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Triptycene Diols: A Strategy for Synthesizing Planar π Systems through Catalytic Conversion of a Poly(*p*-phenylene ethynylene) into a Poly(*p*-phenylene vinylene)**

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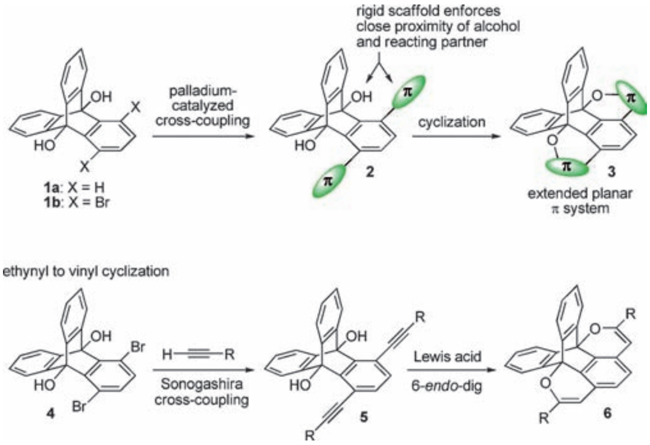
The performance of conjugated electronic polymers is highly dependent on conformation and the limits it places on electronic delocalization. Coplanarity of adjacent segments is generally desired to create the highest π-orbital overlap, thus resulting in less energetic disorder along the backbone. Simply stated, enforced planarity of the π system leads to greater exciton and charge transport (along the π way).[1] Greater chain coplanarity can be achieved by simply polymerizing fused polycyclic planar, π-extended monomers. Alternatively, postpolymerization annulation and rigidification, often taking advantage of reactive side chains,[2] has proven an effective strategy—particularly for phenylene-based ladder polymers.[2a]

Recently, our group reported an efficient synthesis of triptycene diols (TDs; e.g., **1a**) using a rhodium-catalyzed [2+2+2] cycloaddition.[3] The rigid three-dimensional structure of triptycene-derived scaffolds has proven to be a versatile motif for creating new and enhanced material properties.[4] To expand the diversity of iptycene scaffolds for such applications, we envisioned a suitably functionalized TD (e.g., **1b**) might be amenable to additional functionalization through palladium cross-coupling methods (Scheme 1; **1b**→**2**). The resultant extended π system (**2**) has close proximity to the hydroxy group, thus affording the opportunity for cyclization reactions to create higher-order planarized triptycene π systems (Scheme 1; **2**→**3**).

To investigate this strategy for cyclization and planarization we have targeted alkyne π systems because of the significant literature surrounding alcohol–alkyne cyclization reactions (Scheme 1; **4**→**5**→**6**).[5] Furthermore, in the context of polymer chemistry, we envisioned such a transformation might also provide a postpolymerization means of converting the alkyne units of readily available poly(phenylene ethynylene)s (PPEs)[6] to give a new class of poly(phenylene vinylene)s (PPVs)[7] with annulated alkene units (see Scheme 5). This transformation represents a particularly rare form of postpolymerization reactivity for conjugated polymers as the polymer main chain would be chemically altered (in contrast to modification or elaboration of side chains).



Scheme 1. Rationale for the conversion of triptycene diols in cyclization reactions to give planar extended π systems.

Within the context of PPE main-chain alteration, the literature is scarce and the best examples include full[8] and partial[9] hydrogenation of the triple bonds to give respective unconjugated poly(*p*-xylene)s and *cis*-poly(*p*-phenylene vinylene)s. The transformation outlined in Scheme 1 would result in a *trans* PPV. Furthermore, it would provide for a rare substitution of the vinylene segment[10] of a PPV with an electron-donating oxygen group, while simultaneously creating greater planarity in the backbone. Herein we detail the synthesis and tranformation of **1b** to give molecules and polymers with planarized extended π systems.

The synthesis of TDs—bearing the 1,4-halogen substitution pattern (**1b**)—used the previous [2+2+2] cycloaddition strategy.[3] However, the presence of bromine substituents did not permit direct transfer of previous synthetic conditions, and a modified synthesis is presented herein (Scheme 2). Starting from commercially available **7**, a Sandmeyer reaction[11] afforded the dibromoanthroquinone **8** in excellent yield. Double addition of lithium triisopropylsilyl (TIPS) acetylide to **8** in toluene provided the *syn*-addition product **9** with modest selectivity (2.3:1 *syn*/*anti*; the analogous lithium trimethylsilyl (TMS) acetylide gave a mixture of 1:1 *syn*/*anti* addition products. Isomers are separable by chromatography). Finally, removal of the TIPS groups with fluoride gave the cyclization substrate **10**.

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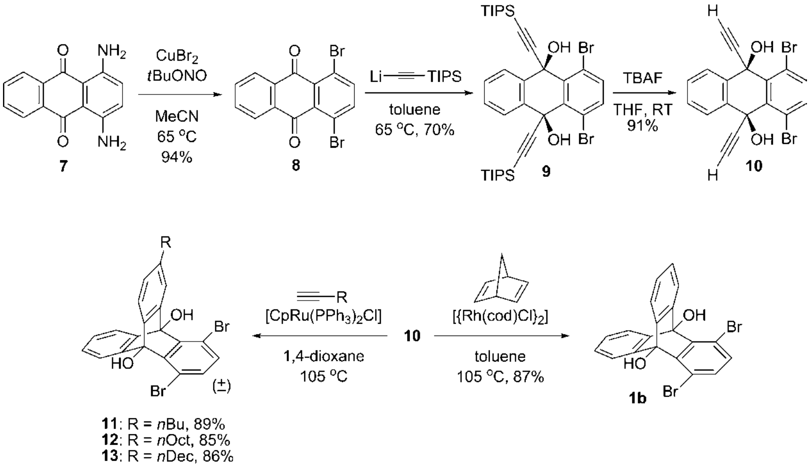


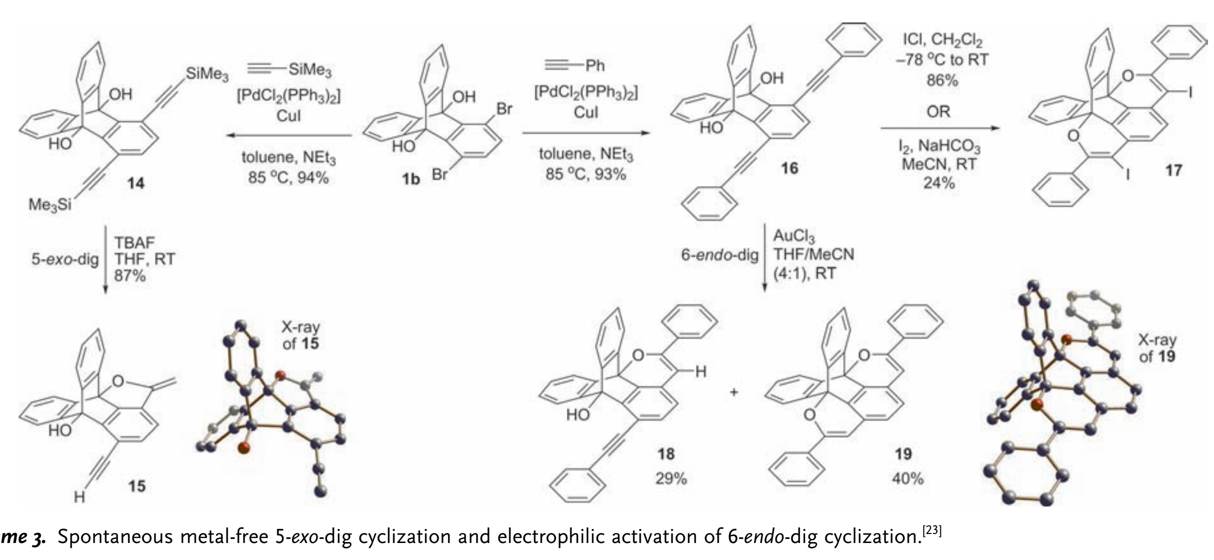
Scheme 2. Synthesis of 1,4-dibromo-substituted triptycene diols. Cp = cyclopentadiene, cod = 1,5,-cyclooctadiene, TBAF = tetra-*n*-butylammonium fluoride, THF = tetrahydrofuran.

The previously effective[3] Wilkinson's catalyst [Rh-$(PPh_3)Cl$] failed to give the [2+2+2] cycloaddition products using **10**. However, the ruthenium catalyst [$CpRu(PPh_3)_2Cl$] readily facilitated [2+2+2] cycloadditions of **10** with terminal alkynes to yield racemic products (**11**–**13**). Finally, the formal cycloaddition of **10** with acetylene to give **1b** was accomplished by using norbornadiene in the presence of [Rh-$(cod)Cl_2$], which promoted a [2+2+2] cycloaddition with a subsequent retro-Diels–Alder reaction and expulsion of cyclopentadiene.[12]

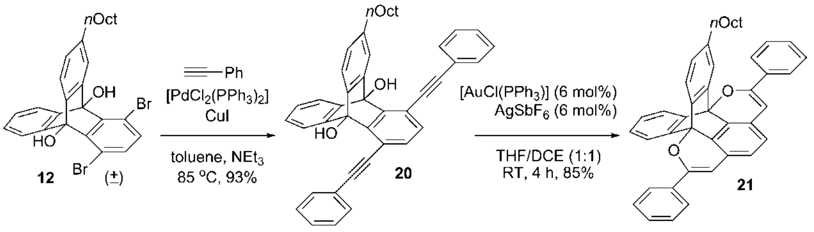
Compound **14** was investigated as a direct precursor to a polymerizable monomer (for PPEs) and was synthesized in a straight forward manner from **1b** by Sonogashira coupling with a TMS-protected acetylene (Scheme 3). However, upon deprotection with either fluoride or basic methanol, spontaneous metal-free cyclization occurred on one side of the molecule to give **15**. NMR analysis indicated the product to be that resulting from the 5-*exo*-dig cyclization (based on vinyl coupling constants), and X-ray crystallography revealed how closure of the five-membered ring creates a geometry that pulls the other alkyne and hydroxy group apart to prevent a second cyclization. We reasoned that cyclization of the alcohol oxygen atom onto the terminal carbon atom of the alkyne (6-*endo*-dig) would lead to a less-strained six-membered ring with less structural distortion and might allow for double cyclization (Scheme 1). To this end, the phenyl acetylene analogue **16** was found to be indefinitely stable to spontaneous cyclization, which allowed for exploration of selective 6-*endo*-dig cyclization through electrophilic activation of the alkyne (Scheme 3).[15]

Treatment with electrophilic iodine sources provided the doubly cyclized product with concomitant installment of iodides on the alkenes.[13] Furthermore, electrophilic gold-(III)[5b] proved moderately effective in promoting the 6-*endo*-dig isomerization of **16** into the mono- and doubly cyclized compounds **18** and **19**. These observations, along with the X-ray crystal structure of **19** shown in Scheme 3, confirm our hypothesis that the 6-*endo*-dig pathway enabled double cyclization to take place. Furthermore, the dihedral angles between the newly formed rings and terminal benzenes were near planarity (1.1 ± 0.8° and 3.4 ± 0.4°). This planarity derives from the less sterically demanding lone pairs on the oxygen atom—in contrast to an analogous biphenyl system—and bodes well for increased monomer coplanarity in polymer **24** (see below).

Compound **19**, with its rigidified structure, displayed poor solubility, thus making analysis and additional method development difficult. To address this issue compound **12**, bearing a solubilizing alkyl side chain, was employed to give the bis(phenyl acetylene) **20** (Scheme 4). Subsequent optimized 6-*endo*-dig isomerization of the alkyne into the oxygen-substituted alkene (**20**→**21**) using a more active gold(I) catalyst system[14] provided **21** in high yield upon isolation (spot to spot conversion was observed when monitoring the reaction by TLC). The high conversion and lack of side



Scheme 3. Spontaneous metal-free 5-*exo*-dig cyclization and electrophilic activation of 6-*endo*-dig cyclization.[23]



Scheme 4. 6-*Endo*-dig cyclization of more soluble model substrate **20**. DCE = 1,2-dichloroethane.

products gave us confidence that we could extend this method to the post polymerization alteration of PPEs into PPVs. Additionally, the resistance to spontaneous cyclization provided by **20** (and **16**) ensures the synthesis and characterization of well-defined PPEs (free of cyclized defects), which could then be catalytically isomerized into the PPVs.

We selected **12** and **22** as monomers for the Sonogashira polymerization to form PPE **23** (Scheme 5). Compound **22** was an attractive monomer as it lacked side-chain substitution on the benzene ring that would adversely affect chain planarity through steric interactions. However, the lack of side chains also presents a challenge for solubility as side chains are typically used to promote polymer solubility. We hoped to offset this issue using the characteristics of the comonomer **12**, with disorder in the solubilizing *n*-octyl side chain arising from its racemic nature and an expected regionrandom orientation in the polymer chain. Additionally, the rigid three-dimensional structure of iptycenes (triptycene in this case) has been observed to impart greater solubility through suppression of interpolymer π–π associations.[16] The polymerization (Scheme 5) successfully produced polymer **23** at reasonably high molecular weight ($M_n = 12500$, PDI = 1.44, DP = 24). However, the yield of the isolated, soluble **23** was low (32 %) because of large quantities of insoluble and presumably high-molecular-weight polymer.[17] In any case, **23** was subjected to a two-stage addition (see the Supporting Information for details) of gold(I) catalyst to produce the cyclized polymer **24** ($M_n = 14700$, PDI = 1.16 DP = 28). The increase in molecular weight of **24** relative to **23** was likely due to increased rigidity along the polymer chain. This rigidity increases the persistence length of the polymer, thus making it appear larger under size-dependent measurements (i.e. GPC).[8b,18]

The effects of the cyclization reaction on the π systems of **21** and **24** were most distinctly visualized in their UV/vis and fluorescence signatures relative to their respective starting materials (Figure 1). The model substrates **20** and **21** both showed very small Stokes shifts, however the absorbance and fluorescence maximums of **21** are red-shifted by almost 100 nm after cyclization (Figure 1 a; Table 1). This closing of the band gap is ascribed to both the increased planarity of **21** and the presence of electron-rich oxygen donor atoms on the alkene that raise the HOMO level. The distinctly sharper emission features of **21** and resolved vibrational transitions also evidence the increased rigidity (enforced planarity).[19] As expected there is also an associated increase in fluorescence quantum yield for **21** compared to **20**, as a result of the removal of vibrational relaxation through planarization and rigidification.

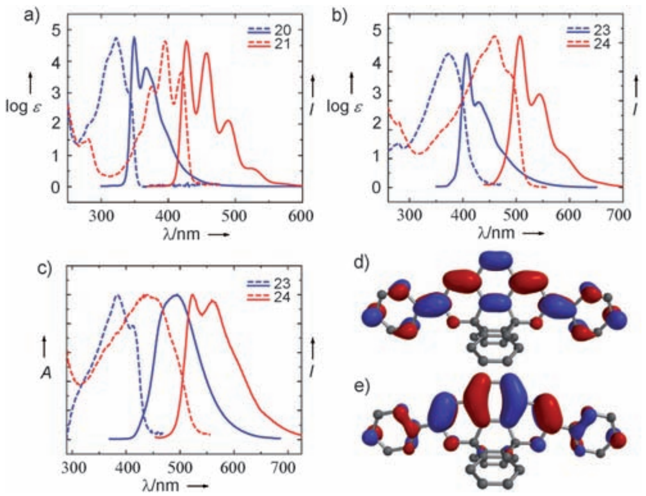
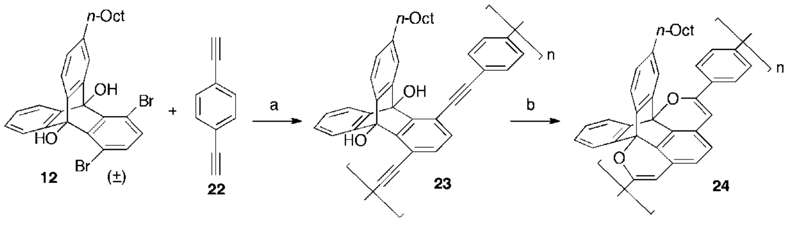


Figure 1. UV/Vis absorbance (dashed) and fluorescence (solid) spectra of a) **20** and **21** in $CHCl_3$, b) **23** and **24** in $CHCl_3$, c) **23** and **24** in thin film. d) LUMO and e) HOMO representations from DFT (B3LYP/6-31G*) calculations for **19**.

Table 1: Summary of photophysical data.

Compound	abs λ_{max}[a] [nm]	em λ_{max}[a] [nm]	log ε[b]	Φ_F	τ_F	$E_{g,optical}$[c] [eV]
20	322	349	4.74	0.65	1.11	3.5
21	395	427	4.63	0.89	1.77	2.8
23	372	408	4.62	0.74	0.53	2.8
24	460	507	5.23	0.46	1.28	2.4
23 (film)	384	495		0.15	1.20[d]	2.8
24 (film)	435	523		0.03	1.10[e]	2.3

[a] Measured in $CHCl_3$. [b] Determined from abs λ_{max}. [c] Band gap estimated by onset of absorption spectrum. [d] Biexponential lifetime 82.9%, second exponential 3.5 ns, 17.1 %. [e] Biexponential lifetime 91.7%, second exponential 3.0 ns, 8.3 %.



Scheme 5. Polymerization and postcyclization, a) $[PdCl_2(PPh_3)_2]$, CuI, toluene, NEt_3, 85 °C, 32 %. b) $[AuCl(PPh_3)]$ (20 mol %), $AgSbF_6$ (20 mol %), THF/DCE (1:1), RT, 24 h, 74 %.

Similar effects were also seen for the polymers **23** and **24** (Figure 1 b), thus confirming a successful extension of the cyclization conditions to the postpolymerization conversion of the PPE **23** into PPV **24**. Small Stokes shifts were observed for both polymers, and **24** showed a red-shift of almost 100 nm in absorbance and emission upon cyclization (Figure 1 b; Table 1). Furthermore, the planarity imparted to **24** produces a clear vibrational fine structure, which is generally less pronounced in conjugated polymers. Finally, the cyclization can also be monitored by ^{1}H NMR spectroscopy with the disappearance of the signal corresponding to the alcohol protons at $\delta = 5.9$ ppm (in **23**) and appearance of those for the vinyl protons at $\delta = 6.2$ ppm (in **24**).

In contrast to **21**, polymer **24** did not have an associated increase in fluorescence quantum yield relative to precursor polymer **23**. This difference may be related to the longer fluorescence lifetime (τ_F) of **24**, which is almost double that of **23** (Table 1), and the lower band gap. As a result, **23** showed a higher quenching response ($K_{SV} = 511$) to 2,4-dinitrotoluene (DNT) than did **24** ($K_{SV} = 92$). Additional discussion of the mode of quenching with respect to fluorescence lifetime can be found in the Supporting Information.

The thin film spectra for both polymers are shown in Figure 1 c. Both polymers remain visibly fluorescent in thin film (Table 1), and **24** maintains a significant red-shift relative to **23**. It would appear that the triptycene group—the smallest member of the iptycene family—was not sufficient to prevent unfavorable π–π interactions between polymer chains as both polymers display significant broadening of their absorbance and fluorescence spectra. However, the rigidified polymer **24** appears to retain vibrational structure in its thin film fluorescence spectrum (Figure 1 c).

The compounds discussed above differ from previous oxygen-substituted PPV systems in that the substitution occurs on the vinyl unit instead of the phenyl. To understand these substitution effects, we performed DFT calculations for the LUMO and HOMO of **19** (Figures 1 d and e). These data show the closing of the band gap for each compound may stem more from the planarization than from the oxygen substitution. In both the HOMO and LUMO there is only a small electron density on the oxygen atom. The band gap of **21** was similar to other ring substituted triphenylene vinylene model systems.[20] However, the band gap of **24** was larger than that for MEH-PPV,[21] which may result from **24** possessing half the oxygen substitution per repeat unit relative to MEH-PPV.[22]

To summarize, we have developed a highly efficient method to introduce planarity and rigidity along a conjugated polymer backbone using a catalytic main-chain alteration to convert the alkynes of the PPE (**23**) into annulated alkenes in the PPV (**24**), thus transitioning between two classes of conjugated polymers. The postpolymerization cyclization provides for a rarely seen oxygen substitution of the vinyl units of a PPV and endows the products with greater planarity and rigidity, thereby resulting in red-shifts in absorbance and fluorescence and defined vibrational features. We hope to extend this cyclization strategy to establish higher order planarity for other conjugated polymer classes.

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[1] *Conjugated Polymers: Theory, Synthesis Properties, and Characterization*, CRC, Boca Raton, FL, **2007**.

[2] a) D. Izuhara, T. M. Swager, *J. Am. Chem. Soc.* **2009**, *131*, 17724 – 17725; b) A. C. Grimsdale, K. Mullen in *Design and Synthesis of Conjugated Polymers* (Eds.: M. Leclerc, J. Morin), Wiley-VCH, Weinheim, **2010**, pp. 227 – 245.

[3] M. S. Taylor, T. M. Swager, *Org. Lett.* **2007**, *9*, 3695 – 3697.

[4] a) T. M. Swager, *Acc. Chem. Res.* **2008**, *41*, 1181 – 1189; b) J. H. Chong, M. J. MacLachlan, *Chem. Soc. Rev.* **2009**, *38*, 3301 – 3315.

[5] a) S. Seo, T. J. Marks, *Chem. Eur. J.* **2010**, *16*, 5148 – 5162; b) A. S. Hashmi, S. Schäfer, M. Wölfle, C. Diez Gil, P. Fischer, A. Laguna, M. C. Blanco, M. C. Gimeno, *Angew. Chem.* **2007**, *119*, 6297 – 6300; *Angew. Chem. Int. Ed.* **2007**, *46*, 6184 – 6187; c) B. Gabriele, G. Salerno, A. Fazio, R. Pittelli, *Tetrahedron* **2003**, *59*, 6251 – 6259; d) M. D. Weingarten, A. Padwa, *Tetrahedron Lett.* **1995**, *36*, 4717 – 4720; e) B. M. Trost, A. C. Gutierrez, R. C. Livingston, *Org. Lett.* **2009**, *11*, 2539 – 2542; f) F. E. McDonald, *Chem. Eur. J.* **1999**, *5*, 3103 – 3106; g) B. M. Trost, Y. H. Rhee, *J. Am. Chem. Soc.* **1999**, *121*, 11680 – 11683; h) P. Compain, J. Goré, J. M. Vatèle, *Tetrahedron* **1996**, *52*, 10405 – 10416; i) P. Compain, J. Goré, J. M. Vatèle, *Tetrahedron Lett.* **1995**, *36*, 4063 – 4064; j) R. Rüttinger, J. Leutzow, M. Wilsdorf, K. Wilckens, C. Czekelius, *Org. Lett.* **2011**, *13*, 224 – 227; k) A. S. Hashmi, M. Bührle, *Aldrichimica Acta* **2010**, *43*, 27 – 33; l) A. S. K. Hashmi, M. Bührle, M. Wölfle, M. Rudolph, M. Wieteck, F. Rominger, W. Frey, *Chem. Eur. J.* **2010**, *16*, 9846 – 9854.

[6] a) B. VanVeller, T. M. Swager in *Design and Synthesis of Conjugated Polymers* (Eds.: M. Leclerc, J. Morin), Wiley-VCH, Weinheim, **2010**, pp. 175 – 200; b) U. H. F. Bunz, *Adv. Polym. Sci.* **2005**, *177*, 1 – 52; c) U. H. F. Bunz, *Chem. Rev.* **2000**, *100*, 1605 – 1644.

[7] Y. Pang in *Design and Synthesis of Conjugated Polymers* (Eds.: M. Leclerc, J. Morin), Wiley-VCH, Weinheim, **2010**, pp. 147 – 170.

[8] a) A. R. Marshall, U. H. F. Bunz, *Macromolecules* **2001**, *34*, 4688 – 4690; b) H. L. Ricks, U. H. Choudry, A. R. Marshall, U. H. F. Bunz, *Macromolecules* **2003**, *36*, 1424 – 1425; c) J. B. Beck, A. Kokil, D. Ray, S. J. Rowan, C. Weder, *Macromolecules* **2002**, *35*, 590 – 593.

[9] R. M. Moslin, C. G. Espino, T. M. Swager, *Macromolecules* **2009**, *42*, 452 – 454.

[10] a) R. M. Moslin, T. L. Andrew, S. E. Kooi, T. M. Swager, *J. Am. Chem. Soc.* **2009**, *131*, 20 – 21; b) N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, A. B. Holmes, *Nature* **1993**, *365*, 628 – 630.

[11] a) C. Galli, *Chem. Rev.* **1988**, *88*, 765 – 792; b) R. Bohlmann in *Comp. Org. Synth.*, *Vol. 6* (Eds.: B. M. Trost, I. Flemming), Pergamon, Oxford, **1991**, pp. 203 – 223.

[12] Y. T. Wu, T. Hayama, K. K. Baldridge, A. Linden, J. S. Siegel, *J. Am. Chem. Soc.* **2006**, *128*, 6870 – 6884.

[13] R. Mancuso, S. Mehta, B. Gabriele, G. Salerno, W. S. Jenks, R. C. Larock, *J. Org. Chem.* **2010**, *75*, 897 – 901.

[14] D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351 – 3378.

[15] I. V. Alabugin, K. Gilmore, M. Manoharan, *J. Am. Chem. Soc.* **2011**, *133*, 12608 – 12623; K. Gilmore, I. V. Alabugin, *Chem. Rev.* **2011**, *111*, 6513 – 6556, and references therein.

[16] a) V. E. Williams, T. M. Swager, *Macromolecules* **2000**, *33*, 4069 – 4073; b) D. Zhao, T. M. Swager, *Macromolecules* **2005**, *38*, 9377 –

9384; c) D. H. Zhao, T. M. Swager, *Org. Lett.* **2005**, *7*, 4357–4360.

[17] This insolubility is likely responsible for the small PDI values observed, as longer, more disperse chains are excluded from the GPC analysis.

[18] P. M. Cotts, T. M. Swager, Q. Zhou, *Macromolecules* **1996**, *29*, 7323–7328.

[19] Additionally, consistent with triphenylene vinylene systems, the (0,0) transition of **21** was not the most intense band in the absorption spectrum (Figure 1 a), but was the most intense in the emission spectrum. This indicates that the terminal phenyl rings for **21** may not be coplanar in the ground state but are so in the excited state.

[20] H. C. Lin, C. M. Tsai, G. H. Huang, J. M. Lin, *J. Polym. Sci. Part A* **2006**, *44*, 783–800.

[21] F. Wudl, G. Srdanov, US Patent No. 5 189 136, **1993**.

[22] A brief description of the electrochemistry of **21** and **24** can be found in the Supporting Information.

[23] CCDC 835368 (**15**) and CCDC 835369 (**19**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.