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Synthesis and electronic properties of nanometer-size symmetrical *tetrakis*(poly-*p*-phenylene)ethylenes

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ABSTRACT

A simple synthesis of soluble *tetrakis*(poly-*p*-phenylene)ethylenes (TPEs), where poly-*p*-phenylene units contain up to 4 phenylene moieties, is accomplished using an easily available *tetrakis*(4-bromophenyl)ethylene and phenyl, biphenyl, and *p*-terphenylboronic acids, containing solubilizing *iso*-alkyl groups as the end-capping substituents. Electrochemical oxidation of TPEs (i.e., **T1–T4**) showed that they undergo reversible electrochemical oxidations and form stable cation-radical salts in solution. The evaluation of absorption and emissions characteristics of **T1–T4** in solution indicated that unlike parent tetratolylethylene (**T1**), the higher homologues (i.e., **T2–T4**) show emission centered at 520 nm and the quantum efficiency of emission increases with the increasing number of phenylene moieties in poly-*p*-phenylene units in various TPEs.

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The design and synthesis of new electro-active organic materials based on polyaromatic hydrocarbons continue to attract considerable attention owing to their potential for the practical applications in the emerging areas ranging from molecular electronics and nanotechnology to solar energy storage.¹ Of these, poly-*p*-phenylenes (**PPn**) are especially important due to their high conductivity and high thermal and oxidative stability.² We recently carried out a careful study of the optical and electronic properties of a series of well-defined oligomers of the poly-*p*-phenylenes containing up to 7 phenylene moieties; and demonstrated that all the optical and electrochemical properties followed an inverse relationship with the number of phenylene moieties.³ Longer poly-*p*-phenylenes could not be obtained owing to limitation posed by solubility despite having long alkyl chains at the apical positions (see Fig. 1).³

A need for conducting molecules with increased effective conjugation lengths⁴ led us to conjecture that if the smaller poly-*p*-phenylenes are incorporated at the vertices of tetraphenylethylene core, nanometer-size electro-active molecules should become readily accessible. For example, an incorporation of a modest length *p*-terphenyl unit onto the vertices of tetraphenylethylene alone would lead to a conducting single molecule which is longer than the largest known (soluble) poly-*p*-phenylene,³ that is, Figure 1.

Accordingly, herein we describe an efficient synthesis of a welldefined series of *tetrakis*(poly-*p*-phenylene)ethylenes (TPEs), where poly-*p*-phenylene units contain 2, 3, and 4 phenylene moieties, respectively. The availability of a homologous series of TPEs allows us to evaluate their optical and electrochemical properties as well as the optical characteristics of their cation radicals with increasing number of phenylene units in TPEs. The details of these preliminary findings are presented herein.

Various soluble *tetrakis*(poly-*p*-phenylene)ethylenes (**T2-T4**) were synthesized in excellent yields by Suzuki reaction⁵ between phenyl, biphenyl, and *p*-terphenylboronic acids (**B1–B3**), containing solubilizing *iso*-alkyl groups as the end-capping substituents, and *tetrakis*(4-bromophenyl)ethylene (Scheme 1). The desired *tetrakis*(*p*-bromophenyl)ethylene⁶ was easily prepared from tetraphenylethylene via a solid-phase reaction with gaseous bromine while the synthesis of boronic acids **B1–B3** has been described earlier.³ A model tetratolylethylene (**T1**) was also obtained by a simple









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Scheme 1. Synthesis of various tetrakis(poly-*p*-phenylene)ethylenes. Reagents: (a) Bromine vapors; (b) Pd(PPh₃)₄ (2 mol %), dioxane-H₂O (2:1), Na₂CO₃, reflux.

McMurry coupling of 4,4-dimethylbenzophenone.⁷ The structures of **T2–T4** were easily established by 1 H/ 13 C NMR spectroscopy and were further confirmed by MALDI mass spectrometry (see Supplementary data section for the experimental details).

The redox properties of T1-T4 were evaluated by electrochemical oxidation at a platinum electrode as a 1×10^{-3} M solution in dichloromethane containing 0.2 M tetra-n-butylammonium hexafluorophosphate $(n-Bu_4NPF_6)$ as the supporting electrolyte. The common unifying feature in the cyclic voltammograms of T1-T4 (Fig. 2) is the presence of two 1-electron oxidation waves with the first wave being completely reversible while the second wave was found to be somewhat quasi reversible.^{8a} The oxidation potentials of **T1-T4** corresponding to the first and second oxidations (i.e., loss of one and two electrons, respectively) were referenced to added ferrocene, as an internal standard ($E_{ox} = 0.45$ V vs SCE),^{8b} and the E_{ox} values are compiled in Table 1. With the increasing number of phenylene moieties in **T1** to **T4**, there is a modest increase in their first oxidation potential (\sim 50 mV), while the second oxidation potential largely remain unchanged (Table 1). The modest increase in the oxidation potentials going from **T1** to **T4** is understandable from the fact that HOMO largely resides on the tetraphenylethylene core (vide infra), and the substitution of electron-releasing alkyl groups in T1 by electron-withdrawing phenyl, biphenyl, and terphenyl in T2, T3, and T4, respectively, contribute to the progressive increase in the first oxidation potentials of T2-T4.

The reversibility of 1-electron oxidation by cyclic voltammetry of various TPE's prompted us to evaluate the stability of their cation radical salts using stable triarylamine (**MB**)⁹ and/or a hydroquinone ether (**MA**)¹⁰ cation-radical salt as robust 1-electron oxidants.



Thus, Figure 3 shows the spectral changes attendant upon the reduction of **MB**⁺ SbCl₆⁻ [λ_{max} (log ε) = 728 nm (4.45)] by an incremental addition of **T2** to its cation radical **T2**⁺ in dichloromethane at 22 °C. The presence of well-defined isosbestic points at



Figure 2. Cyclic voltammograms (blue) and the corresponding square-wave voltammogram (red) of 1×10^{-3} M **T1–T4** in CH₂Cl₂ containing 0.2 M (*n*-Bu)₄NPF₆ at 22 °C at scan rate of 200 mV s⁻¹.

 λ_{max} = 678 and 766 nm in Figure 3A established the uncluttered character of the electron transfer.

Furthermore, a plot of the depletion of **MB**^{.+} and formation of **T2**^{.+} against the increments of added neutral **T2** (Fig. 3B) established that **MB**^{.+} was completely consumed after the addition of 1 equiv of **T2**; the resulting absorption spectrum of **T2**^{.+} remained unchanged upon further addition of neutral **T2** (i.e., Eq. 1).

$$\mathbf{T2} + \mathbf{MB}^{\cdot +} \to \mathbf{MB} + \mathbf{T2}^{\cdot +} \tag{1}$$

The radical-cation absorption spectra of **T2**⁺ [λ_{max} (log ε) = 660, 1160 (4.38)], **T3**⁺ [λ_{max} (log ε) = 454, 670, 1292 (4.39)], and **T4**⁺ [λ_{max} (log ε) = 458, 622, 1300 (4.40)] contained a pair of absorption bands characteristic of the parent tetratolylethylene cation radical **T1**⁺⁺ [λ_{max} (log ε) = 522, 882 (3.95)];¹¹ and the twin absorption bands of the purple-colored **T1**⁺⁺ not only considerably red shifted in the green-colored **T2**⁺⁺, but there was also a considerable increase in its molar absorptivity (vide infra). However, the absorption spectra of **T3**⁺⁺ and **T4**⁺⁺ were rather similar and were only slightly red shifted (~150 nm) when compared to **T2**⁺⁺. Furthermore, the molar absorptivities of **T2**-**T4** cation radical were similar but considerably higher as compared to parent **T1** cation radical (Fig. 3C and Table 1).

As such, the observed saturation of the low-energy transition as well as molar absorptivity beyond **T3**⁺ suggests that conjugation length for the stabilization of the cationic charge in TPEs is limited to only 2–3 phenylene moieties on each poly-*p*-phenylene arm connected to ethylenic core. Furthermore, this observation is also consistent with the localization of HOMO in **T4** which extends only up to 3 phenylene moieties of quarter-*p*-phenylene arms of **T4**, see Figure 4.

Table 1	
Optical and	electrochemical data of T1-T4

Properties		T1	T2	T3	T4
E _{ox1}	V vs SCE	1.11	1.12	1.15	1.16
E _{ox2}	V vs SCE	1.38	1.29	1.29	1.29
UV-vis $\lambda_{max}(\varepsilon_{max})$	nm (M^{-1} cm ⁻¹)	246 (29,227)	291 (69,650)	315 (89,172)	326 (157,062)
		313 (16,451)	~346 (30,734)	~352 (37,854)	(~356) 68,378
$\lambda_{\rm max}$ (emission)	nm	_	520	520	520
Quantum yield	Φ_{F}	_	0.01	0.02	0.04
Normalized intensity		_	71	237	492
$TPE^+ \lambda_{max} (\varepsilon_{max})$	nm $(M^{-1} cm^{-1})$	522 (11,763)	428 (22,969)	454 (25,295)	458 (26,218)
		880 (8838)	660 (14,023)	670 (12,063)	622 (12,640)
			1160 (24,045)	1292 (24,307)	1300 (25,391)



Figure 3. (A) Spectral changes upon the reduction of 5.5×10^{-5} M **MB**⁺ (blue line) by incremental addition of 2.0×10^{-3} M **T2** to its radical cation (green line) in CH₂Cl₂ at 22 °C. (B) A plot of depletion of absorbance of **MB**⁺ (blue circles, at 728 nm) and an increase of the absorbance of **T2**⁺ (green triangles, at 1158 nm) against the equivalent of added neutral **T2**. (C) Comparison of the absorption spectra and molar absorptivity of **T1**⁺ (blue line), **T2**⁺ (gruple line), **T3**⁺ (graven line).

The optical properties of neutral TPEs were evaluated with the aid of UV-vis and emission spectroscopy as follows. The electronic absorption spectra of **T1–T4**, in dichloromethane, were recorded under identical concentration and temperature (22 °C) and are compiled in Figure 5. All TPEs showed a characteristic twin absorption band that shifted bathochromically with the increasing number of phenylene moieties in **T1–T4**. Although, the molar extinction coefficients exhibited almost a linear increase with the increasing



Figure 4. Showing the HOMO of **T4** with quarter-*p*-phenylene arms, calculated using Density Functional Theory (DFT) at B3LYP/6-31G* level, extends only up to 3 phenylene moieties in each arm.



Figure 5. (A) Comparison of the UV-vis absorption spectra and molar absorptivity of **T1–T4** as dilute solutions in CH₂Cl₂ at 22 °C. **B.** Comparison of the excitation (left) and emission spectra (right) of **T2–T4** as 6.7×10^{-6} M solutions in CH₂Cl₂ at 22 °C upon excitation at the low-energy absorption bands (see Table 1).

number of phenylene units in **T1–T4** (Table 1, vide supra), the absorption maxima did not show a similar linear red shift but exhibited a saturation behavior akin to that observed above for the electronic transitions in their cation radical spectra (compare Figs. 3C and 5A).

The emission spectra of **T1–T4** were recorded under conditions of constant concentration (6.7×10^{-6} M solution in dichloromethane) and temperature (22 °C) and are compared along with their excitation spectra in Figure 5. Expectedly, the parent tetratolylethylene (**T1**) did not show an observable emission owing to the fact that the excited state in terarylethylenes and stilbenes undergoes a facile radiation less deactivation owing to a twisting motion around the C=C bond.¹² Interestingly, however, **T2-T4** showed an (invariant) emission band centered at 520 nm, and the emission intensity linearly increased with the increasing number of phenylene moieties from **T2** to **T4** (see Fig. 5B). The fluorescence quantum yields for **T2-T4** were also determined using 9,10-diphenylanthracene ($\Phi = 0.91$)¹³ as a standard (see the Supplementary data for the experimental details) and the values are compiled in Table 1. The quantum yield data in Table 1 show that there is a modest increase in the fluorescence quantum yield from **T2** ($\Phi = 0.01$) to **T3** ($\Phi = 0.02$) to **T4** ($\Phi = 0.04$).

As such, the observation of relatively weak emission from **T2– T4** suggests that the emission largely arises from a reorganization of the ethylenic-centered exciton to the poly-*p*-phenylene groups of the **T2–T4**.¹⁴ Indeed, a comparison of the emission spectra of poly-*p*-phenylenes³ with that of **T2–T4** show a reasonable spectral similarity, however, at this juncture, we are unable to reconcile the invariance of the emission bands of **T2–T4**. Further studies using time-resolved spectroscopy as well as theoretical calculations will be required to pinpoint the origin of the observed emission of **T2–T4**.

In summary, we have developed an efficient synthesis of soluble *tetrakis*(poly-*p*-phenylene)ethylenes (TPEs), where poly-*p*-phenylene units contain up to 4 phenylene moieties, from easily available precursors. Various TPEs undergo reversible electrochemical oxidations and form stable cation-radical salts in solution which are stabilized by charge delocalization onto the poly-*p*-phenylene arms. The evaluation of absorption/emission properties of various TPEs showed that the intramolecular reorganization of exciton energy from the non-emissive tetraphenylethylene core to the poly-*p*-phenylene arms allows them to emit. Efforts are underway to develop more effective emitters based on *tetrakis*(poly-*p*-phenylene) derivatives in which C=C bond rotations, responsible for the radiation-less deactivation of the excited state, are hampered.

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Supplementary data

Synthetic details, spectral data, and NMR spectra/mass spectra of various compounds in Scheme 1 are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.08.077.

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