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ScienceDirect
Tetrahedron 63 (2007) 2907–2914
Tetrahedron

Star-shaped oligo(*p*-phenylene)-functionalized truxenes as blue-light-emitting materials: synthesis and the structure–property relationship

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Received 15 November 2006; revised 16 January 2007; accepted 16 January 2007
Available online 20 January 2007

Abstract—In this contribution, we described a strategy to prepare a series of well-defined, blue-light-emitting materials with truxene unit as the core and oligo(*p*-phenylene) (from one to four phenyl units) as the branches. The Suzuki coupling reactions between truxene bromide derivatives and phenylboronic acid or 1,1′-biphenyl-4-boronic acid catalyzed by Pd(0) afforded the desired compounds **Tr-1-Ph**, **Tr-2-Ph**, **Tr-3-Ph** and **Tr-4-Ph**. With stepwise increases of the benzene rings, the desired molecules exhibited exceptional photophysical properties as well as increasing thermal stability. T_gs increased from 39 °C for **Tr-1-Ph** to 192 °C for **Tr-4-Ph**. The absorption and the emission maximum peaks of these four compounds were red-shifted from the ultraviolet to the blue region with the increase of effective conjugation length. All results demonstrated that the physical properties were facilely tuned by connecting different types and different conjugated lengths to C-2, C-7, and C-12 positions of the truxene core.

1. Introduction

π-Conjugated organic materials have received intensive research interest both in academic and industry due to their potential application in a wide range of electronic and optoelectronic devices.[1] New synthetic methodologies and novel structures are continuously introduced into this blooming field. Most recently, star-shaped molecules have become an inspiring aspect of material chemistry because it can lead to a strong enhancement of physical properties.[2] Its combination with conjugated character within the arms brings novel electrical, optical, and morphological properties, as well as intrinsic two- or three-dimensional character.[3] Meanwhile, these monodisperse, well-defined π-conjugated oligomers serve as important and perfect model compounds for the corresponding conductive polymers, providing deep insight into the structure–property relationship of conductive polymers.[4] Among π-conjugated organic materials with large energy band gaps, oligo- and poly-*p*-phenylene (PPP),[5,6] ladder-poly-*p*-phenylene (LPPP),[7] polyfluorene (PF),[8] and oligofluorene[9] derivatives have been recognized as the most promising blue-light emitters due to their high photoluminescence (PL) efficiency, good charge transportation, thermal stability, and facile tunability of physical properties through chemical modification.

Oligo(*p*-phenylenes), as mentioned above, an important class of conjugated redox and chromophore materials have been attracted considerable interests in the past decades. The well-defined models for poly(*p*-phenylenes)[10] not only achieved blue-light-emitting OLED in 1991,[6a] and offered materials with chemically tailored properties,[11] but was also employed as rigid-rod building blocks for constructing novel supramolecules,[12] as well as for molecular wires or linkages or spacers in molecular electronics,[13] and as synthetic ionophores to facilitate ion migration through lipid bilayers,[14] and as chain-stiffening building blocks in liquid crystalline materials and semiflexible polymers to tailor properties such as crystallinity, fluorescence behavior, and stability.[15]

Truxene, 10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene, has been recognized as an attractive building block for the construction of novel π-conjugated star-shaped molecules due to its unique three-dimensional topology and easy functionalization at both methylene groups and C-2, C-7, and C-12 positions. Previously, it has been used as a potential starting material for the construction of bowl-shaped fragments of the fullerenes,[16] C_3 tripodal materials in asymmetric catalysis and chiral recognition,[17] and liquid crystalline compounds.[18] Some *syn*-trialkylated truxenes and sterically crowded 5,10,15-triarylated- and 5,10,15-tri(9-fluorenylidene) truxenes have been synthesized and their self-associate behavior in solution or reversible reduction behavior in

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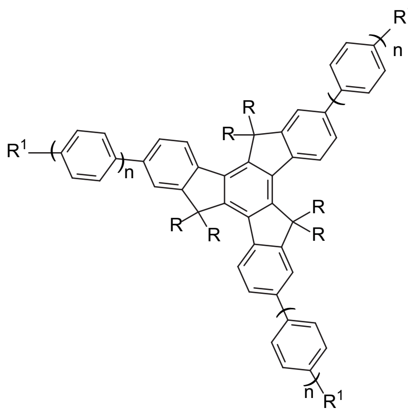
doi:10.1016/j.tet.2007.01.025

cyclic voltammetry was carefully investigated.[19] Our group has successfully introduced oligothiophene arms to the truxene core[20a] and developed novel π-conjugated truxene-based dendrimers, which have larger molecular weight for **G1** (M_w=7908).[20b,c] Therefore, Skabara and co-workers reported on employing the truxene core for the construction of virtually 'no-core' star-shaped oligofluorene architectures.[3a] All these results and the ongoing research in our group show that truxene-based materials exhibit excellent photophysical properties, such as highly efficient emission and facile emissive wavelength tuning, high thermal and electrochemical stability, as well as ready synthesis, and demonstrate that truxene derivatives are an important class of organic light-emitting materials and their thermal and photophysical properties could be facilely tuned by connecting different types and lengths of conjugated chains to C-2, C-7, and C-12 positions of the truxene core.[3a,20]

In this contribution, we report the design, synthesis, and characterization of star-shaped oligo(*p*-phenylene)-functionalized truxenes, **Tr-*n*-Ph** (Chart 1) with up to quaterphenylene arms, as potential blue-light-emitting materials. These nanosized macromolecules (radius 2.3 nm for **Tr-4-Ph**) were still readily soluble in common organic solvents, exhibiting good film forming properties. Their absorption and emission properties and thermal stability, as well as structure–property relationships, were investigated. The highly efficient blue-light emission, together with remarkably high T_g, demonstrated these compounds as the promising candidates for blue-light-emitting materials.



R = *n*-C_6H_{13};
n = 0: R^1 = Br: **1;**
n = 1, R^1 = H: **Tr-1-Ph;**
n = 1, R^1 = Br: **2;**
n = 2, R^1 = H: **Tr-2-Ph;**
n = 2, R^1 = Br: **3;**
n = 3, R^1 = H: **Tr-3-Ph;**
n = 4, R^1 = H: **Tr-4-Ph.**

Chart 1.

2. Results and discussion

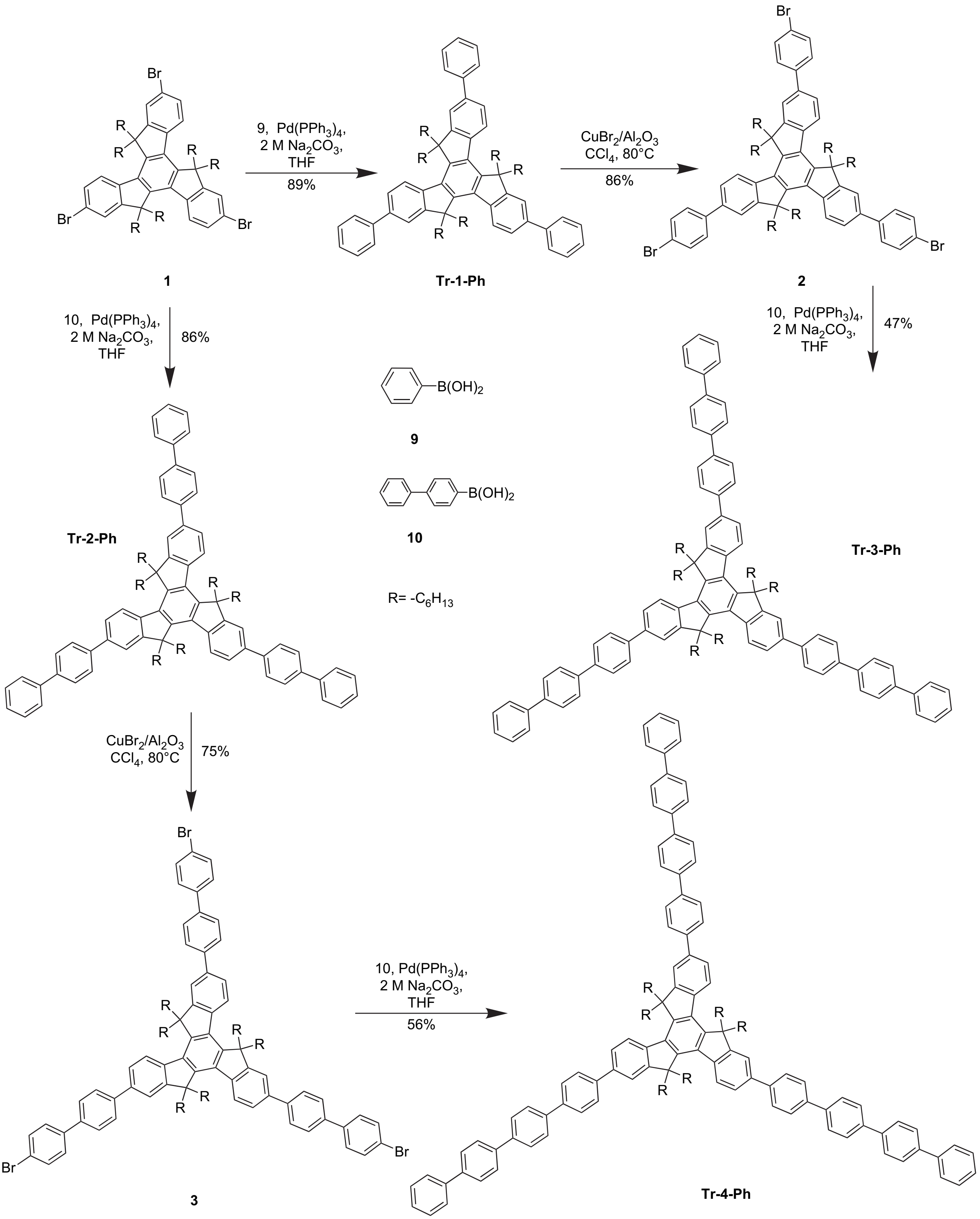
2.1. Synthesis

The synthetic route is sketched in Scheme 1. The repetitive divergent approach was exploited to give the desired materials, which was similar to that reported by our group for the synthesis of star-shaped oligofluorenes in which the branch size was increased by repetitive addition of arm units to the star-shaped oligomer through the Suzuki coupling.[3d] One of the barriers toward the full realization of oligo(*p*-phenylene)s' potential is their challenging synthesis and purification.[21] The difficulty associated with poor solubility of oligo(*p*-phenylene)s partially addressed by introducing various side chains to the phenylene unit. In this project, the problem was strategically circumvented by introducing six stretched hexyl chains to the truxene core prior to oligophenylene modification. First, truxene was alkylated to give readily soluble hexahexylated truxene and following subsequent bromination afforded hexahexylated truxene tribromide **1** in high yield as reported both in our previous contributions[22] and by Skabara et al.[3a] Phenylboronic acid and 1,1′-biphenyl-4-boronic acid were readily prepared in excellent yield from the reaction of corresponding Grignard reagents with trimethyl borate followed by hydrolysis. The Suzuki cross-coupling reactions of **1** with phenyl or biphenylboronic acids afforded **Tr-1-Ph** and **Tr-2-Ph**, respectively. The method employing bromine in methylene chloride failed to give the desired bromides **2** and **3**. ^{1}H NMR spectrum showed that bromination occurred not only at the *para* site of the benzene unit but also at the C-4, C-9, and C-14 positions of the truxene core, which might be inferred from the appearance of a singlet at about δ 8.7 ppm. This might be due to the relatively averaged electron density between the truxene core and the conjugated arms. For **Tr-1-Ph**, pure tribromide could not be obtained but instead, when excess bromine was applied, pure hexabromide was afforded. For **Tr-2-Ph**, excess bromine resulted in further bromination at the biphenyl unit. The similar polarity of our products made the separation very difficult. The attempt to iodinate **Tr-1-Ph** and **Tr-2-Ph** using $I_2/HIO_4/HOAc$ also failed, in which both **Tr-1-Ph** and **Tr-2-Ph** aggregated and gave no reaction even in the presence of excess I_2/HIO_4 after reflux for three days. In our recent report on the monodisperse star-shaped oligofluorenes,[3d] alumina-supported copper(II) bromide was found to selectively brominate aromatic hydrocarbons at the outermost positions of the system under mild conditions. Its application in this system also gave very good results. After bromination, for **Tr-1-Ph** and **Tr-2-Ph**, the triplet centered at about δ 7.40 ppm, which belongs to the *para* site protons of outermost benzene rings, gradually disappeared and the multiple signal arising around δ 7.50 ppm moved downfield to about δ 7.60 ppm while the doublet signals around δ 8.45 ppm, which was assigned to the protons at C-3, C-8, and C-13 positions, did not show significant change. The convenient Suzuki cross-coupling[3d,20a,22] between tribromide compounds (**2** and **3**) with 1,1′-biphenyl-4-boronic acid finally yielded **Tr-3-Ph** and **Tr-4-Ph**, respectively. Not only they were adequately characterized by the appropriate ^{1}H and ^{13}C NMR spectra and elemental analysis, MALDI-TOF MS measurement was also employed to determine the structure, the molecular weight, and the purity of these new compounds.

2.2. Photophysical properties

The normalized absorption and emission spectra of compounds **Tr-1-Ph**, **Tr-2-Ph**, **Tr-3-Ph**, and **Tr-4-Ph** in THF solutions are shown in Figure 1. They all showed strong π–π* electron absorption bands in the near violet region. The continuous red-shift of the absorption maximum was observed with a successive increase of benzene rings in each conjugated branch.

The absorption maximums of compounds **Tr-1-Ph**, **Tr-2-Ph**, **Tr-3-Ph**, and **Tr-4-Ph** were 326, 336, 340, and



Scheme 1.

341 nm, respectively, which were substantially red-shifted in comparison with those of benzene, biphenyl (246 nm), *p*-terphenyl (278 nm), and *p*-quaterphenyl (294 nm).[23] Considering the fact that the truxene core has an absorption maximum at 301 nm, we speculated that a highly extended π-delocalized system was formed throughout the truxene core, which contributed the most to the system's absorption. The band gaps for compounds **Tr-1-Ph**, **Tr-2-Ph**, **Tr-3-Ph**, and **Tr-4-Ph** of 3.20–3.49 eV, estimated from the red edge of the longest wavelength absorption in the electronic

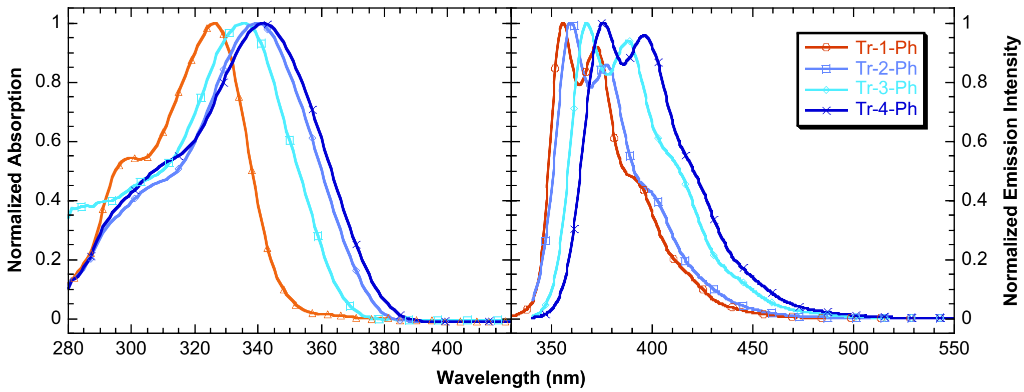


Figure 1. Absorption and emission spectra of compounds **3**, **5**, **7**, and **8** in THF solutions at room temperature.

spectra in THF solutions, exhibited a perfect linear correlation (r=0.999) with the inverse number of benzene units (n) in each conjugated arm as shown in Figure 2.

The fitted linear equation as shown in Figure 3 indicated a saturation limit for ΔE versus the number (n) of benzene rings, which could also be seen from the trend of the curve about the lowest energy transition versus the numbers of benzene rings in the conjugated branches.

$$E(\mathrm{eV}) = 3.11 + 0.38/n$$

The photoluminescence (PL) spectrum of compounds **Tr-1-Ph**, **Tr-2-Ph**, **Tr-3-Ph**, and **Tr-4-Ph** exhibited a well-defined vibronic feature and the difference of peaks was enlarged with increase of benzene rings, which suggested the relative enhancement of vibronic transition. Moreover, the results also demonstrated that the emission spectra of truxene derivatives were liable to be tuned by introducing conjugated segments of different types and lengths.

We also investigated the absorption and emission spectra of compounds **Tr-1-Ph**, **Tr-2-Ph**, **Tr-3-Ph**, and **Tr-4-Ph** in films spin-coated from toluene solutions are shown in Figure 4. Similar red-shift trend with increase of benzene rings was also observed. For compounds **Tr-1-Ph** and **Tr-2-Ph**, their absorption maximum peaks in THF solutions were identical with those in solid states. Due to aggregation in solid states, PL spectra of compounds **Tr-1-Ph**, **Tr-2-Ph**, **Tr-3-Ph**, and **Tr-4-Ph** in films were substantially red-shifted in comparison with those in solutions. Moreover, the molecular vibronic features disappeared for compounds **Tr-2-Ph**, **Tr-3-Ph**, and **Tr-4-Ph** gave out bright blue emission with high quantum efficiency. The fluorescence quantum yields (Φ_f) in dilute THF solution using 9,10-diphenylanthracene (Φ_f=0.91 in ethanol) as standard were measured to be 0.91 for **Tr-1-Ph**, 0.93 for **Tr-2-Ph**, 0.98 for **Tr-3-Ph**, and 0.96 for **Tr-4-Ph**, respectively, as summarized in Table 1.[24]

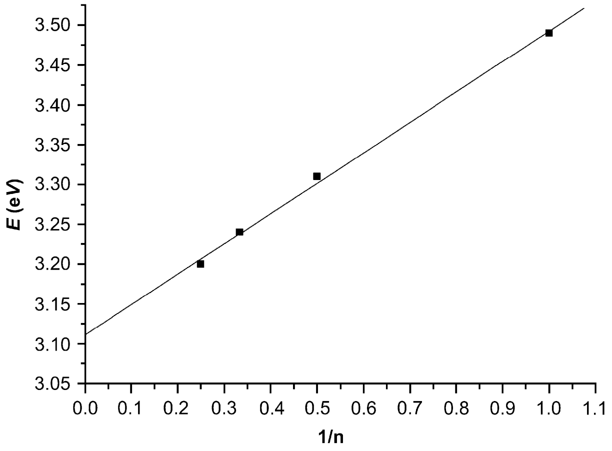


Figure 2. Energy (ΔE) of the lowest electronic transition for compounds **Tr-1-Ph**, **Tr-2-Ph**, **Tr-3-Ph**, and **Tr-4-Ph** in THF solutions versus the inverse number ($1/n$) of benzene ring units in each conjugated branch.

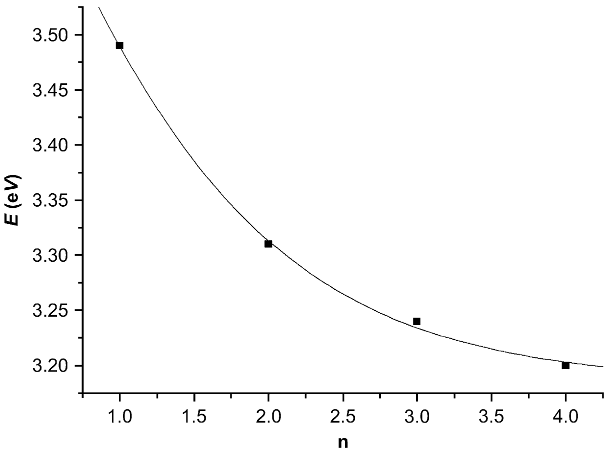


Figure 3. Energy (ΔE) of the lowest electronic transition for compounds **Tr-1-Ph**, **Tr-2-Ph**, **Tr-3-Ph**, and **Tr-4-Ph** in THF solutions versus the number ($1/n$) of benzene ring units in each conjugated arm.

2.3. Thermal analysis

In comparison with polymers, oligomers are more liable to form a crystalline state than polymers, which can scatter the light and limit charge injection and transport in OLEDs. Thus, oligomeric materials capable of demonstrating a glass transition state while resisting crystallization are more preferred. For the photoelectronic applications, the thermal stability of organic materials is critical for device stability and lifetime because during the electroluminescent process, heat is generated that can affect the material morphology and the device performance, finally leading to the degradation of OLEDs.[25] The rapid molecular motion near the glass transition temperature (T_g) might promote such morphological change. Hence, the relatively high T_g is essential

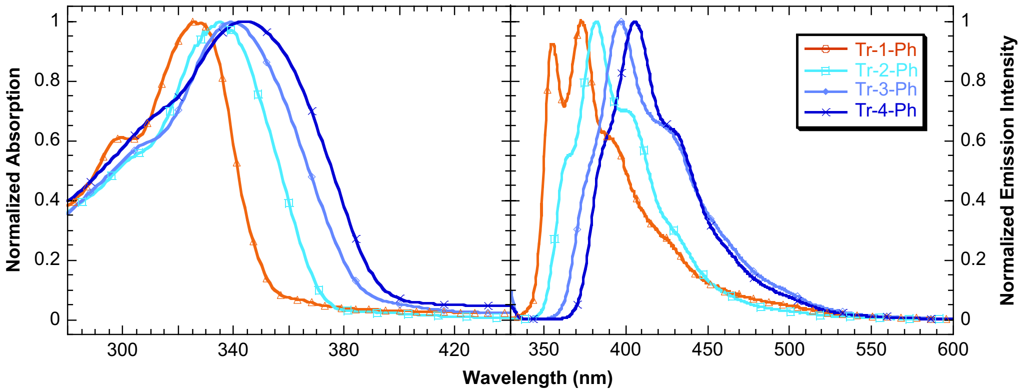


Figure 4. Absorption and emission spectra of compounds **3**, **5**, **7**, and **8** in solid states at room temperature.

Table 1. Physical properties of compounds **Tr-1-ph**, **Tr-2-ph**, **Tr-3-ph**, and **Tr-4-ph**

Compd	λ_{max} abs in solution	λ_{max} abs in film	λ_{max} PL in solution	λ_{max} PL in film	T_g	Band gap	Quantum yields Φ_f
Tr-1-Ph	326	326	356 (372)	373 (357)	39	3.49	0.91
Tr-2-Ph	336	336	359 (377)	382	77	3.31	0.93
Tr-3-Ph	340	342	368 (388)	397	125	3.24	0.98
Tr-4-Ph	341	345	376 (396)	405	192	3.20	0.96

for materials used as emissive materials for optoelectronic applications. In this series of compounds, we found that **Tr-1-Ph** was somewhat crystalline while the other three compounds were amorphous at room temperature. The thermally induced phase transition behaviors of these compounds were investigated with differential scanning calorimetry (DSC) in nitrogen at a heating rate of 10 °C min^{-1}. In the first heating cycle, the samples had been heated to 300 °C and then allowed to slowly cool to room temperature to remove the residual solvent molecules and to afford stable amorphous phases. Typically, this cycle showed a weak and broad melting endothermic peak. It is at the second run when the residual solvents in samples had been removed that the amorphous phases could be observed. The T_g of **Tr-1-Ph** was around 39 °C. Then the increasing length of rigid oligo (*p*-phenylene) units seemed to improve the glass transition temperature a great deal to 192 °C for **Tr-4-Ph**, which was quite remarkable. The differential scanning calorimetric thermogram of compounds **Tr-1-Ph**, **Tr-2-Ph**, **Tr-3-Ph**, and **Tr-4-Ph** is shown in Figure 5. All the characterization of physical properties of compounds **Tr-1-Ph**, **Tr-2-Ph**, **Tr-3-Ph**, and **Tr-4-Ph** is summarized in Table 1.

3. Conclusion

In summary, we developed a series of well-defined, readily soluble, blue-light-emitting materials with truxene as the core and oligo(*p*-phenylene) as the branches employing the Suzuki cross-coupling reactions in good yields. The materials exhibited exceptional photophysical properties as well as good thermal stability. The absorption and emission

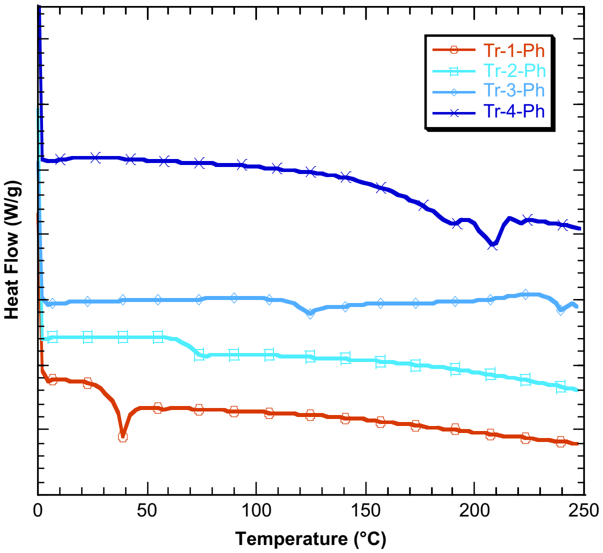


Figure 5. DSC curves (second run) of compounds **3**, **5**, **7**, and **8**.

spectra of these materials in THF solutions and in solid states were readily tuned by varying the number of phenyl units. The relatively narrow emission spectra as well as structure-unrelated features in solid states might be contributed to the star-shaped two-dimensional architecture, which also improved their amorphous properties. A significant increase of glass transition temperature (T_g) was observed from 39 °C for **Tr-1-Ph** to 192 °C for **Tr-4-Ph**. Together with their excellent film forming property and free solubility in common organic solvents, these high-generation nano-sized oligomers (radius ≈ 2.3 nm for **Tr-4-Ph**) might be the promising candidates for blue-light-emitting materials. This work should also be of great interest and very helpful for the systematic investigation of structure–property relationships. The investigation on their practical optoelectronic application is still ongoing.

4. Experimental section

4.1. General methods

Commercial chemicals were purchased and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 (300 MHz) or 200 (200 MHz) spectrometer in $CDCl_3$ with TMS as the reference. Elemental analysis of all new compounds was performed on a Elementar Vario EL (Germany) instrument. Both the absorption and emission spectra were measured in the degassed dilute THF solution (about 1.0×10^{-6} mol/L) at room temperature and were recorded on Perkin–Elmer Lambda 35 UV–vis spectrometer and LS 55 Luminescence Spectrometer. Fluorescence quantum yields (Φ_f) of the samples in THF solutions were measured by using 9,10-diphenylanthracene (Φ_f=0.91 in ethanol) as standard. Values are calculated according to the following equation, where Φ_{unk} is the fluorescence quantum yield of the sample, Φ_{std} is the fluorescence quantum yield of 9,10-diphenylanthracene, I_{unk} and I_{std} are the integrated emission intensities of the sample and 9,10-diphenylanthracene, respectively; A_{unk} and A_{std} are the absorbance of the sample and 9,10-diphenylanthracene at the excitation wavelength, respectively, and η_{unk} and η_{std} are the refractive indexes of the corresponding solutions (pure solvents were assumed).

$$\Phi_{unk} = \Phi_{std}(I_{unk}/A_{unk})(A_{std}/I_{std})(\eta_{unk}/\eta_{std})^2$$

4.1.1. 5,5,10,10,15,15-Hexahexyl-2,7,12-triphenyl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (Tr-1-Ph). To a degassed solution of 2,7,12-tribromo-5,5′,10,10′,15,15′-hexahexyltruxene (4.0 g, 3.67 mmol) and 1-phenylboronic acid (2.7 g, 22.14 mmol) in 50 mL of THF were added $Pd(PPh_3)_4$ (30 mg) and 36 mL of 2 M aqueous Na_2CO_3 solution. The mixture was refluxed under nitrogen for 20 h and then poured into a saturated solution of ammonium chloride followed by extracting with ethyl acetate for three times. The combined organic phases were washed with brine and dried over $MgSO_4$. After the removal of the solvent, the residue was purified by flash column chromatography using petroleum ether as eluent to give the product as a white solid (3.5 g, 89%). ^{1}H NMR ($CDCl_3$, 300 Hz, ppm): δ 8.44 (3H, d, *J*=8.4 Hz, Ar-H), 7.77 (6H, m, Ar-H), 7.68 (6H, m, Ar-H), 7.54 (6H, t, *J*=7.5 Hz, Ar-H), 7.39 (3H, t, *J*=7.2 Hz, Ar-H), 3.00–3.05 (6H, m, CH_2), 2.14–2.21 (6H, m, CH_2), 0.89–0.93 (36H, m, CH_2), 0.50–0.62 (30H, m, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 100 Hz, ppm): δ 154.3, 145.2, 145.4, 139.6, 139.1, 138.1, 128.8, 127.2, 127.1, 125.1, 124.9, 120.6, 55.8, 37.1, 31.5, 29.5, 23.9, 22.3, 13.9. MALDI-TOF MS: 1075 (M^++H). Anal. Calcd for $C_{81}H_{102}$: C, 90.44; H, 9.56. Found: C, 90.23; H, 9.61.

4.1.2. 2,7,12-Tris-(4′-bromo-biphenyl-4-yl)-5,5,10,10,15,15-hexahexyl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorine (2). A mixture of **Tr-1-Ph** (1.00 g, 0.93 mmol) and $CuBr_2$–Al_2O_3 (6.21 g, 9.28 mmol) in CCl_4 was stirred at 80 °C for 24 h. The reaction mixture was filtered and the resulting precipitate was washed with CCl_4. After removal of the solvents, the residue was purified by column chromatography using CH_2Cl_2/petroleum ether and then recrystallized from CH_2Cl_2/ethanol to afford the product as a white solid (1.08 g, 88%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.42 (3H, d, *J*=8.1 Hz, Ar-H), 7.49–7.78 (18H, m, Ar-H), 2.98–3.05 (6H, m, CH_2), 2.10–2.20 (6H, m, CH_2), 0.88–0.93 (36H, m, CH_2), 0.46–0.62 (30H, m, CH_2, CH_3). MALDI-TOF MS: 1312 (M^+). Anal. Calcd for $C_{81}H_{99}Br_3$: C, 74.13; H, 7.60; Br, 18.27. Found: C, 74.02; H, 7.64; Br, 18.46.

4.1.3. 2,7,12-Tris-biphenyl-4-yl-5,5,10,10,15,15-hexahexyl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorine (Tr-2-Ph). To a degassed solution of 2,7,12-tribromo-5,5′,10,10′,15,15′-hexahexyltruxene (4.0 g, 3.67 mmol) and 4′-biphenylboronic acid (4.4 g, 22.14 mmol) in 50 mL of THF were added $Pd(PPh_3)_4$ (30 mg) and 36 mL of 2 M aqueous Na_2CO_3 solution. The mixture was refluxed under nitrogen for 20 h and then poured into a saturated solution of ammonium chloride followed by extracting with ethyl acetate for three times. The combined organic phases were washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash column chromatography using CH_2Cl_2/petroleum ether as eluent, to afford the product as a white solid (4.1 g, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.52 (3H, d, *J*=8.4 Hz, Ar-H), 7.94 (6H, d, *J*=8.0 Hz, Ar-H), 7.76–7.85 (18H, m, Ar-H), 7.56 (6H, t, *J*=7.4 Hz, Ar-H), 7.45 (3H, t, *J*=7.2 Hz, Ar-H), 3.10–3.18 (6H, m, CH_2), 2.25–2.35 (6H, m, CH_2), 0.86–1.04 (36H, m, CH_2), 0.68–0.74 (30H, m, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 154.8, 145.7, 141.3, 140.7, 140.5, 140.2, 139.0, 138.6, 129.3, 128.0, 127.9, 127.8, 127.5, 125.5, 125.4, 121.0, 56.3, 37.6, 31.9, 30.0, 24.5, 22.7, 14.3. MALDI-TOF MS: 1304 (M^+). Anal. Calcd for $C_{99}H_{114}$: C, 91.19; H, 8.81. Found: C, 91.38; H, 8.80.

4.1.4. 2,7,12-Tris-(4′-bromo-biphenyl-4-yl)-5,5,10,10,15,15-hexahexyl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3). The procedure was analogous to that for **2** using **Tr-2-Ph** (1.0 g, 0.77 mmol) and $CuBr_2/Al_2O_3$ (5.2 g, 7.7 mmol), giving the product as a white solid (0.89 g, 75%) after recrystallization from CH_2Cl_2/ethanol. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.47 (3H, d, *J*=7.5 Hz, Ar-H), 7.84–7.87 (6H, m, Ar-H), 7.71–7.77 (18H, m, Ar-H), 7.52–7.63 (6H, m, Ar-H), 3.00–3.10 (6H, m, CH_2), 2.18–2.24 (6H, m, CH_2), 0.90–0.95 (36H, m, CH_2), 0.44–0.63 (30H, m, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 153.5, 146.6, 141.2, 141.0, 140.7, 140.5, 137.7, 132.4, 130.5, 129.5, 129.3, 127.9, 127.6, 127.2, 125.2, 120.7, 56.3, 37.3, 31.9, 29.8, 24.4, 22.7, 14.3. MALDI-TOF

MS: 1540 (M$^+$). Anal. Calcd for $C_{99}H_{111}Br_3$: C, 77.18; H, 7.26; Br, 15.56. Found: C, 77.13; H, 7.25; Br, 15.07.

4.1.5. 5,5,10,10,15,15-Hexahexyl-2,7,12-tris-[1,1′;4′,1″]-terphenyl-4-yl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]-fluorene (Tr-3-Ph). To a degassed solution of **2** (0.5 g, 0.38 mmol) and 4′-biphenylboronic acid (0.45 g, 2.28 mmol) in 12 mL of toluene were added $Pd(PPh_3)_4$ (10 mg) and 8 mL of 2 M aqueous Na_2CO_3 solution. The mixture was refluxed for 20 h and then poured into a saturated solution of ammonium chloride, followed by extracting with ethyl acetate for three times. The combined organic phases were washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash column chromatography using petroleum ether/CH_2Cl_2 (v/v=15:1) to afford the product as a white solid (0.28 g, 47%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.49 (3H, d, J=8.4 Hz, Ar-H), 7.90 (6H, d, s, J=8.4 Hz, Ar-H), 7.68–7.84 (30H, m, Ar-H), 7.50 (6H, t, J=6.5 Hz, Ar-H), 7.39 (3H, t, J=7.4 Hz, Ar-H), 3.06–3.10 (6H, m, CH_2), 2.18–2.27 (6H, m, CH_2), 0.84–1.00 (36H, m, CH_2), 0.51–0.66 (30H, m, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 155.0, 154.4, 145.3, 145.3, 140.7, 140.4, 140.2, 139.8, 139.7, 139.5, 138.5, 138.1, 128.8, 127.6, 127.5, 127.4, 127.4, 127.1, 125.0, 120.5, 55.8, 37.2, 31.5, 29.5, 24.0, 22.3, 13.9. MALDI-TOF MS: 1532. (M$^+$). Anal. Calcd for $C_{117}H_{126}$: C, 91.71; H, 8.29. Found: C, 91.55; H, 8.37.

4.1.6. 5,5,10,10,15,15-Hexahexyl-2,7,12-Tris-[1,1′;4′,1″;4″,1‴]quaterphenyl-4-yl-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (Tr-4-Ph). To a degassed solution of **3** (0.39 g, 0.25 mmol) and 4′-biphenylboronic acid (0.25 g, 1.27 mmol) in 12 mL of toluene were added $Pd(PPh_3)_4$ (10 mg) and 8 mL of 2 M aqueous Na_2CO_3 solution. The mixture was refluxed for 20 h and then poured into a saturated solution of ammonium chloride, followed by extracting with ethyl acetate for three times. The combined organic phases were washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash column chromatography using petroleum ether/CH_2Cl_2 (v/v=12:1) to afford the product as a white solid (0.25 g, 56%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.49 (3H, d, J=7.8 Hz, Ar-H), 7.90 (6H, d, s, J=8.1 Hz, Ar-H), 7.59–7.87 (42H, m, Ar-H), 7.44–7.51 (6H, m, Ar-H), 7.35–7.42 (3H, m, Ar-H), 3.06–3.10 (6H, m, CH_2), 2.18–2.27 (6H, m, CH_2), 0.93–0.97 (36H, m, CH_2), 0.50–0.65 (30H, m, CH_2, CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 155.0, 154.4, 145.7, 145.4, 140.7, 140.4, 140.3, 139.8, 139.6, 139.5, 138.6, 138.2, 130.7, 128.8, 127.6, 127.5, 127.2, 127.1, 125.1, 120.5, 119.8, 114.1, 55.9, 37.2, 31.5, 29.5, 24.1, 22.3, 13.9. MALDI-TOF MS: 1760 (M$^+$). Anal. Calcd for $C_{135}H_{138}$: C, 92.10; H, 7.90. Found: C, 91.87; H, 7.94.

Acknowledgements

This work was supported by National Natural Science Foundation of China (NSFC 20425207, 50473016, and 20521202).

References and notes

1. (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539; (b) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Ed.; Dekker: New York, NY, 1997; (c) *Conjugated Conducting Polymers*; Kies, H., Ed.; Springer: Berlin, 1992; Vol. 102; (d) *Conjugated Polymers*; Bredas, J. L., Sylbey, R., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; (e) Roncali, J. *Chem. Rev.* **1992**, *92*, 711; (f) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477; (g) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430; (h) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402; (i) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. S. *Adv. Mater.* **2000**, *12*, 1737; (j) Ho, P. K. H.; Kim, J. S.; Burroughes, J. H.; Becker, H.; Li, S. F. Y.; Brown, T. M.; Cacialli, F.; Friend, R. H. *Nature* **2000**, *404*, 481; (k) Gross, M.; Müller, D. C.; Nothofer, H.-G.; Scherf, U.; Neher, D.; Bräuchle, C.; Meerholz, K. *Nature* **2000**, *405*, 661.
2. (a) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747; (b) Zyss, J.; Ledoux, I. *Chem. Rev.* **1994**, *94*, 77; (c) Dhenault, C.; Ledoux, I.; Samuel, I. D. W.; Bourgault, M.; Le Bozec, H. *Nature* **1995**, *374*, 339.
3. (a) Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695; (b) Li, B.; Li, J.; Fu, Y.; Bo, Z. *J. Am. Chem. Soc.* **2004**, *126*, 3430; (c) de Bettignies, R.; Nicolas, Y.; Blanchard, P.; Levillain, E.; Nunzi, J.-M.; Roncali, J. *Adv. Mater.* **2003**, *15*, 1939; (d) Zhou, X.-H.; Yan, J.-C.; Pei, J. *Org. Lett.* **2003**, *5*, 3543; (e) Ponomarenko, S. A.; Kirchmeyer, S.; Elschner, A.; Huisman, B.-H.; Karbach, A.; Drechsler, D. *Adv. Funct. Mater.* **2003**, *13*, 591; (f) Lin, W.-J.; Chen, W.-C.; Wu, W.-C.; Niu, Y.-H.; Jen, A. K.-Y. *Chem. Mater.* **2004**, *37*, 2335.
4. *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, New York, NY, 1998.
5. (a) McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. *Adv. Mater.* **1999**, *11*, 1349; (b) Virgili, T.; Lidzey, D. G.; Bradley, D. D. C. *Adv. Mater.* **2000**, *12*, 58; (c) Jiang, X.-Z.; Liu, S.; Ma, H.; Jen, A. K.-Y. *Appl. Phys. Lett.* **2000**, *76*, 1813.
6. (a) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36; (b) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934; (c) *Advances in Synthetic Metals—Twenty Years of Progress in Science and Technology*; Bernier, P., Lefrant, S., Bidan, G., Eds.; Elsevier: Amsterdam, 1999; pp 1–97.
7. (a) Scherf, U.; Müllen, K. *Macromol. Rapid Commun.* **1991**, *12*, 489; (b) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853.
8. (a) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416; (b) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946; (c) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965; (d) Müller, D. C.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wlederhirm, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. *Nature* **2003**, *421*, 829.
9. (a) Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C.-H.; Su, Y.-O.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 11576; (b) Katsis, D.; Geng, Y. H.; Ou, J.-J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 1332; (c) Geng, Y. H.; Katsis, D.; Culligan, S. W.; Ou, J.-J.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.*

2002, *14*, 463; (d) Wu, C.-C.; Liu, T.-L.; Hung, W.-Y.; Lin, Y.-T.; Wong, K.-T.; Chen, R.-T.; Chen, Y.-M.; Chien, Y.-Y. *J. Am. Chem. Soc.* **2003**, *125*, 3710; (e) Geng, Y. H.; Culligan, S. W.; Trajkovska, A.; Wallace, J. U.; Chen, S. H. *Chem. Mater.* **2003**, *15*, 542; (f) Wu, F.-I.; Reddy, D. S.; Shu, C.-F.; Liu, M. S.; Jen, A. K.-Y. *Chem. Mater.* **2003**, *15*, 269.

10. (a) Remmers, M.; Neher, D.; Gruner, J.; Friend, R. H.; Gelinck, G. H.; Warman, J. M.; Quattrocchi, C.; Dossantos, D. A.; Bredas, J. L. *Macromolecules* **1996**, *29*, 7432; (b) Schlüter, A. D.; Wegner, G. *Acta Polym.* **1993**, *44*, 59; (c) Vanhee, S.; Rulkens, R.; Lehmann, U.; Rosenauer, C.; Schulze, M.; Kohler, W.; Wegner, G. *Macromolecules* **1996**, *29*, 5136.
11. (a) Winkler, B.; Meghdadi, F.; Tasch, S.; Mullner, R.; Stelzer, F. *Opt. Mater.* **1998**, *9*, 159; (b) Heidenhain, S. B.; Sakamoto, Y.; Suzuki, T.; Miura, A.; Fujikawa, H.; Mori, T.; Tokito, S.; Taga, Y. *J. Am. Chem. Soc.* **2000**, *122*, 10240; (c) Era, M.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1995**, *67*, 2436; (d) Wang, Y. Z.; Sun, R. G.; Meghdadi, F.; Leising, G.; Epstein, A. J. *Appl. Phys. Lett.* **1999**, *74*, 3613; (e) Kim, H. K.; Kim, K. D.; Zyung, T. *Mol. Cryst. Liq. Cryst.* **1997**, *295*, 27; (f) Shin, S. H.; Oh, D. J.; Kim, H. K. *Mol. Cryst. Liq. Cryst.* **2000**, *349*, 423.
12. (a) For example, see: Hyslop, A. G.; Therien, M. J. *Inorg. Chim. Acta* **1998**, *275–276*, 427; (b) Schlicke, B.; Belser, P.; Cola, L. D.; Sabbioni, E.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 4207; (c) Schlicke, B.; De Cola, L.; Belser, P.; Balzani, V. *Coord. Chem. Rev.* **2000**, *208*, 267; (d) Taylor, P. N.; O'Connell, M. J.; McNeill, L. A.; Hall, M. J.; Aplin, R. T.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3456; (e) Yoo, Y. S.; Choi, J. H.; Song, J. H.; Oh, N. K.; Zin, W. C.; Park, S.; Chang, T.; Lee, M. *J. Am. Chem. Soc.* **2004**, *126*, 6294.
13. (a) Li, Z.-H.; Wong, M.-S.; Tao, Y.; D'Iorio, M. *J. Org. Chem.* **2004**, *69*, 921; (b) Weiss, E. A.; Ahrens, M. J.; Sinks, L. E.; Gusev, A. V.; Ratner, M. A.; Wasielewski, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 5577.
14. (a) Robert, F.; Winum, J.-Y.; Sakai, N.; Gerard, D.; Matile, S. *Org. Lett.* **2000**, *2*, 37; (b) Sakai, N.; Majumdar, N.; Matile, S. *J. Am. Chem. Soc.* **1999**, *121*, 4294; (c) Ghebremariam, B.; Sidorov, V.; Matile, S. *Tetrahedron Lett.* **1999**, *40*, 1445; (d) Ni, C.; Matile, S. *Chem. Commun.* **1998**, 755.
15. (a) Deimede, V.; Andrikopoulos, K. S.; Voyiatzis, G. A.; Konstandakopoulou, F.; Kallitsis, J. K. *Macromolecules* **1999**, *32*, 8848; (b) Mikroyannidis, J. A. *Macromol. Chem. Phys.* **1999**, *200*, 2327; (c) Konstandakopoulou, F. D.; Gravalos, K. G.; Kallitsis, J. K. *Macromolecules* **1998**, *31*, 5264.
16. (a) Boorum, M. M.; Vasilév, Y. V.; Drewello, T.; Scott, L. T. *Science* **2001**, *294*, 828; (b) Gómez-Lor, B.; de Frutos, Ó.; Echavarren, A. M. *Chem. Commun.* **1999**, 2431; (c) Rabideau, P. W.; Abdourazak, A. H.; Marcinow, Z.; Sygula, R.; Sygula, A. *J. Am. Chem. Soc.* **1995**, *117*, 6410; (d) Demlow, E. V.; Kelle, T. *Synth. Commun.* **1997**, *27*, 2021; (e) Gómez-Lor, B.; González-Cantalapiedra, E.; de Frutos, Ó.; Cárdenas, D. J.; Santos, A.; Echavarren, A. M. *Chem.—Eur. J.* **2004**, *10*, 2601.
17. Moberg, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 248.
18. (a) For example, see: Destrade, C.; Malthete, J.; Tinh, N. H.; Gasparoux, H. *Phys. Lett. A* **1980**, *78*, 82; (b) Destrade, C.; Gasparoux, H.; Babeau, A.; Tinh, N. H.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 693; (c) Tinh, N. H.; Foucher, P.; Destrade, C.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *111*, 277; (d) Buisine, J. M.; Cayuela, R.; Destrade, C.; Tinh, N. H. *Mol. Cryst. Liq. Cryst.* **1987**, *144*, 137.
19. (a) de Frutos, Ó.; Granier, T.; Gómez-Lor, B.; Jiménez-Berbero, J.; Monge, A.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Chem.—Eur. J.* **2002**, *8*, 2879; (b) de Frutos, Ó.; Gómez-Lor, B.; Granier, T.; Monge, M. A.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 204; (c) Ruiz, M.; Gómez-Lor, B.; Santos, A.; Echavarren, A. M. *Eur. J. Org. Chem.* **2004**, 858.
20. (a) Pei, J.; Wang, J.-L.; Cao, X.-Y.; Zhou, X.-H.; Zhang, W.-B. *J. Am. Chem. Soc.* **2003**, *125*, 9944; (b) Cao, X.-Y.; Zhang, W.-B.; Wang, J.-L.; Zhou, X.-H.; Lu, H.; Pei, J. *J. Am. Chem. Soc.* **2003**, *125*, 12430; (c) Cao, X.-Y.; Liu, X.-H.; Zhou, X.-H.; Zhang, Y.; Jiang, Y.; Cao, Y.; Cui, Y.-X.; Pei, J. *J. Org. Chem.* **2004**, *69*, 6050.
21. (a) See Ref. 14a. (b) Read, M. W.; Escobedo, J. O.; Willis, D. M.; Beck, P. A.; Strongin, R. M. *Org. Lett.* **2000**, *2*, 3201.
22. Pei, J.; Ni, J.; Zhou, X.-H.; Cao, X.-Y.; Lai, Y.-H. *J. Org. Chem.* **2002**, *67*, 4924.
23. (a) Berlman, I. B.; Wirth, H. O.; Steingraber, O. J. *J. Phys. Chem.* **1971**, *76*, 318; (b) Nijegorodova, N. I.; Downeya, W. S.; Danailov, M. B. *Spectrochim. Acta, Part A* **2000**, *56*, 783.
24. Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic/Plenum: New York, NY, 1999.
25. (a) Kagan, J.; Arora, S. K. *J. Org. Chem.* **1983**, *48*, 4317; (b) Han, E. M.; Do, L. M.; Nkiidome, Y.; Fujihira, M. *Chem. Lett.* **1994**, 969.