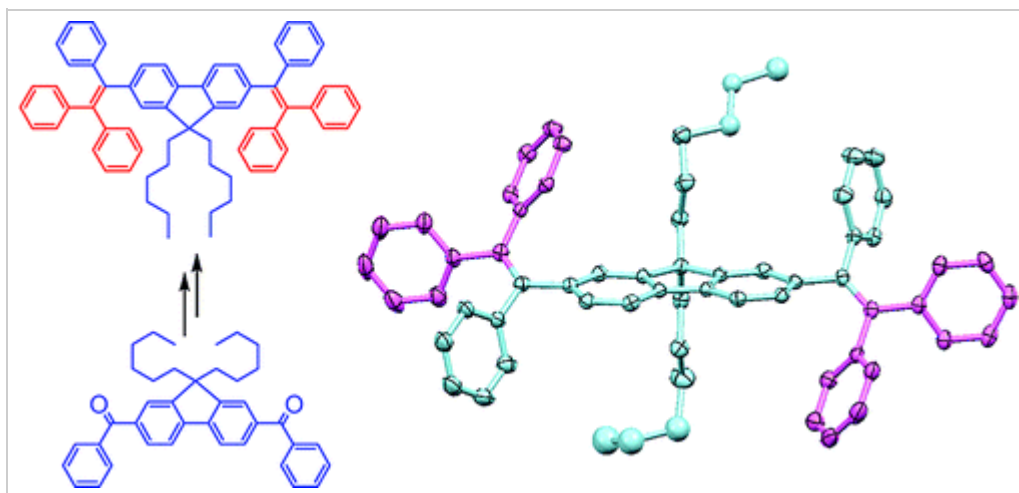Sergey V. Lindeman
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Abstract

We have demonstrated that reactions of diphenylmethyllithium with a variety of substituted benzophenones produces corresponding tertiary alcohols that are easily dehydrated, without any need for purification, to produce various unsymmetrical and symmetrical tetraarylethylenes in excellent yields. The simplicity of the method allows for the preparation of a variety of ethylenic derivatives in multigram (10–50 g) quantities with great ease. The methodology was successfully employed for the preparation of various triphenylethylene (TPE)-based triads (i.e., TPE–spacer–TPE) containing polyphenylene and fluoranyl-based spacers. The ready availability of various substituted tetraarylethylenes allowed us to shed light on the effect of substituents on the oxidation potentials (E_{ox}) of various tetraarylethylenes. Moreover, the electronic coupling among the triphenylethylene moieties in various TPE–spacer–TPE triads was briefly probed by electrochemical and optical methods.

Introduction

The tetraphenylethylene (TPE) motif has attracted considerable attention by virtue of its rich electrochemical[1] and excited-state properties[2] as well as its extensive usage as an electron-transfer catalyst in a variety of polymerization[3] and coupling reactions.[4] For several decades, TPE and its derivatives have served as models to study photoinduced cis–trans isomerization of ethylenic double bonds — a process of fundamental importance both in biological and in materials chemistry.[5] For example, the mechanism of vision is believed to occur by a rotation around a carbon–carbon double bond, following a photon absorption, that sets off a chain of events that leads to data storage of enormous complexity.[6] The extended π-systems based on tetraarylethylenes are also potentially important candidates for incorporation into various organic optoelectronic and optomechanical switching and storage devices,[7] as well as for the preparation of two-dimensional molecular scaffolds for bichromophoric donor–acceptor dyads for energy/charge transport.[8]

Thus, an efficient and scalable methodology for the preparation of these tetraarylethylenes is imperative. Although symmetrical tetraarylethylenes are easily prepared via McMurry coupling of corresponding benzophenones by low-valent titanium,[9] the unsymmetrical tetraarylethylenes are, however, not as readily accessible. McMurry coupling of two different benzophenones is not of general

synthetic use as it produces a mixture of symmetrical and mixed products in a nearly statistical mixture, unless one of the components is used in sacrificial excess.[10] Furthermore, the procedures that are generally utilized for the preparation of unsymmetrical tetraarylethylenes either require the multistep synthesis of precursors or suffer from low yields. The reactions of resonance stabilized selenoketones with diaryldiazomethane,[11] benzophenone hydrazones with diselenium dibromide,[12] the Pd-catalyzed three-component coupling of aryl iodides/internal alkynes/arylboronic acids,[13] and the Pd-catalyzed sequential assembly using a vinyl 2-pyrimidyl sulfide core[14] give either a mixture of products or are not amenable for large-scale syntheses.

We have recently reported[15] that easily prepared diphenylmethyllithium from diphenylmethane and n-butyllithium in tetrahydrofuran at 0 °C add to hexakis(4-benzoylphenyl)benzene to afford the corresponding hexaalcohol, which can be readily dehydrated using an acid catalyst to afford hexakis(tetraphenylethylene)benzene in nearly quantitative yield[15] (i.e., Scheme 1).
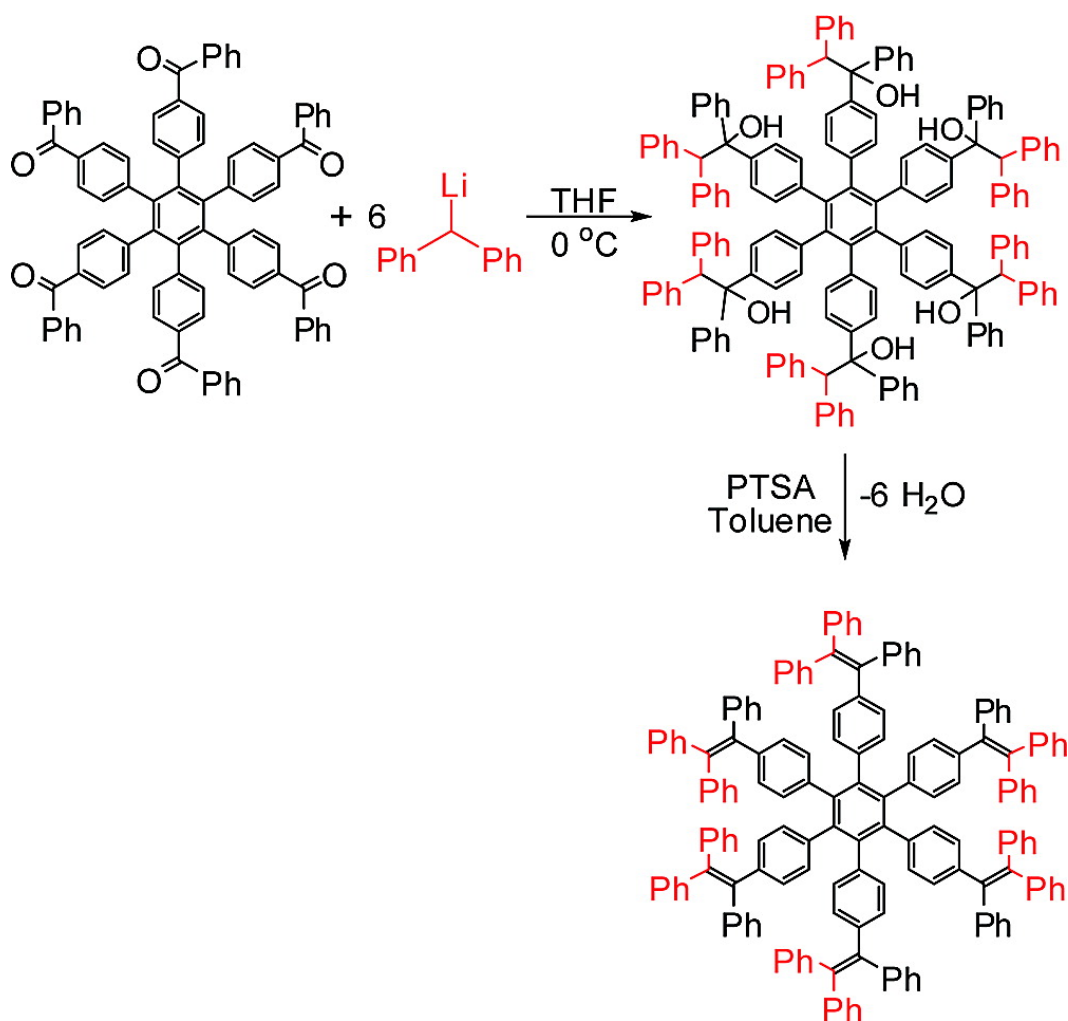

Scheme 1. Two-Step Synthesis of Polychromophoric Hexakis-(tetraphenylethylene) Benzene

Herein, we report that the reaction sequence depicted in Scheme 1 is general and can be applied for the preparation of multigram quantities of unsymmetrical tetraarylethylenes as well as the parent tetraphenylethylene with remarkable ease using appropriately substituted benzophenones. The ready availability of multigram quantities of mono-bromoTPE (i.e., 4-bromophenyltriphenylethylene), using the protocol in Scheme 1, allowed the preparation of a number of TPE-based triads (TPE–spacer–TPE) by palladium-catalyzed coupling reactions. Also, various tetraarylethylenes and polychromophoric triads, prepared herein, were utilized for the exploration of the structure–property relationship of their electrochemical and spectral behavior as follows.

Results and Discussion

Synthesis of Tetraarylethylenes. Thus, an addition of *n*-butyllithium (2.5 M in hexanes, 100 mmol) to a solution of diphenylmethane (105 mmol) in tetrahydrofuran (100 mL) at 0 °C produced an orange–red solution of diphenylmethyllithium within 30 min. To this highly colored solution was added solid 4-methylbenzophenone (100 mmol) at 0 °C, and the resulting mixture was allowed to warm to room temperature and was stirred for 6 h. The reaction was quenched with saturated aqueous ammonium chloride solution followed by a standard aqueous workup, affording the corresponding alcohol in nearly quantitative yield (see Scheme 2). The crude alcohol was dissolved in toluene and refluxed in the presence of a catalytic amount of *p*-toluenesulfonic acid with an azeotropic removal of water using a Dean–Stark trap to furnish tolyltriphenylethylene (**2**) in 96% isolated yield (33.5 g, ~97 mmol) by simple crystallization from a mixture of dichloromethane and methanol (i.e., Scheme 2).
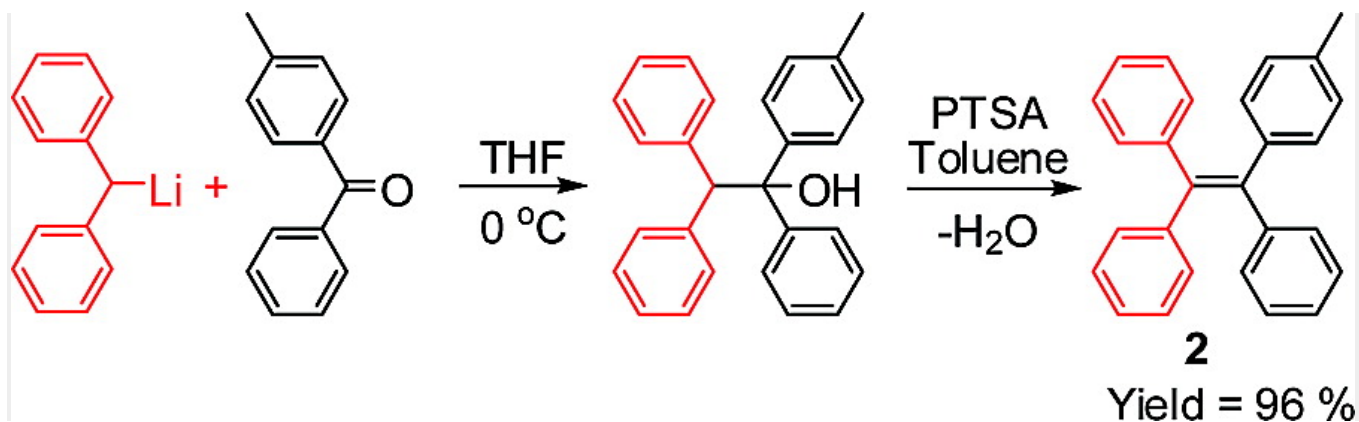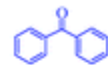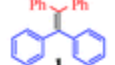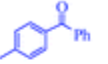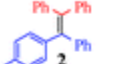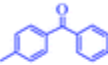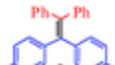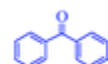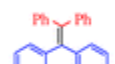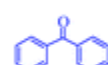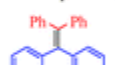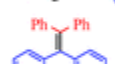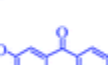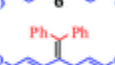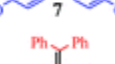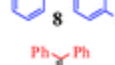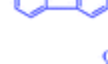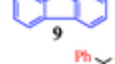

Scheme 2. Representative Two-Step Reaction Sequence for Synthesis of Various Tetraaryllethylenes

Using a procedure akin to that in Scheme 2, a number of benzophenone derivatives were reacted with freshly prepared diphenylmethyllithium to afford the corresponding alcohols, which were dehydrated, without any purification, to produce the corresponding tetraarylethylenes in excellent yield as listed in Table 1. The efficacy of the synthetic protocol in Scheme 2 is clearly evident by excellent yields of various substituted tetraarylethylenes using methoxy-, methyl-, or phenyl-substituted benzophenones

(see Table 1). The structures of various tetraarylethylenes were established by $^{1}H/^{13}C$ NMR spectroscopy, comparison with the authentic samples where available, and X-ray crystallography of a representative example (**6**). Various characterization data are compiled in the Supporting Information.

Table 1. Tetraarylethylenes Synthesized Using the Two-Step Procedure in Scheme 2[a,b]

Benzophenone derivative	Ar$_2$CHLi	Tetraryl-ethylene	% Yield[c]
		1	94
		2	96
		3	92
		4	81
		5	86
		6	90
		7	84
		8	79
		9	93
		10	91
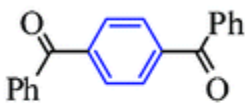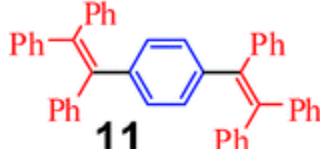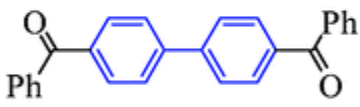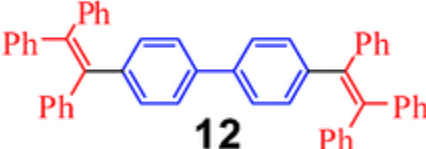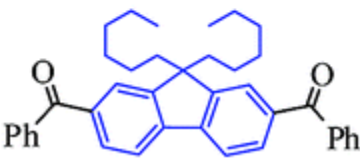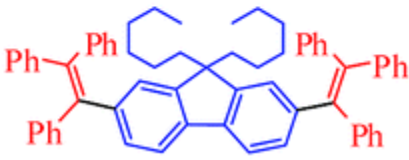
[a] All reactions were performed using the genral procedure (see text). [b] Progress of the reactions was monitored by TLC. [c] Isolated yield. Pure products were obtained in most cases by simple crystallization from a mixture of dichloromethane and methanol acetonitrile.

It is to be further noted that the reaction of 4-bromobenzophenone (entry **4**) with diphenylmethyllithium was carried out at a lower temperature (−78 °C) for 3 h followed by slowwarming to 22 °C to avoid halogen−metal exchange. Dehydration of the resulting alcohol afforded

the mono-bromotetraphenylethylene **4** in good yield. This particular ethylene derivative holds the potential to be utilized for the preparation of a variety of macromolecular derivatives by palladium-catalyzed coupling reactions (vide infra).

Preparation of TPE-Based Triads (TPE−Spacer−TPE). The reaction of diphenylmethyllithium with bis-benzoyl substrates according to the procedure in Scheme 2, with a simple change in the stoichiometries, provided ready access to TPE−spacer−TPE triads with phenylene, bis-phenylene, and 9,9-dihexylfluorene as spacers. Various triads in Table 2 were obtained in excellent yields with the reactions being clean and complete and having no traces of the products arising from incomplete reactions of the bis-benzoyl substrates (Table 2).

Table 2. Synthesis of TPE−Spacer−TPE Triads Using the Two-Step Procedure in Scheme 2[a,b]

Bis-Benzoyl substrate	TPE-spacer-TPE	% Yield[c]
	11	92
	12	95
	13	92

[a] All reactions were performed using the genral procedure (see text). [b] Progress of the reactions was monitored by TLC. [c] Isolated yield.

The molecular structure of TPE−Ph−TPE (**11**) was established by X-ray crystallography and is displayed in Figure 1. It is interesting to note that a pair of dichloromethane molecules is sandwiched between two pairs of cofacially juxtaposed phenyl moieties in **11** in a way that they allow effective C−H···π interactions, as shown by a partial space-filling representation in Figure 1 (right). Moreover, Figure 1

(left) also shows that a cofacial juxtaposition of the phenyls and central phenylene in **11** should allow an effective electronic coupling between the two triphenylethylene moieties via a contribution from through-space electronic coupling[16] (vide infra). The X-ray structure of **13** was also established by X-ray crystallography, and the structural details are available in the Supporting Information.
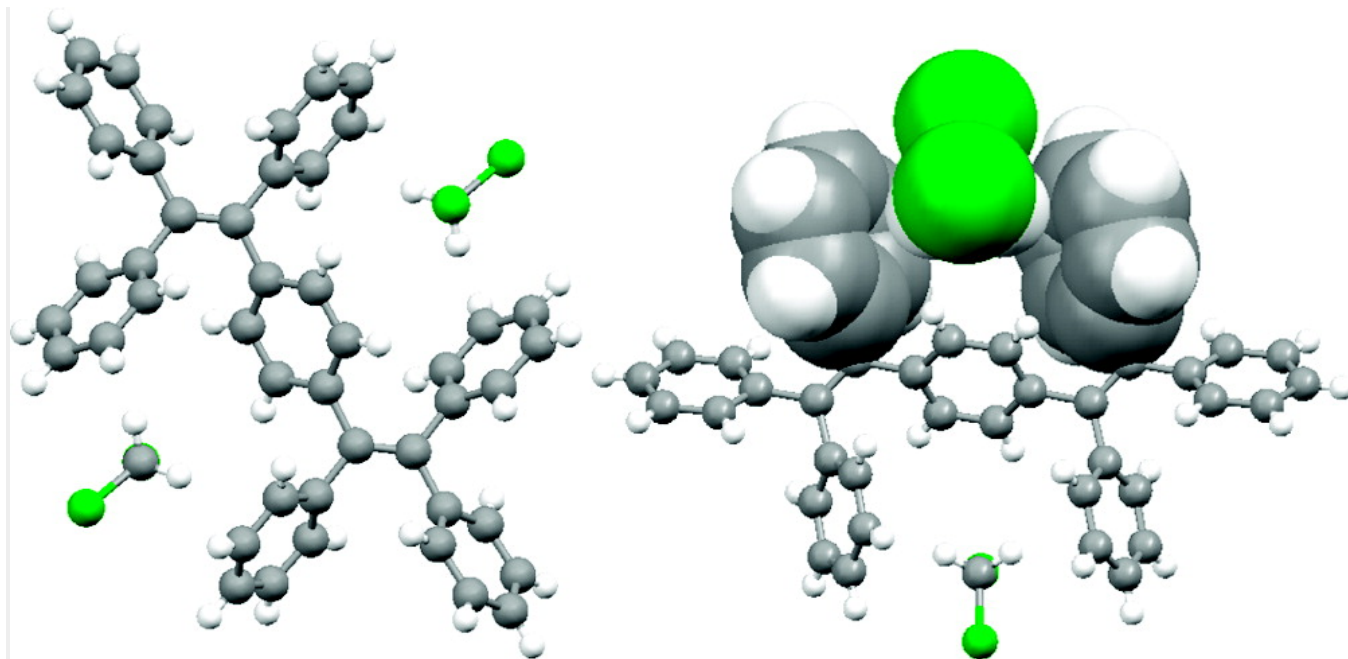
Figure 1 (Left) Ball-and-stick model of the molecular structure of **11** obtained by X-ray crystallography. (Right) Partial space-filling representation of [**11**·2CH$_2$Cl$_2$] showing the sandwiching of CH$_2$Cl$_2$ molecules between a pair of phenyls via C−H···π interactions.

The ready availability of triphenylethylene-based triads separated by mono- and di-phenylene spacers (i.e., **11** and **12**) prompted us to obtain the higher homologues containing longer polyphenylene spacers using mono-bromotetraphenylene (**4**) (vide infra). Indeed, a standard Suzuki coupling of 2 equiv of **4** with the benzene-1,4-diboronate ester, biphenyl-4,4'-diboronate ester, or 9,9'-dihexylfluorene-2,7-diboronic acid afforded the corresponding bichromophoric TPE derivatives (**14−16**) in excellent yields (i.e., Scheme 3). With a series of TPE-based triads (Table 2 and Scheme 3) and various tetraarylethylenes (Table 1) at our disposal, we next examined their electrochemical and optical properties as follows.
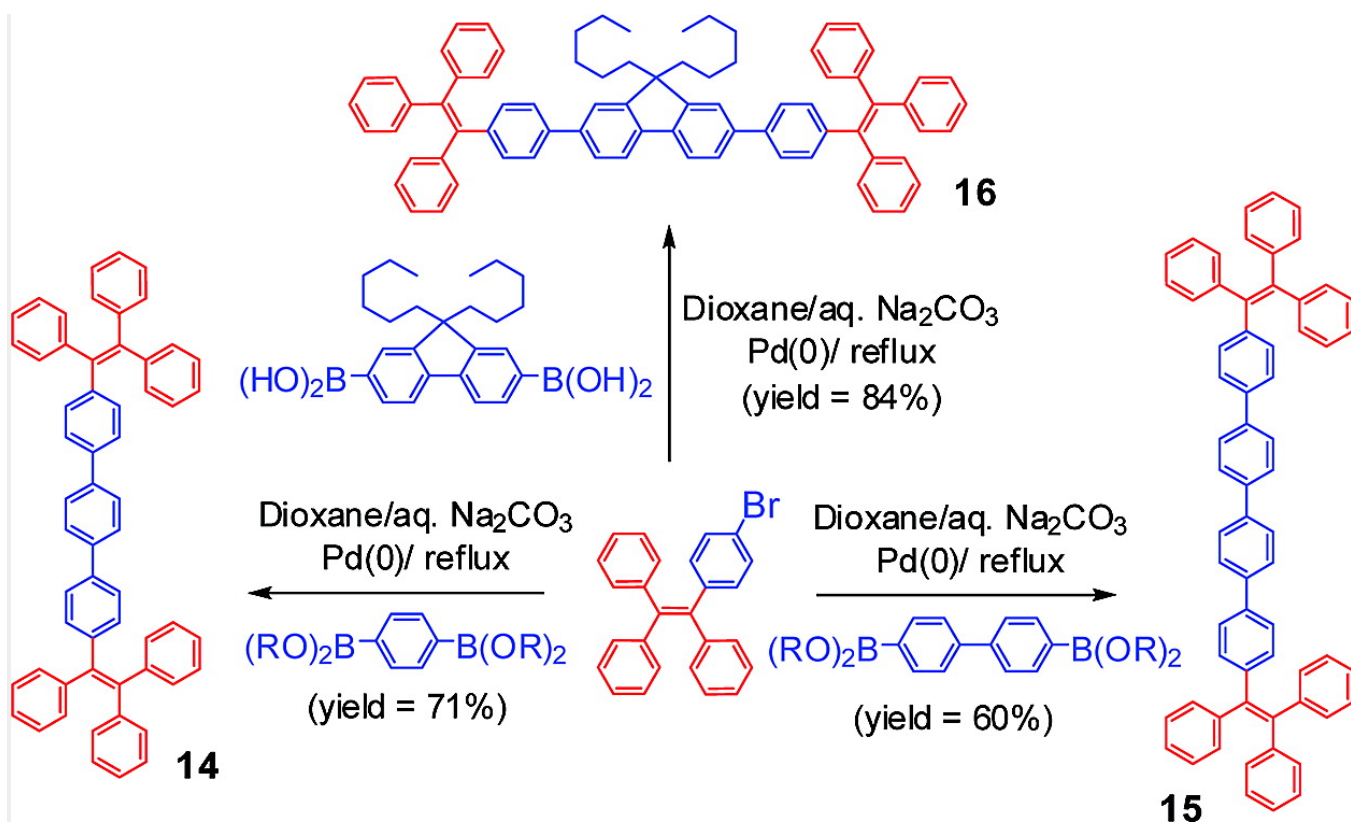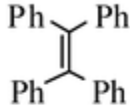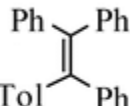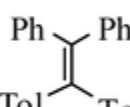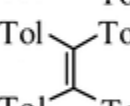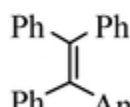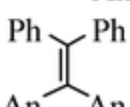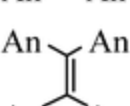
Scheme 3. Suzuki Coupling of Mono-bromotetraphenylethylene **4** with Various Diboronic Acid Spacers

Electrochemical Studies of the Tetraarylethylenes. A number of studies[17] on the tetraarylethylene systems has shown that they are generally oxidized and reduced in two successive one-electron transfer steps and that the one-electron oxidation/reduction products have a tendency to disproportionate with the position of equilibrium dependent upon ion-pairing and solvation. Herein, we examine the effect of substitutions on the oxidation potentials (E_{ox}) of various tetraarylethylenes as follows.

Table 3. Electrochemical Oxidation Potentials of Representative Tetraarylethylenes[a]

Tetraethylene Derivative	E^0_{ox} (I) (V vs. SCE)	E^0_{ox} (II) (V vs. SCE)	Δ(mV) E^0_{ox} (II)-E^0_{ox} (I)
Ph, Ph / Ph, Ph **1**	1.36	1.67	350
Ph, Ph / Tol, Ph **2**	1.29	1.57	276
Ph, Ph / Tol, Tol **3**	1.23	1.53	300
Tol, Tol / Tol, Tol **17**	1.11	1.39	272
Ph, Ph / Ph, An **5**	1.17	1.41	232
Ph, Ph / An, An **6**	1.06	1.33	268
An, An / An, An **18**	0.79	0.91	120

[a] In anhydrous dichloromethane as a 0.2 mM solution containing 0.2 M TBAP at a scan rate of 200 mV/S and at 25 °C. All potentials were calibrated with ferrocene as an added internal standard [E_{ox} (ferrocene) = 0.45 V vs SCE].

The E_{ox} values for various tetraarylethylenes were determined electrochemically at a platinum electrode as 2 × 10^{-3} M solutions in anhydrous dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. The common unifying feature in all the cyclic voltammograms of tetraarylethylenes (in Table 1) is the presence of two closely coupled one-electron oxidation waves with the first wave completely reversible and the degree of reversibility of the second wave dependent upon the nature and substitution pattern and the possibility of electrochemically induced chemical reactions at the electrode (vide infra).[18] The potentials corresponding to the first and second oxidations were referenced to added ferrocene, as an

internal standard, and are compiled in Table S1 in the Supporting Information along with the separation between the two oxidation potentials ($\Delta E_{1/2}$). To briefly comment on the effect of substitution patterns on the first and second oxidation potentials of various methyl- and methoxy-substituted tetraarylethylenes, their E_{ox} values together with tetratolylethylene (**17**)[19] and tetraanisylethylene (**18**)[19] are shown in Table 3.
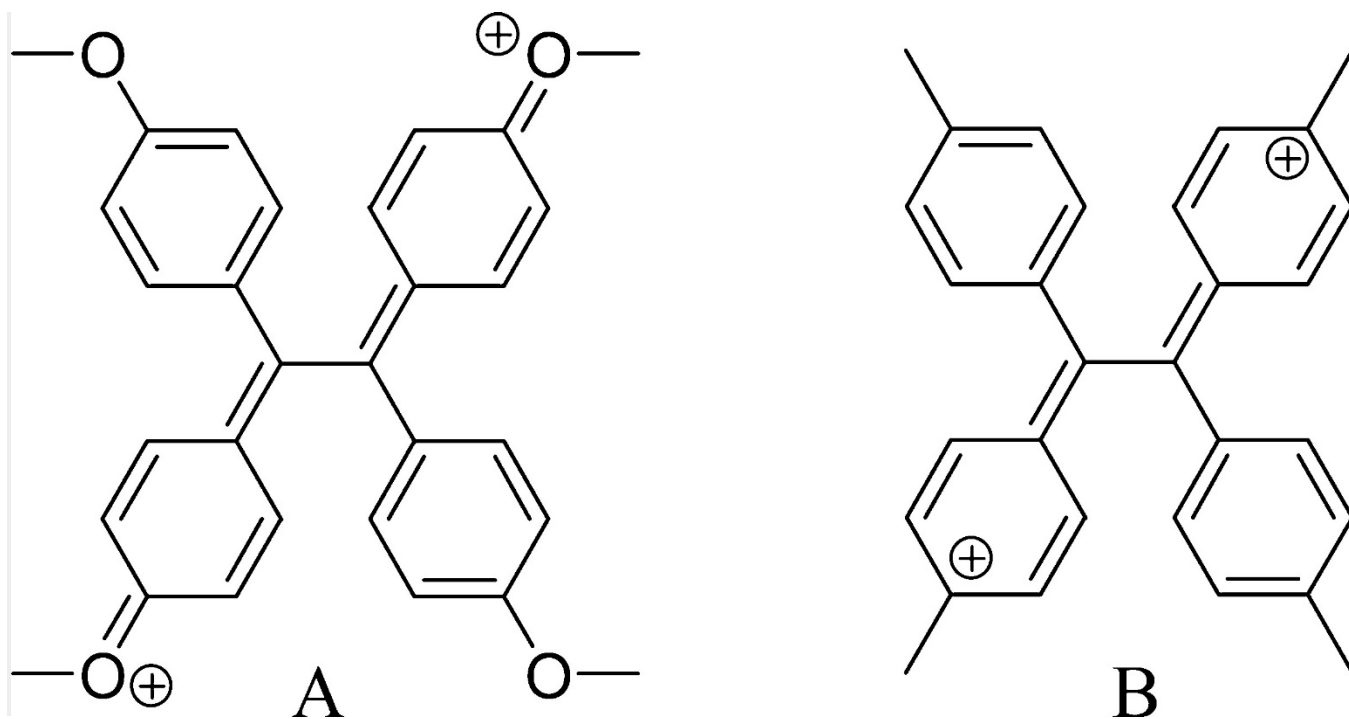
Chart 1. Anisyl versus Tolyl Stabilization of Cationic Charge

Predictably, both the first and the second oxidation potentials of various tetraarylethylenes decrease with an increasing number of electron-donating methyl or methoxy substituents in comparison to the parent tetraphenylethylene. Also the reversibility of the two redox processes (or the stability of the cation radical and dication) reaches a maximum in tetra-substituted derivatives **17** and **18**.[19]

Also noteworthy are the ΔE_{ox} values (i.e., the separation between the first and the second oxidation potentials), which are relatively larger for unsymmetrical methoxy-substituted derivatives **5** and **6** (i.e., 232 and 268 mV, respectively) as compared to the symmetrical tetraanisylethylene (120 mV) (see Figure 2). In contrast, however, both symmetrical and unsymmetrical methyl-substituted tetraphenylethylene **18**, **2**, and **3** showed rather similar ΔE_{ox} values (~300 ± 25 mV). Such a disparate behavior among the methyl- and methoxy-substituted tetraphenylethylene derivatives arise, at least in part, due to the fact that a single *p*-anisyl group stabilizes a cationic charge much more effectively than the *p*-tolyl or phenyl groups (see Chart 1).[19]
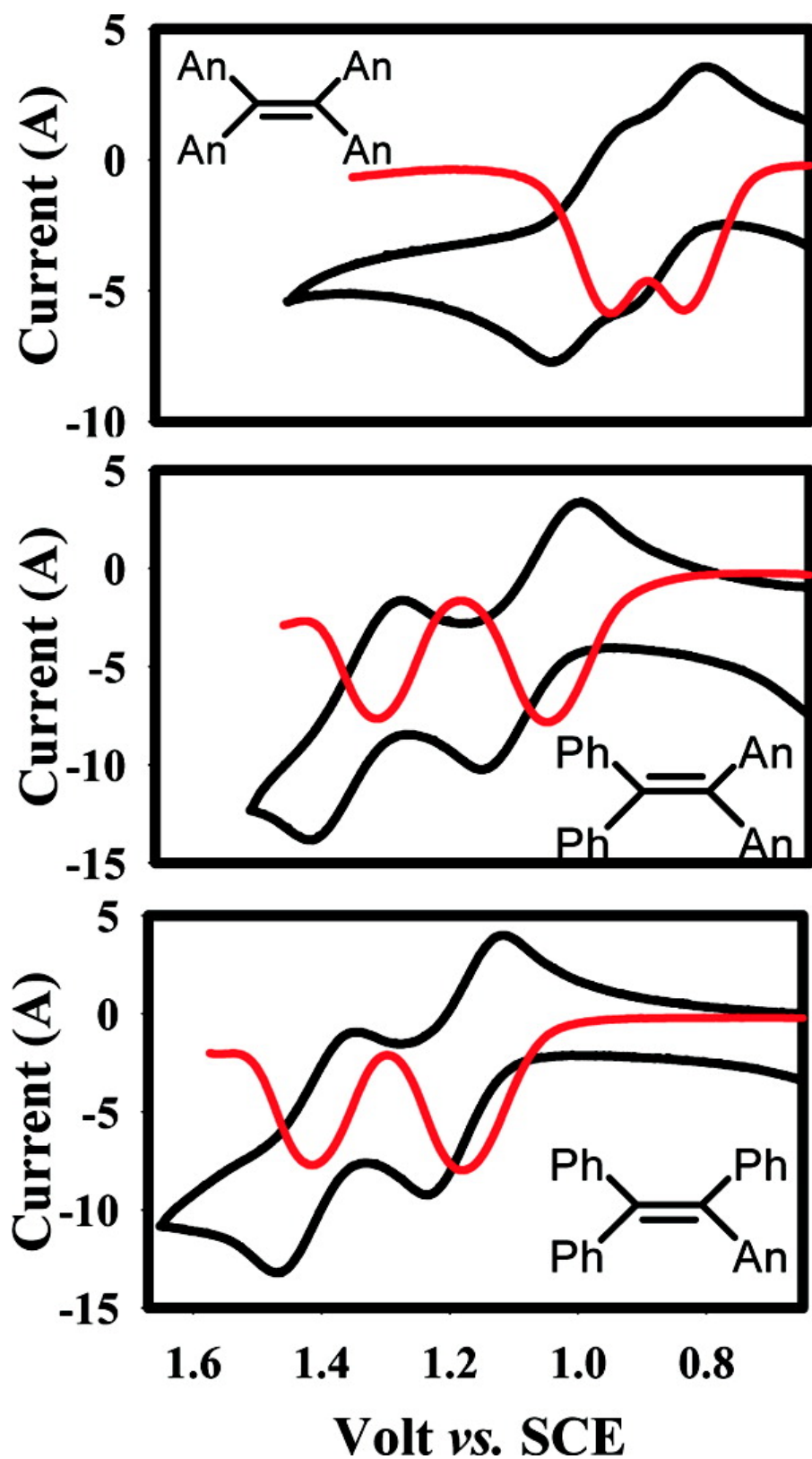
Figure 2 Cyclic- and square-wave voltammogram of the methoxy-substituted tetraphenylethylene derivatives **5**, **6**, and **18** as a 0.2 mM solution in dichloromethane containing 0.2 M TBAH as the supporting electrolyte at 22 °C and scan rate of 200 mV s^{-1}.

Owing to the extensive interest in poly(phenylenevinylene) derivatives for the preparation of electroactive materials,[20] herein, we briefly apply electrochemical techniques to probe electronic coupling between the two triphenylethylene moieties separated by either a poly-p-phenylene spacer of increasing length or the fluorene and 2,7-diphenylfluorene spacers as well-defined triads (TPE–spacer–TPE). The square-wave voltammograms of various triads recoded under identical conditions are displayed in Figure 3, and the E_{ox} values are compiled in Table 4.

When the two TPE moieties were separated through a single p-phenylene bridge as in **11**, two well-resolved reversible oxidation waves centered at 1.22 and 1.38 V with a separation of ΔE_{ox} = 162 mV were observed (Figure 3). Varying the spacer from a simple p-phenylene to bis-p-phenylene to tris-p-phenylene to tetrakis-p-phenylene showed a steady decrease in ΔE_{ox} values of 162 to 125 to 45 mV to an eventual merger of the two oxidation waves in triad **15** (with tetrakis-p-phenylene as a spacer) into a single two-electron oxidation wave at 1.29 V (Figure 3).[21]
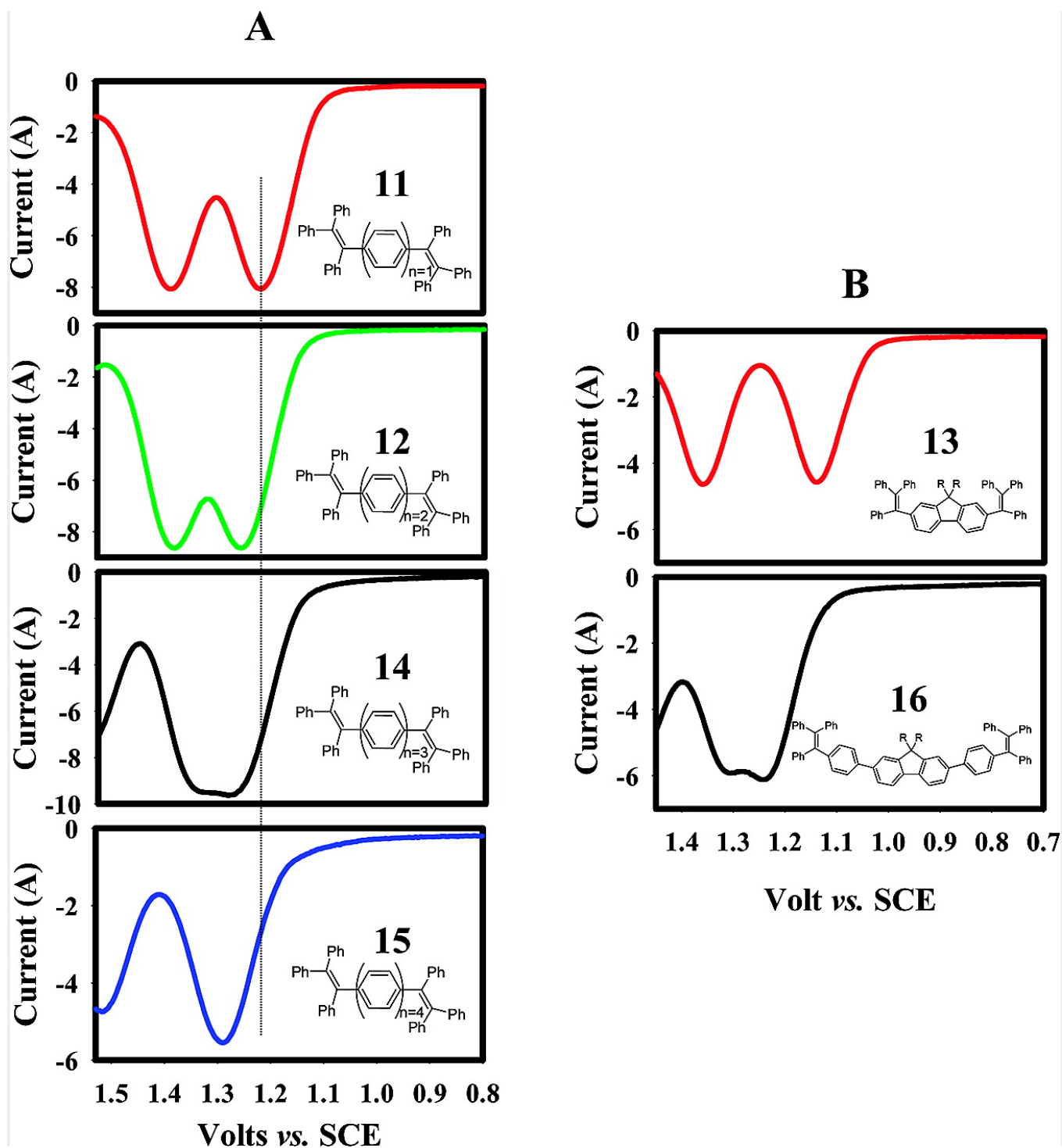
Figure 3 (A) Coalescence of two one-electron waves with increasing length of poly-*p*-phenylene spacer to a single two-electron wave in the case of the quaterphenyl spacer. (B) Square-wave voltammograms showing the effect of planarization of the spacers in the form of incorporation of fluorene moieties in **13** and **16** in comparison to **12** and **15**, respectively.

Table 4. Electrochemical Oxidation Potentials of Various TPE–Spacer–TPE Triads[a]

triad	E^0_{ox} (I) (V vs SCE)	E^0_{ox} (II) (V vs SCE)	Δ (mV) E^0_{ox} (II) − E^0_{ox} (I)
11	1.218	1.38	162

12	1.258	1.383	125
14	1.286	1.331	45
15	1.29		0
13	1.142	1.362	220
16	1.246	1.313	67

[a] In anhydrous dichloromethane as a 0.2 mM solution containing 0.2 M TBAHP at a scan rate of 200 mV/s and at 25 °C.

As such, the magnitude of the observed splitting of the oxidation waves (ΔE_{ox}) in various triads qualitatively reflects the extent of electronic coupling between the two TPE moieties, and the electronic interaction is highly dependent on the planarity of the (poly)phenylene bridge (vide infra).[21] With an increasing degree of torsional freedom between the phenylene rings going from one phenylene spacer (in **11**) to four phenylene spacers (in **15**) completely prevents electronic coupling between the TPE moieties.

Qualitatively, the electronic coupling between the TPE moieties can be enhanced by deliberate planarization of the molecular conformation of the bridging spacer. For example, the electronic coupling through the bis-*p*-phenylene spacer can be dramatically improved by bridging the two *p*-phenylene units together in a rigid coplanar conformation by a chemical $-CR_2-$ link between their ortho positions. The resulting fluorene-bridged triad **13** showed a greater splitting of the oxidation waves (ΔE_{ox} = 220 mV) than the bis-*p*-phenylene spacer (ΔE_{ox} = 125 mV) in **12**. In fact, the more planar 2,7-diphenylfluorene spacer in **16** allows a weak electronic interaction between the TPE moieties when compared to the structurally similar tetrakis-*p*-phenylene spacer in **15**, with multiple degrees of torsional freedom, which shows only a single two-electron oxidation wave (compare Figure 3A,B). We hope that spectroscopic and X-ray crystallographic studies of the one- and two-electron oxidized triads (Table 4) presently underway will provide further insight into the mechanism of electronic coupling in the various triads presented previously.

Absorption and Emission Studies of TPE–Spacer–TPE Triads. Tetraphenylethylene and its derivatives are known to have exceedingly short singlet excited-state lifetimes, negligible fluorescence quantum yields in solution, and slow rates of intersystem crossing.[22] Herein, we explore the emission/optical behavior of tetraphenylethylene moieties when incorporated into various triads (vide infra).

For example, the absorption spectra as a 2.2×10^{-5} M solution in dichloromethane showed the same general spectral band shape as in tetraphenylethylene with a poorly resolved vibrational structure for the various triads with poly-*p*-phenylene (Figure 4A) and fluoranyl-based (Figure 4B) spacers. The absorption maxima of various TPE–(Ph)$_n$–TPE triads show slight bathochromic shifts up to the bis-phenylene spacer while the molar absorptivity increases with an increasing number of phenylene rings

in the spacer up to the tris-phenylene spacer. The increase in molar absorptivity is, however, modest and in fact dies down at the tris-phenylene spacer (Figure 4A). The spacer has a more pronounced effect on the absorption intensity in the case of the fluoranyl containing triads (see Figure 4B).
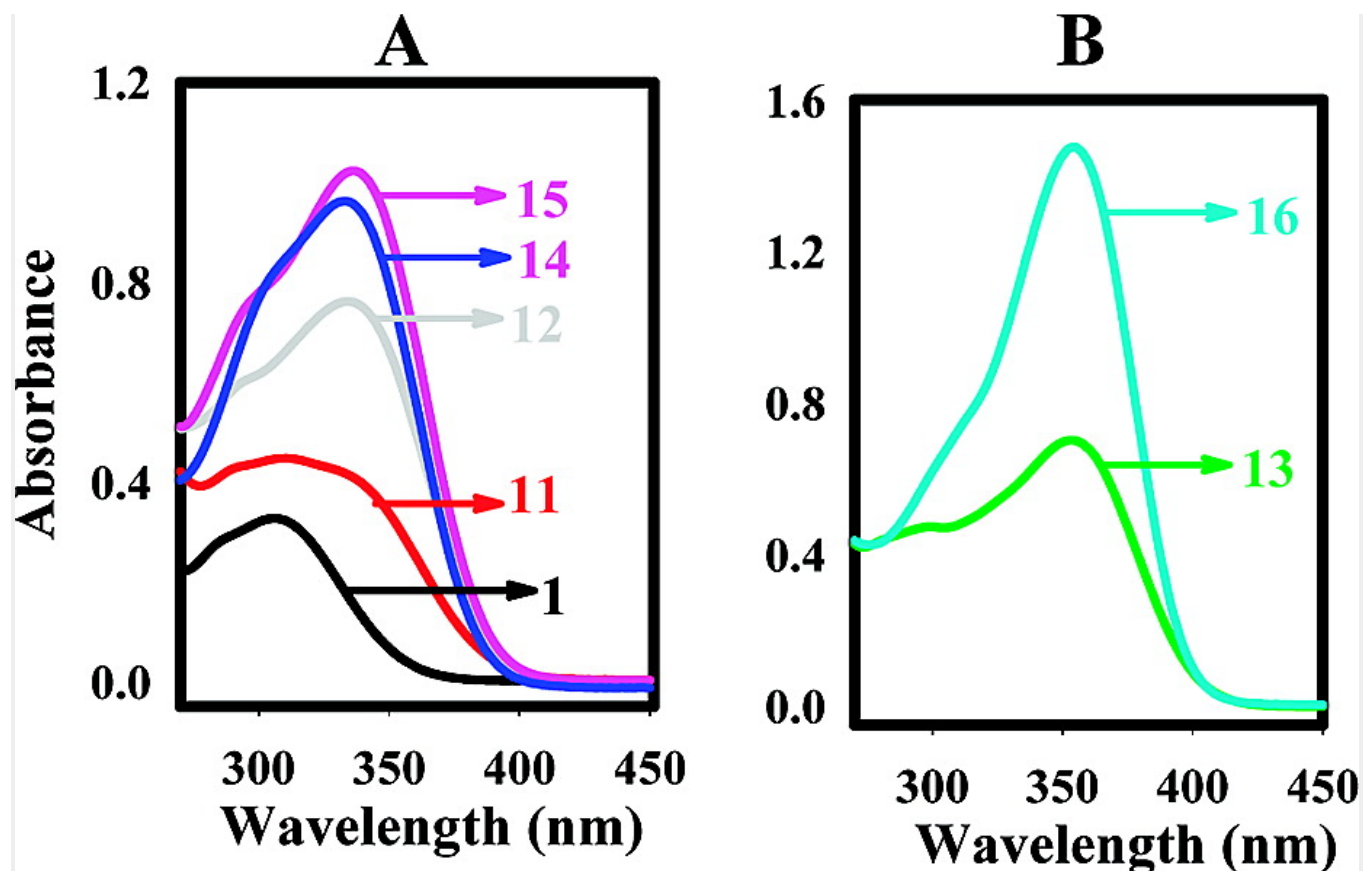
Figure 4 Comparison of the UV–vis spectral profile of the TPE–spacer–TPE triads as a 2.2 × 10^{-5} M solution in dichloromethane.

The emission spectra were recorded as a 3 × 10^{-4} M solution in dichloromethane, but no emission was detected at that concentration for the parent tetraphenylethylene and the triads containing the *p*-phenylene, bis-*p*-phenylene, and tris-*p*-phenylene spacers. The triad containing the quaterphenyl spacer (i.e., **15**), however, showed an intense emission, while the triads with fluoranyl spacers (**13** and **16**) yielded only weak fluorescence emissions (Figure 5).
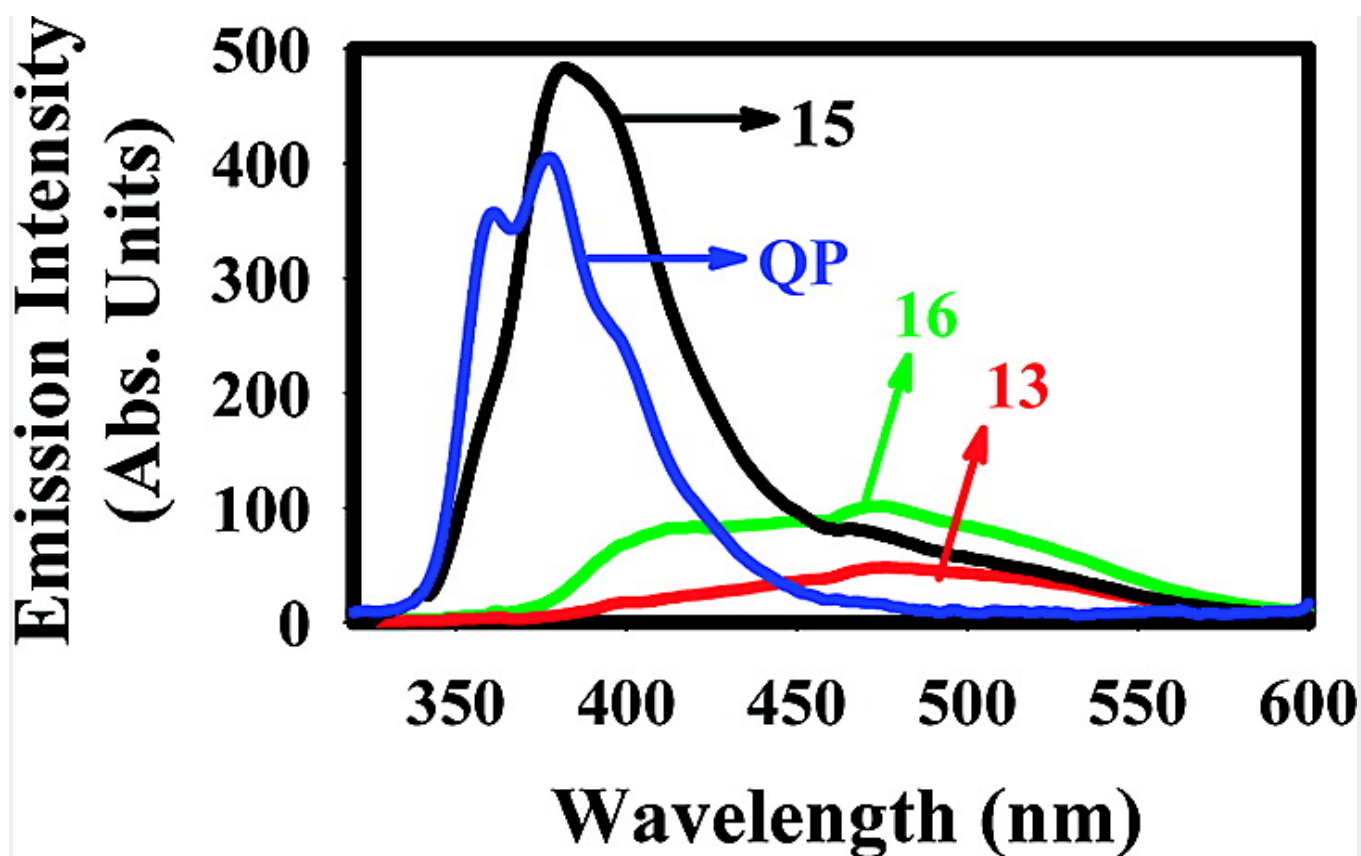
Figure 5 Emission spectral profile of the various triads and 4,4-di-*t*-butylquaterphenyl (QP) as a 3 × 10⁻⁴ M solution in dichloromethane at 22 °C.

As such, the observation of an intense emission from the triad **15**, containing a quaterphenyl spacer, is surprising and would suggest that the emission must be arising from a singlet energy transfer from TPE moieties to the quaterphenyl spacer. Indeed, a comparison of the emission spectrum of 4,4-di-*t*-butylquaterphenyl (QP),[23] obtained under similar conditions with that of **15,**showed a reasonable spectral similarity (see Figure 5). Further studies, using time-resolved spectroscopy, will be required to pinpoint the origin of observed emission in various triads.

Conclusion

We have described herein a scalable and simple methodology for the preparation of various unsymmetrical tetraarylethylenes in excellent yields. The synthetic strategy was also employed for the preparation of various TPE-based triads (TPE–spacer–TPE) using bis-benzoyl substrates as well as palladium-catalyzed coupling reactions using mono-bromotriphenylethylene. Redox and photophysical properties were also evaluated to shed light onto the structure–property relationships of various tetraarylethylene derivatives and triads. Studies are underway, especially for the TPE–spacer–TPE triads, to establish the extent of the electronic coupling among the triphenylethylenic donor moieties when connected to various poly-*p*-phenylene spacers. These studies will be reported in due course.

Experimental Section

General Procedure for the Preparation of Tetraarylethylene Derivatives. To a solution of diphenylmethane (2.02 g, 12 mmol) in dry tetrahydrofuran (20 mL) was added 4 mL of a 2.5 M solution of *n*-butyllithium in hexane (10 mmol) at 0 °C under an argon atmosphere. The resulting orange−red solution was stirred for 30 min at that temperature. To this solution was added the appropriate benzophenone (9 mmol) or bis-benzoyl derivative (4 mmol), and the reaction mixture was allowed to warm to room temperature with stirring during a 6 h period. The reaction was quenched with the addition of an aqueous solution of ammonium chloride, the organic layer was extracted with dichloromethane (3 × 50 mL), and the combined organic layers were washed with a saturated brine solution and dried over anhydrous MgSO$_4$. The solvent was evaporated, and the resulting crude alcohol (containing excess diphenylmethane) was subjected to acid-catalyzed dehydration as follows.

The crude alcohol was dissolved in about 80 mL of toluene in a 100 mL Schlenk flask fitted with a Dean−Stark trap. A catalytic amount of *p*-toluenesulphonic acid (342 mg, 1.8 mmol) was added, and the mixture was refluxed for 3−4 h and cooled to room temperature. The toluene layer was washed with 10% aqueous NaHCO$_3$ solution (2 × 25 mL) and dried over anhydrous magnesium sulfate and evaporated to afford the crude tetraphenylethylene derivative. The crude product was purified by a simple recrystallization from a mixture of dichloromethane and methanol or acetonitrile or by column chromatography. The spectral data of various TPE derivatives are summarized next.

1,1,2,2-Tetraphenylethylene (1). White solid, mp 222−224 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.05−7.08 (m, 8H), 7.10−7.13 (m, 12H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 126.6, 127.8, 131.5, 141.1, 143.9.

1-(4-Methylphenyl)-l,2,2-triphenylethylene (2). White solid, mp 153−155 °C (lit.[13b] mp 146−148 °C); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.31 (s, 3H), 6.97 (s, 4H), 7.07−7.17 (m, 15H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 21.4, 126.48, 126.52, 127.80, 127.86, 128.6, 131.4, 131.51, 131.55, 136.2, 140.6, 140.9, 141.1, 144.10, 144.13, 144.14.

1,1-Diphenyl-2,2-di-*p*-tolylethylene (3). White solid, mp 161−163 °C (lit.[24] mp 152−154 °C); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.29 (s, 6H), 6.95 (s, 8H), 7.06−7.15 (m, 10H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 21.4, 127.8, 128.5, 131.45, 131.53, 136.1, 140.2, 141.0, 141.1, 144.3.

1-(4-Bromophenyl)-1,2,2-triphenylethylene (4). White solid, mp 148−150 °C (lit.[25] mp 151−152 °C); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.88 (d, *J* = 8.52 Hz, 2H), 6.99−7.03 (m, 6H), 7.07−7.12 (m, 9H), 7.20 (d, *J* = 8.52 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 120.6, 126.8, 126.8, 126.9, 127.9, 128.0, 128.1, 131.0, 131.42, 131.44, 131.5, 133.2, 139.8, 141.8, 142.9, 143.4, 143.5, 143.6.

1-(4-Methoxyphenyl)-1,2,2-triphenylethylene (5). Light yellow solid, mp 130−132 °C (lit.[13b] mp 132−134 °C); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.76 (s, 3H), 6.68 (d, *J* = 8.88 Hz, 2H), 6.99 (d, *J* = 8.88 Hz, 2H),

7.05–7.17 (m, 10H);^{13}C NMR (CDCl$_3$, 100 MHz) δ 55.2, 113.2, 126.42, 126.43, 126.5, 127.8, 127.9, 131.52, 131.55, 131.57, 132.7, 136.3, 140.2, 140.7, 144.16, 144.21, 158.2.

1,1-Diphenyl-2,2-di-(*p*-methoxyphenyl)ethylene (6). Light yellow solid, mp 156–158 °C (lit.[24] mp 154–158 °C); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.76 (s, 6H), 6.68 (d, *J* = 8.84 Hz, 4H), 6.99 (d, *J* = 8.84 Hz, 4H), 7.06–7.16 (m, 10H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 55.2, 113.1, 126.2, 127.8, 131.5, 132.8, 136.5, 139.4, 140.2, 144.5, 158.2.

1,1-Diphenyl-2,2-di-(3,4-dimethoxyphenyl)ethylene (7). Yellow solid, mp 167–168 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 3.48 (s, 6H), 3.82 (s, 6H), 6.56–6.65 (m, 6H), 7.02–7.14 (m, 10H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 55.7, 55.8, 110.3, 115.3, 124.2, 126.3, 127.9, 131.3, 136.2, 139.5, 140.6, 144.5, 147.7, 147.9.

1-(4-Biphenyl)-l,2,2-triphenylethylene (8). White solid, mp 187–189 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.00–7.46 (m, 24H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 126.4, 126.63, 126.69, 127.0, 127.3, 127.85, 127.90, 127.96, 128.9, 131.55, 131.63, 132.0, 139.0, 140.7, 140.8, 141.3, 143.0, 143.93, 143.97.

Diphenylmethylidenefluorene (9). Pale yellow solid, mp 232–234 °C (lit.[26] mp 235 °C); ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.66 (d, *J* = 7.96 Hz, 2H), 6.96 (t, *J* = 6.96 Hz, 2H), 6.27 (t, *J* = 7.1 Hz, 2H), 7.41–7.45 (m, 10H), 7.73 (d, *J* = 7.36 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 119.5, 125.1, 126.6, 127.8, 128.4, 129.0, 129.9, 134.4, 138.9, 140.7, 143.1, 145.7.

(4-Triphenylethenylphenyl)pentaphenylbenzene (10). White solid, mp 342–344 °C (lit.[15b] mp >350 °C);^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.54–6.61 (m, 4H), 6.75–7.08 (m, 40H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 125.4, 126.33, 126.40, 126.46, 126.73, 126.78, 127.5, 127.7, 127.8, 130.1, 131.0, 131.49, 131.54, 131.61, 131.66, 139.1, 140.2, 140.3, 140.40, 140.42, 140.6, 140.76, 140.78, 140.83, 140.89, 143.8, 143.9, 144.1.

1,4-Bis(triphenylethenyl)benzene (11). White solid, mp 242–244 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.80 (s, 4H), 7.03–7.15 (m, 30H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 126.57, 126.65, 127.75, 127.81, 130.9, 131.54, 131.59, 141.0, 142.1, 143.7, 143.94, 143.97.

4,4′-Bis(triphenylethenyl)-1,1′-Biphenyl (12). White solid, mp 288–290 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.03–7.14 (m, 34H), 7.33 (d, *J* = 8.44 Hz, 4H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 126.1, 126.6, 126.67, 127.8, 127.9, 128.0, 131.55, 131.6, 131.9, 138.4, 140.7, 141.2, 142.9, 143.92, 143.94, 143.97.

2,7-Bis(triphenylethenyl)-9,9-dihexylfluorene (13). Yellow solid, mp 174–176 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.26–0.33 (m, 4H), 0.84–0.95 (m, 10H), 0.99–1.06 (m, 4H), 1.14–1.22 (m, 4H), 1.48–1.52 (m, 4H), 6.91–6.94 (m, 4H), 7.00–7.12 (m, 30H), 7.36–7.38 (m, 2H).; ^{13}C NMR (CDCl$_3$, 100 MHz) δ 14.4, 22.9, 23.6, 29.8, 31.8, 40.5, 54.8, 119.1, 126.1, 126.56, 126.60, 127.74, 127.76, 127.86, 130.4, 131.6, 139.4, 140.7, 141.7, 143.0, 144.1, 144.2, 150.5.

General Procedure for the Suzuki Coupling for the Preparation of Triads 14–16. A mixture of aqueous 2 M Na_2CO_3 (4 mL) and dioxane (12 mL) was repeatedly degassed by evacuation and purging with argon gas and into it, 1-(4-bromophenyl)-1,2,2-triphenylethylene (822 mg, 2 mmol) and the appropriate diboronic acid (1 mmol) along with 3 mol % $Pd(PPh_3)_4$ (70 mg) were added. The mixture was refluxed in an argon atmosphere under the complete exclusion of light for 16 h after which it was quenched with the addition of 10% aqueous HCl. The organic layer was extracted with dichloromethane and washed consecutively with water and brine before being dried over $MgSO_4$ and concentrated. The crude product was then chromatographed over silica gel, using ethyl acetate/hexanes as the eluent to afford the coupled products. The spectral data of various triads are summarized next.

4,4'-Bis(triphenylethenyl)-1,1':4',1'-terphenyl (14). White solid, mp 294–296 °C; ^{1}H NMR (CDCl₃, 400 MHz) δ 7.03–7.14 (m, 34H), 7.38 (d, J = 8.48 Hz, 4H), 7.59 (s, 4H); ^{13}C NMR (CDCl₃, 100 MHz) δ 126.2, 126.63, 126.69, 126.71, 127.3, 127.84, 127.90, 127.98, 131.56, 131.63, 132.0, 138.5, 139.5, 140.7, 141.3, 143.0, 143.92, 143.97.

4,4''-Bis(triphenylethenyl)-1,1':4',1'':4'',1'''-quaterphenyl (15). Pale yellow solid, mp 320–324 °C; ^{1}H NMR (CDCl₃, 400 MHz) δ 7.03–7.14 (m, 38H), 7.39–7.41 (m 4H), 7.65–7.71 (m, 4H); ^{13}C NMR (CDCl₃, 100 MHz) δ 126.3, 126.7, 127.4, 127.85, 127.92, 127.98, 131.57, 131.6, 132.1, 138.5, 139.56, 139.77, 140.7, 141.4, 143.1, 143.92, 143.96.

2,7-Bis(tetraphenylethenyl)-9,9-dihexylfluorene (16). Yellow solid, mp 207–209 °C; ^{1}H NMR (CDCl₃, 400 MHz) δ 0.71 (m, 4H), 0.79 (t, J = 7.06 Hz, 6H), 1.04–1.17 (m, 12H), 2.02–2.06 (m, 4H), 7.09–7.20 (m, 34H), 7.47–7.49 (m, 4H), 7.56–7.58 (m, 4H), 7.73–7.75 (m, 2H); ^{13}C NMR (CDCl₃, 100 MHz) δ 13.2, 21.8, 22.9, 28.9, 30.7, 39.7, 54.4, 119.1, 120.2, 125.0, 125.4, 125.7, 126.8, 126.9, 127.0, 130.6, 131.0, 138.5, 139.2, 139.7, 141.8, 143.0, 150.8.

Acknowledgment

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