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Tunable blue-emitting fluorophores—benzo[1,2-*b*:4,3-*b*′]dithiophene and trithia[5]helicene end-capped with electron-rich or electron-deficient aryl substituents

Ying Hu [a], Brigitte Wex [b], Marc W. Perkovic [c], Douglas C. Neckers [a,*]

[a] *Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403, United States*
[b] *Division of Natural Sciences, Lebanese American University, Byblos, Lebanon*
[c] *Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008, United States*

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It is with sorrow that we dedicate this paper to the memory of Professor Perkovic

Abstract

Light-emitting fluorophores **1–10b** based on aryl substituted benzo[1,2-*b*:4,3-*b*′]dithiophenes (**BDT**) and trithia[5]helicenes (**T5H**) have been synthesized using various combinations of Suzuki coupling, the Wittig, or McMurry reaction, and subsequent photocyclization of the dithienylethenes thus obtained. Photophysical properties of the helical compounds end-capped with different electron-rich and electron-deficient aryl moieties thus resulting were evaluated. Photocyclization of a dithienylethene derivative **10a** was investigated, and the X-ray crystal structure of dinaphthyl-substituted **BDT** (**4**) was obtained. With this series of compounds **1–10b**, we demonstrate that the optical properties of all of the new compounds, and by extension many conjugated materials, can be tuned over the entire blue range (400–480 nm).

1. Introduction

Organic semiconducting molecules particularly for applications as organic light-emitting diodes (OLED), organic field-effect transistors (OFET), in nonlinear optics (NLO), and as photovoltaic cells have attracted considerable attention. Nonlinear polycyclic compounds used as NLO materials have been studied both theoretically and experimentally.[1–3] They serve as model compounds for understanding the chemical and physical properties of related materials as well as for the investigation of structure–property correlations among similar electronic materials. Our particular interest was in probing structural features to affect useful functions and properties using materials comprised of aryl substituted heterohelicenes in that these compounds are essential toward the rational design and the optimization of functional organic helical conjugated materials.

The helix is a common structure in nature, and its intrinsic 3-D architecture also offers much interest to synthetic chemists because of the potential interactions between overlapping layers, and the presence of a powerful inherent chirality.[4–6] In biology, important life secrets lie in helical DNA, and many proteins adopt a helical structure. In chemistry, since Newman synthesized and resolved hexahelicene,[7,8] Martin (Brussels)[9] and Wynberg (Groningen)[10] developed numerous helicenes of all types, including carbohelicenes, double helicenes, and heterohelicenes. Replacing benzenes with thiophenes has beneficial effects on the nonlinear optical properties of previously known achiral conjugated helicene structures, due to the unique 2-position of thiophene and the electron-rich sulfur atoms. In principle, these features make functionalization of helicene systems possible, thus opening the way for obtaining modified helicenes targeted for specific uses, and for tuning and monitoring properties.[11]

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* Corresponding author.
E-mail address: neckers@photo.bgsu.edu (D.C. Neckers).

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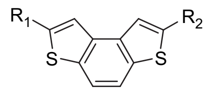
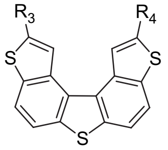


1. R_1 = 4-methoxyphenyl, R_2 = H
2. R_1 = α–naphthyl, R_2 = H
3. R_1 = 4-cyanophenyl, R_2 = H
4. R_1 = R_2 = α–naphthyl
5. R_1 = 4-acetylphenyl, R_2 = H
6. R_1 = 4-methoxyphenyl, R_2 = (*E*)-2-thienylethenyl



7. R_3 = 4-methoxyphenyl, R_4 = H
8. R_3 = 4-methoxyphenyl, R_4 = 4-cyanophenyl
9. R_3 = 4-methoxyphenyl, R_4 = 4-acetylphenyl

Chart 1. Molecular structures of **BDT** and **T5H** derivatives **1**–**9**.

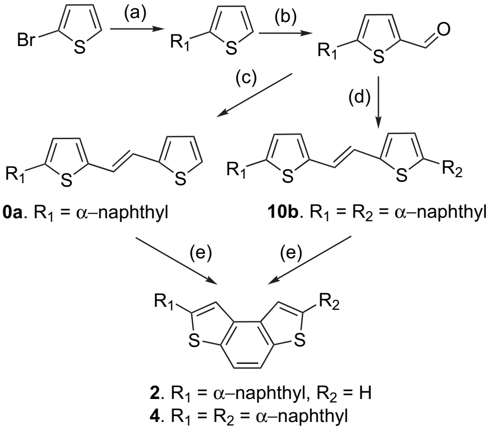
Many alkyl thia[*n*]helicenes, $n<9$, have been reported,[11–15] but aryl thia[*n*]helicenes have never been prepared. We herein report the first synthesis of helicenes end-capped with electron-rich and electron-deficient aryl moieties (Chart 1). Tunable blue-emitting π-conjugated helical compounds based on benzo[1,2-*b*:4,3-*b′*]dithiophene (**BDT**) and trithia[5]helicene (**T5H**) were synthesized, and their structure–function relationships were investigated.[16] Both **BDT** and **T5H** emit in the UV region at 333 nm, 365 and 379 nm, respectively. Therefore, tunable blue-emitting compounds can be obtained by carefully choosing the number of aromatic substituents and end-capped moieties. The parent BDT itself is planar. Aryl substituents increase steric crowding on **BDT** molecule and thereby induce helicity. We attribute the good photo and thermal stability in **1**–**5** and **7**–**9** to their non-planarity and higher percentage of benzene character.[17,18]

2. Results and discussion

2.1. Synthesis

Photocyclization of stilbene-like olefins followed by in situ oxidation using iodine is a crucial step in the synthesis of higher numbered helicenes.[13,19] This reaction requires dilute solutions and is typically carried out in toluene. Application to higher helicenes and heterohelicenes is limited due to their poor solubility, the small scale of the synthesis, and the fact that the products act as filters for incident radiation.[12]

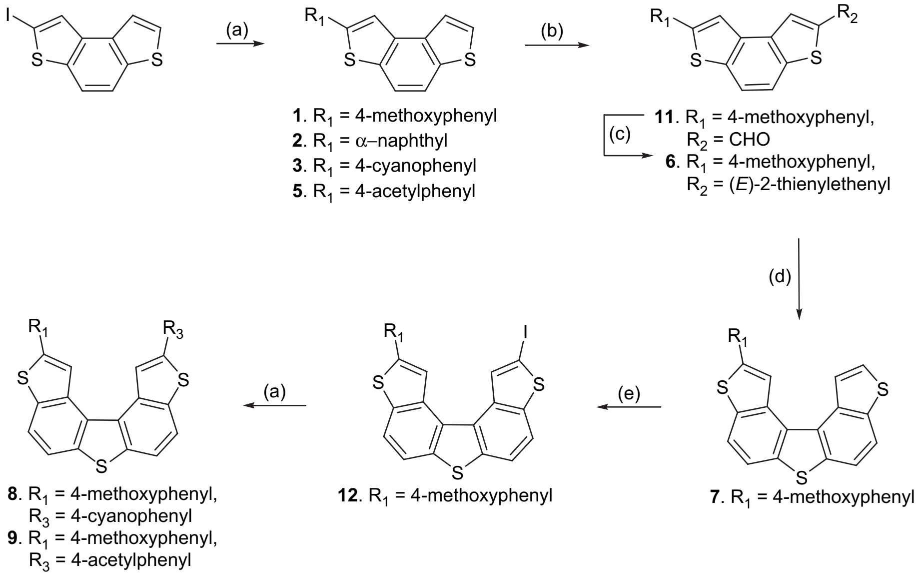
Suzuki coupling is an efficient method for introducing aryl groups. In this method, a palladium catalyst is used to cross-couple an organoboronic acid with an aryl halide. For our target compounds **1**–**9**, there are theoretically two approaches, i.e., Suzuki coupling followed by Wittig/McMurry reaction or Wittig/McMurry reaction followed by Suzuki coupling. Compounds **2** and **4** were synthesized by the former approach in overall yield of 27–47%, Scheme 1. Decomposition products were detected by NMR spectroscopy during photochemical cyclization (step e, Scheme 1). When the latter approach was applied, the synthesis of **2** was achieved in ~80%, Scheme 2. 2-Arylthiophenes are susceptible to rearrangement on irradiation.[20] Photolysis of 2-(α-naphthyl)thiophene in dilute solution, for example, yields 3-(α-naphthyl)thiophene as the only product.[10,21,22] Photolysis of 3-(α-naphthyl)thiophene in dilute solution led to slow decomposition, and no migration of the naphthalene ring was observed.[10,21,22] In contrast, 2- and 3-arylbenzo[*b*]thiophenes show no significant migration of the aryl group or decomposition upon photolysis.[23,24] Our materials, 2-arylbenzo[1,2-*b*:4,3-*b′*]dithiophenes, showed no evidence of group migration as verified by gas chromatography, NMR, and UV absorption spectroscopies, or X-ray crystallography. In this case, conjugation might stabilize carbons 2 and 3 of the thiophene moiety toward rearrangement by rigidifying the structure and delocalizing the electrons.



Scheme 1. Reagents and conditions: (a) $R_1B(OH)_2$, toluene, $(C_4H_9)_4NOH$, $Pd(PPh_3)_4$, reflux, overnight. (b) *n*-BuLi, DMF, −78 °C, 40 min. (c) Diethyl(2-thienylmethyl)phosphonate, NaH, DME, 0 °C for 30 min, reflux 3 h. (d) $TiCl_4$, Zn, THF, −18 °C for 1 h, reflux 4 h. (e) I_2, propylene oxide, *hν*, 1 day.

Photocyclization of **10a**, the precursor of **2**, was carried out in C_6D_6 in an NMR tube. The solution was irradiated under 350 nm light and proton NMR spectra were recorded every 10 min. Selected spectra are shown in Figure 1. During irradiation, **10a**, i.e., (*E*)-1-{2-[5-(1-naphthyl)thienyl]}-2-(2-thienyl)-ethene, was photochemically isomerized to the *Z*-isomer, i.e., (*Z*)-1-{2-[5-(1-naphthyl)thienyl]}-2-(2-thienyl)ethene. This *Z*-isomer then underwent photocyclization and oxidation to form the desired product **2**.

At t=0 min, only the starting **10a** existed. The protons of the ethene group appeared around 7.11 ppm as a singlet. The formation of the *Z*-isomer was confirmed by appearance and disappearance of peaks in the 6.35–6.45 ppm region of the spectra. At t=570 min, the signal of the proton at the 2-position of thiophene changed to a doublet at 7.08 ppm. Peaks above 9.50 ppm were assigned to aldehydic oxidation products of the double bond. Chart 2 shows a plot of the change in the percentage of starting material (**10a**), intermediates, product (**2**), and by-products. At the beginning of the reaction, **10a** photoisomerized to the *Z*-isomer and immediately formed a 1:1 photostationery state of both isomers. This 1:1 ratio of



Scheme 2. (a) DME, K_2CO_3 (2 M), $Pd(PPh_3)_4$, $R_3B(OH)_2$, reflux, overnight. (b) *n*-BuLi, DMF, −78 °C, 40 min. (c) Diethyl(2-thienylmethyl)phosphonate, NaH, DME, 0 °C for 30 min, reflux 3 h. (d) I_2, propylene oxide, *hv*, 1 day. (e) *n*-BuLi, I_2, DME, −78 °C, 1 h.

isomers was observed until the end of the photocyclization reaction.

In order to avoid solubility problems, **7–9** were synthesized by a combination of both approaches (Scheme 2). Our attempts to purify **12** have continually failed due to similarities in polarity of **7** and **12**. The Suzuki cross-coupling of crude **12** with the corresponding boronic acid afforded **8** and **9**, respectively. For both products, **8** and **9**, bright yellow solids were recrystallized from dichloromethane. The yields for **8** and **9** over these two steps starting from **7** were 69–73%. Noteworthy, the synthesis of **8** starting from **3**, did not yield the desired product. The synthesis was attempted in an approach similar to that outlined in Scheme 2. In this case, however, the formylation of **3** did not furnish the desired aldehyde (**11′** with R_1= 4-cyanophenyl, R_2=CHO). This finding is attributed to the deactivation of the formylation site (i.e., R_2, Scheme 2) of **BDT** by the electron-deficient cyanophenyl group. As anticipated, the electron-releasing nature of the methoxyphenyl group stabilized the reaction intermediates and afforded **11**, and hence **7**, **12**, and **8** in satisfactory yields.

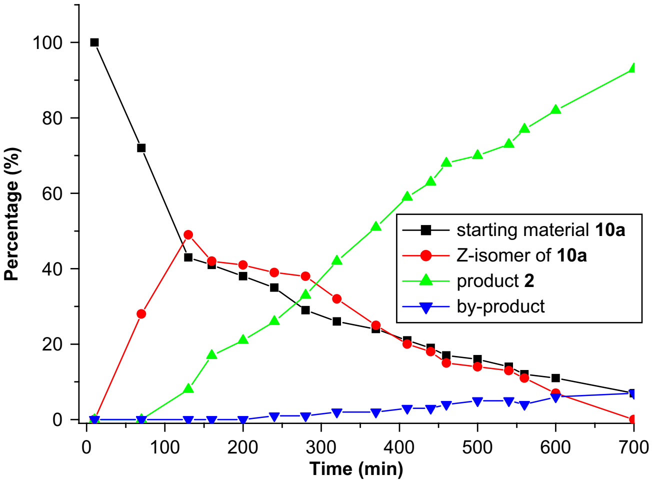


Chart 2. Photocyclization data profile of **10a**.

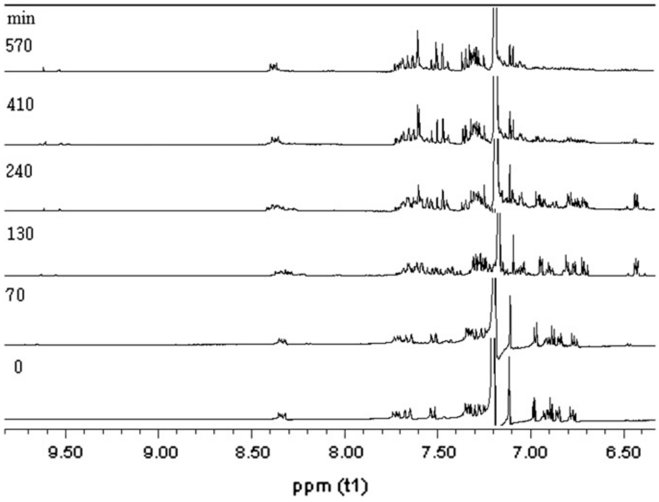


Figure 1. ^1H NMR profile of photocyclization of **10a**.

2.2. Crystal structure

Slow recrystallization of **4** from benzene resulted in wedge-like crystals. Figures 2 and 3 show the molecular structure of **4**[25] and the packing obtained by single-crystal X-ray diffraction. Although both naphthalene and **BDT** are planar, the steric bulk of the naphthyl arms causes a twisting in **4**. It has a C_2 molecular symmetry with the twofold axis bisecting the central ring of the molecules.

The angle between the two naphthalene rings is 114°. Molecules in the crystal are well oriented and exist as a racemic mixture. Pi-stacking is observed between neighboring naphthalene rings and between neighboring **BDT** rings. The 57°

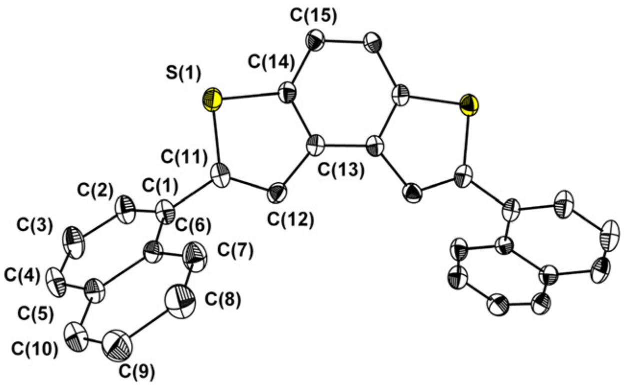


Figure 2. X-ray crystal structure of **4**.

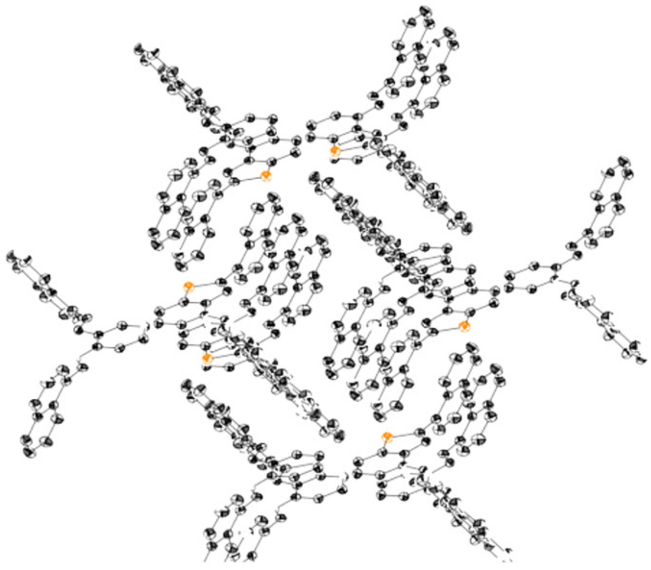


Figure 3. Packing pattern of **4**.

angle may be the reason for the absence of interaction between naphthalene and **BDT**. Figure 4 depicts crystals of **4** under UV light.

2.3. Absorption and emission spectra

Table 1 summarizes absorption and emission properties of compounds **1**–**10b** recorded at room temperature. Normally, π-conjugated systems exhibit strong π–π* electronic absorption in the UV–vis region. Compounds **1**–**10b** fluoresce under UV light, and are mostly blue emitters. For comparison, the absorption and emission spectra of parent **BDT** and **T5H** are shown in Figure 5.

Compounds **1**–**6** showed similar absorption spectra because they have the same heterocyclic backbone. Compounds **7**–**9** also show similar absorption spectra. Compounds with one or two naphthyl substituents, **2** and **4**, exhibited absorption maxima at 307 and 333 nm, respectively. Phenyl-substituted compounds **1**, **3**, and **5** absorb at 333, 346, and 350 nm, respectively. These observations suggest that a chain extension at the 2- and 7-position of **BDT** does not improve the π-orbital conjugation further in the ground state as these structures are non-planar. The electron-rich methoxyphenyl group helps to lower the ground state energy slightly more than the electron-deficient cyano- and acetylphenyl groups do.

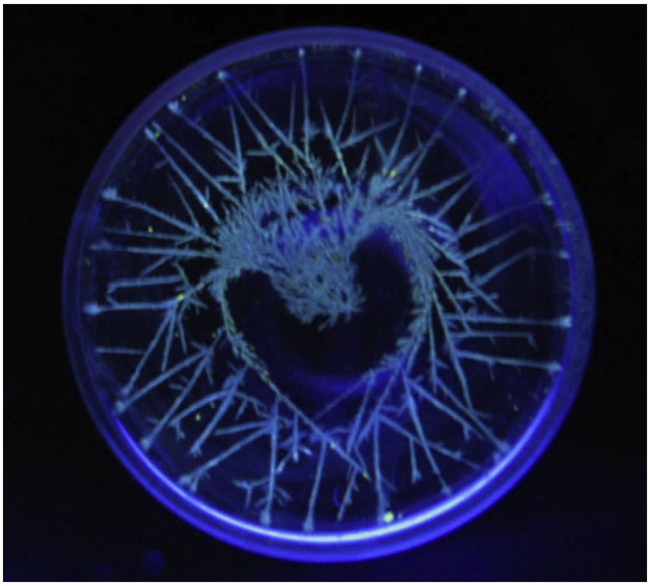


Figure 4. Crystals of **4** under UV irradiation.

A fine emission-color tuning of **1**–**10b** in the region of 380–480 nm is observed in the fluorescence spectra as shown in Figure 6. Comparing the emission maxima of **1** (379 nm), **3** (413 nm), and **5** (430 nm) with those of parent **BDT** (333 nm) shows that aryl substituents introduce a red-shift of emission. The electron-rich aryl group, methoxyphenyl, introduces a red-shift of 46 nm, while the electron-deficient aryl groups, cyanophenyl and acetylphenyl, introduce red-shifts of more than 80 nm in dichloromethane. Likewise, the emission maxima of **7** (409 nm), **8** (469 nm), and **9** (477 nm) show the same trend when compared with **T5H** (363 nm). The fluorescence quantum yields of **1** and **7** are 0.55 and 0.12, respectively. In comparison, the fluorescence quantum yield of **BDT** is 0.08 and that of **T5H** is 0.02.[13] This implies that the

Table 1
Photophysical properties of **1**–**10** in CH_2Cl_2

Compound	λ_{max}[a] (nm)	ε[b] ($\times 10^4\ M^{-1}\ cm^{-1}$)	$\lambda_{F,max}$[c] (nm)	Φ_F[d]
1	333	3.0	379	0.55
2	307	2.4	405	0.17
3	346	3.2	413	0.22
4	333	2.7	423	0.25
5	350	3.2	430	0.12
6	376	4.8	445	0.28
7	295, 357	3.5, 4.1	409	0.12
8	323, 383	4.9, 4.3	469	0.09
9	324, 380	5.4, 4.9	477	0.07
10a	370	3.8	453	0.25
10b	388	4.2	475	0.19

[a] λ_{max}=absorption maximum.
[b] ε=molar decadic absorption coefficient.
[c] $\lambda_{F,max}$=fluorescence maximum.
[d] Φ_F=fluorescence quantum yield.

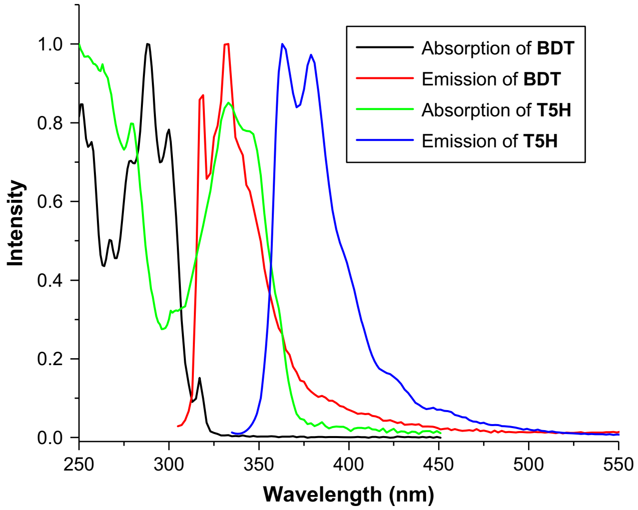


Figure 5. Normalized absorption and emission spectra of **BDT** and **T5H** in CH_2Cl_2.

electron-rich aryl moiety affects a smaller red-shift in fluorescence while dramatically increasing the fluorescence quantum yields. Fluorescence quantum yields of compounds **1** (0.64), **3** (0.56), and **7** (0.07) were also measured in the solid-state. The solid-state fluorescence spectra are provided in Supplementary data.

Interestingly, the emission pattern and quantum yields of fluorescence of **1** and **7** show no significant solvatochromism. However, compounds with electron-deficient cyanophenyl substituents (**3** and **8**) exhibit a large solvatochromic effect, Figure 7 and Table 2. This observation hints of a polar fluorophore.[26] In the polar solvents, dichloromethane and acetonitrile, a shift in fluorescence to a longer wavelength and a loss of the structured fluorescence were observed, Figure 7. Polar solvents stabilize a more polarized excited state, such as an internal charge-transfer (ICT) state, more effectively, which may explain the observed pattern difference and red-shift of the emission maximum. This suggests that the excited states of compounds with the electron-deficient cyanophenyl moieties (**3** and **8**) might be more polar than their ground states.

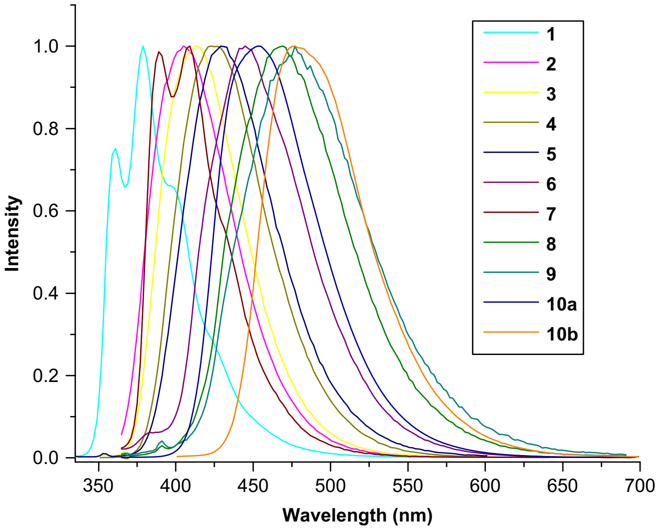


Figure 6. Normalized fluorescence spectra of compounds **1**–**10b** in CH_2Cl_2 solution at room temperature.

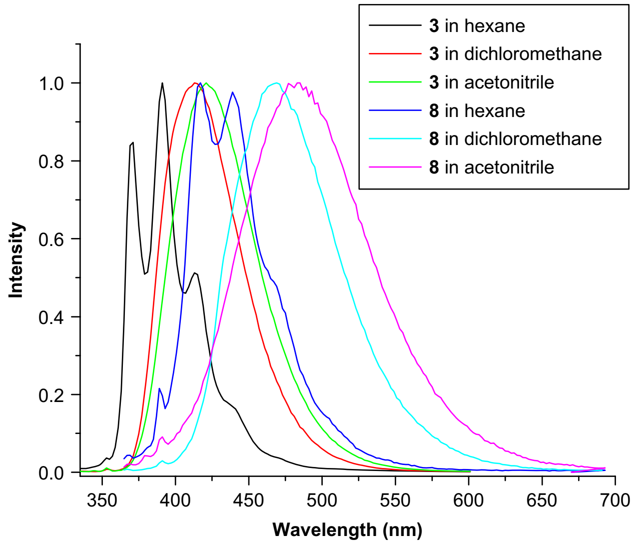


Figure 7. Normalized fluorescence spectra of compounds **3** and **8** in different solvents.

Table 2
Fluorescence quantum yields of **1**, **3**, **7**, and **8** in different solvents

Compound	Φ_F		
	Hexane	Dichloromethane	Acetonitrile
1	0.55	0.55	0.55
3	0.16	0.22	0.41
7	0.12	0.12	0.12
8	0.10	0.09	0.05

3. Conclusions

Two series of blue-emitting aryl substituted helical compounds were successfully synthesized. Compound **2** was prepared by two approaches. The photocyclization of **10a** was carried out in an NMR tube and followed by ^{1}H NMR spectroscopy. Compound **10a** immediately formed an equilibrium 1:1 photostationery state with the *Z*-isomer. Single-crystal X-ray crystallographic analysis carried out on **4** shows that the molecules exist as a racemic mixture in the crystal. From the packing pattern, interaction between aryl substituents was observed and their contribution to the self-assembly was confirmed. The photophysical properties of all the new compounds were studied. By carefully choosing different electron-deficient and electron-rich aryl substituents, the emission of **BDT** and **T5H** parent compounds can be well tuned in the blue region of about 400–480 nm. Solvent polarity has a stronger effect on the fluorescence of compounds with electron-deficient groups than on the fluorescence of those with electron-rich groups. The substantial changes in fluorescence spectra and quantum yields of **3** and **8** imply that their excited states might form ICT or even charge-separated diradical states. A detailed photophysical study is currently underway.

4. Experimental section

4.1. General

Solvents were dried and freshly distilled following usual protocols prior to use. Reagents were used as received from commercial suppliers. Standard grade silica gel (60 Å, 32–63 μm) and silica gel plates (200 μm) were purchased from Sorbent Technologies. Reactions that required anhydrous conditions were carried out under argon in oven-dried glassware.

Mass spectra were recorded on a Shimadzu GCMS-QP5050A instrument equipped with a direct probe (ionization 70 eV). Melting points are uncorrected. A Bruker spectrometer (working frequency 300.0 MHz for ^{1}H and 75.0 MHz for ^{13}C) was used to record the NMR spectra with $CDCl_3$ and C_6D_6 as solvents. Chemical shifts relative to TMS at 0.00 ppm are reported in parts per million (ppm) on the δ-scale for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to $CDCl_3$ at 77.00 ppm and C_6D_6 at 128.00 ppm. Absorption and fluorescence spectra were recorded on a Shimadzu UV-2401 spectrophotometer and a Fluorolog-3 spectrometer, respectively. All measurements were carried out at room temperature.

2-(α-Naphthyl)thiophene, 5-(α-naphthyl)thiophene-2-carbaldehyde, benzo[1,2-*b*;4,3-*b*′]dithiophene, and 2-iodobenzo-[1,2-*b*;4,3-*b*′]dithiophene were synthesized following the literature procedures.[27–30]

4.2. General procedure for Wittig reaction

To a stirred, ice-cooled solution of diethyl(2-thienylmethyl)phosphonate (2.3 g, 10 mmol) in dimethoxyethane (DME) (40 mL) was added sodium hydride (60% dispersion, 0.52 g, 12 mmol). The mixture was stirred for 30 min in an ice bath and then a solution of 5-(α-naphthyl)thiophene-2-carbaldehyde (2.4 g, 10 mmol) in DME (10 mL) was added dropwise over a period of 30 min. The mixture was slowly warmed and refluxed for 3 h. After quenching the reaction by the addition of ice water (50 mL), the mixture was extracted with ether. The extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The residue was recrystallized from cyclohexane or purified by silica gel column chromatography.

4.2.1. (E)-1-{2-[5-(1-Naphthyl)thienyl]}-2-(2-thienyl)ethene (**10a**)

Recrystallization from cyclohexane gave pure yellow solid, yield: 42%, mp 95–96 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.0 (m, 1H), 7.06 (d, 1H), 7.09 (s, 2H), 7.11 (d, 1H), 7.14 (d, 1H), 7.20 (d, 1H), 7.47–7.54 (m, 3H), 7.59 (d, 1H), 7.85–7.91 (m, 2H), 8.28–8.31 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.4, 121.5, 124.4, 125.3, 125.7, 126.0, 126.1, 126.5, 126.6, 127.7, 128.0, 128.1, 128.4, 128.5, 131.7, 132.4, 133.9, 140.8, 142.5, 142.7; HRMS (EI): *m/z* $[M]^+$ calcd for $C_{20}H_{14}S_2$, 318.0537; found, 318.0536.

4.2.2. 2-(4-Methoxyphenyl)-7-[(E)-2-(2-thienyl)ethenyl]-benzo[1,2-b;4,3-b′]dithiophene (**6**)

Silica gel column chromatography with hexane/dichloromethane 1:1 as eluent produced pure **6**, yield: 71%, mp 220–222 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 6.97 (m, 1H), 7.00 (m, 1H), 7.03 (m, 1H), 7.12 (m, 1H), 7.18 (d, 2H), 7.23 (m, 1H), 7.60 (s, 1H), 7.65 (m, 1H), 7.68–7.74 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4, 114.5, 116.3, 118.1, 118.9, 121.1, 121.9, 123.7, 124.9, 126.7, 127.1, 127.7, 127.8, 134.9, 135.5, 135.7, 135.9, 142.1, 142.7, 144.9, 159.9; HRMS (EI): *m/z* $[M^+]$ calcd for $C_{23}H_{16}OS_3$, 404.0363; found, 404.0368.

4.2.3. (E)-1,2-Bis[5-(1-naphthyl)thiophen-2-yl]ethene (**10b**)

To a stirred solution of 5-(α-naphthyl)thiophene-2-carbaldehyde (2.8 g, 10 mmol) in THF (100 mL) was added titanium(IV) chloride (3 mL, 3 mmol) over a period of 30 min at −18 °C (dry ice with ethanol/water=1:4). After stirring at this temperature for 30 min, zinc powder (4 g, 60 mmol) was added in small portions over a period of an additional 30 min. The mixture was stirred at −18 °C for 30 min, warmed to room temperature, and refluxed for 4 h. The reaction was quenched by the addition of ice water (50 mL), and the resulting solid was collected by filtration and dried. The solid was dissolved in dichloromethane (70 mL) and the insoluble inorganic material was removed by filtration. The filtrate was evaporated and the residue was recrystallized from cyclohexane to give orange solid **10b**,[31] yield: 60%, mp 156–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13–7.16 (m, 6H), 7.48–7.55 (m, 6H), 7.60 (d, 2H), 7.85–7.92 (m, 4H), 8.28–8.31 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.4, 125.3, 125.7, 126.1, 126.5, 126.6, 127.9, 128.1, 128.4, 128.5, 131.7, 132.3, 133.9, 140.8, 142.8; HRMS (EI): *m/z* $[M^+]$ calcd for $C_{30}H_{20}S_2$, 444.1006; found, 444.1006.

4.3. General procedure for photocyclization

Compounds **10a**, **10b**, or **6** (0.5 mmol) were dissolved in toluene (300 mL) and exposed to 300 nm light from a UV lamp in a Rayonet reactor for 1 day. I_2 (0.25 g, 0.1 mmol) and propylene oxide (3 mL) were added to the solution and air was bubbled through. The solvent was evaporated and the residue recrystallized from hexane or purified by silica gel column chromatography.

4.3.1. 2-(α-Naphthyl)benzo[1,2-b;4,3-b′]dithiophene (**2**)

Yellow solid, yield: 64%, mp 91–93 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.57 (m, 4H), 7.67–7.71 (m, 2H), 7.82–7.83 (m, 3H), 7.89–7.93 (m, 2H), 8.31–8.34 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 118.3, 118.7, 121.9, 122.2, 125.2, 125.8, 126.2, 126.6, 126.7, 128.4, 128.6, 128.9, 131.9, 132.4, 133.9, 134.6, 135.1, 136.7, 136.9, 142.5; HRMS (EI): *m/z* $[M^+]$ calcd for $C_{20}H_{12}S_2$, 316.0381; found, 316.0382.

4.3.2. 2,7-Di-(α-naphthyl)benzo[1,2-b;4,3-b′]dithiophene (**4**)

Yellow solid, yield: 78%, mp 148–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.57 (m, 6H), 7.71 (d, 2H), 7.86

(s, 2H), 7.88 (s, 2H), 7.90–7.95 (m, 4H), 8.34–8.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 118.4, 122.2, 1253, 125.8, 126.2, 126.7, 128.4, 128.6, 129.0, 131.9, 132.5, 133.9, 135.1, 137.2, 142.7; HRMS (EI): *m/z* $[M]^+$ calcd for $C_{30}H_{18}S_2$, 442.0850; found, 442.0843.

*4.3.3. 2-(4-Methoxyphenyl)trithia[5]helicene (**7**)*

Silica gel column chromatography with hexane/dichloromethane (1:2), yield: 80%, mp 152–153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 7.02 (d, 2H), 7.73–7.76 (m, 3H), 7.81 (d, 1H), 7.87 (d, 1H), 7.93 (d, 1H), 8.02 (d, 1H), 8.41–8.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4, 114.6, 118.6, 119.0, 119.2, 120.7, 121.0, 124.4, 126.2, 127.1, 127.8, 130.4, 134.7, 135.8, 136.9, 137.0, 137.4, 138.1, 144.3; HRMS (EI): *m/z* $[M]^+$ calcd for $C_{23}H_{14}OS_3$, 402.0207; found, 402.0208.

*4.3.4. 2-Iodo-11-(4-methoxyphenyl)trithia[5]helicene (**12**)*

A 2.5 M solution of *n*-BuLi in hexane (0.44 mL, 1.1 mmol) was added dropwise under stirring to a solution of 2-(4-methoxyphenyl)trithia[5]helicene **7** (0.4 g, 1 mmol) in 20 mL of dry THF at −78 °C. The solution was stirred for 10 min at −78 °C and for 15 min at room temperature. The resulting light yellow solution was cooled at −78 °C, and a solution of I_2 (0.27 g, 1.05 mmol) in 5 mL of dry THF was added dropwise. After 2 h, the reaction was quenched with aqueous Na_2SO_3 (5%, 20 mL) and warmed to room temperature. The THF was removed under reduced pressure. The yellow material that precipitated was filtered and washed with water. The crude compound was dried under vacuum and used without further purification.

4.4. General procedure for Suzuki reaction

Under argon, a mixture of 2-iodobenzo[1,2-*b*;4,3-*b*′]dithiophene (1 mmol, 316 mg), aryl boronic acid (1.05 mmol), and $Pd(PPh_3)_4$ (0.03 mmol, 3.0%) in a mixed solvent of DME (3 mL) and aqueous K_2CO_3 (2 M, 1 mL) was refluxed for overnight. Then, water (5 mL) was added. After separation, the organic phase was washed twice with water (2×5 mL) and the collected aqueous phases were extracted twice with 5 mL dichloromethane. The organic phases were collected, dried over Na_2SO_4, and the solvent was removed under reduced pressure to give a residue that was subjected to silica gel chromatography to obtain the pure products.

*4.4.1. 2-(4-Methoxyphenyl)benzo[1,2-b;4,3-b′]dithiophene (**1**)*

Elution with hexane/dichloromethane (1:1) gave yellow solid, yield: 77%, mp 168–169 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.87 (s, 3H), 6.97 (m, 1H), 7.00 (m, 1H), 7.65 (d, 1H), 7.72–7.70 (m, 3H), 7.76 (d, 2H), 7.80 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4, 114.4, 116.4, 118.4, 118.5, 121.9, 126.4, 127.2, 127.8, 134.4, 135.7, 135.8, 136.7, 144.7, 159.8; HRMS (EI): *m/z* $[M]^+$ calcd for $C_{17}H_{12}OS_2$, 296.0330; found, 296.0338.

*4.4.2. 2-(α-Naphthyl)benzo[1,2-b;4,3-b′]dithiophene (**2**)*

Elution with hexane/dichloromethane (10:1) gave a yellow solid in 89%.

*4.4.3. 2-(4-Cyanophenyl)benzo[1,2-b;4,3-b′]dithiophene (**3**)*

Elution with hexane/dichloromethane (1:1) gave yellow solid, yield: 83%, mp 181–183 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, 1H), 7.71–7.75 (m, 3H), 7.78 (d, 1H), 7.85 (m, 2H), 7.88 (m, 1H), 8.03 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.7, 111.4, 118.4, 119.8, 120.0, 121.7, 126.7, 127.2, 132.8, 134.8, 136.9, 138.7, 141.9; HRMS (EI): *m/z* $[M]^+$ calcd for $C_{17}H_9NS_2$, 291.0176; found, 291.0175.

*4.4.4. 2-(4-Acetylphenyl)benzo[1,2-b;4,3-b′]dithiophene (**5**)*

Elution with hexane/dichloromethane (1:1) gave yellow solid, yield: 78%, mp 175–176 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.65 (s, 3H), 7.61 (d, 1H), 7.75 (d, 1H), 7.78 (d, 1H), 7.83 (s, 1H), 7.85 (m, 1H), 7.88 (m, 1H), 8.02 (m, 1H), 8.04–8.05 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.3, 143.0, 138.8, 137.0, 136.8, 136.4, 135.5, 134.8, 129.2, 127.0, 126.3, 121.8, 119.6, 119.2, 118.5, 26.6; HRMS (EI): *m/z* $[M]^+$ calcd for $C_{18}H_{12}OS_2$, 308.0330; found, 308.0332.

*4.4.5. 2-(4-Cyanophenyl)-10-(4-methoxyphenyl)trithia[5]-helicene (**8**)*

Bright yellow solid was precipitated from dichloromethane. The yield starting from **7** was 73%; mp 295–296 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 3H), 6.98 (d, 2H), 7.70–7.75 (m, 4H), 7.83 (d, 1H), 7.88–7.97 (m, 5H), 8.46 (s, 1H), 8.79 (s, 1H); HRMS (EI): *m/z* $[M]^+$ calcd for $C_{30}H_{17}ONS_3$, 503.0472; found, 503.0467.

*4.4.6. 2-(4-Acetylphenyl)-10-(4-methoxyphenyl)trithia[5]-helicene (**9**)*

Bright yellow solid was precipitated from dichloromethane. The yield starting from **7** was 69%; mp 289–291 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.66 (s, 3H), 3.89 (s, 3H), 6.98 (d, 2H), 7.76 (d, 2H), 7.83 (d, 1H), 7.88 (d, 1H), 7.93–7.98 (m, 4H), 8.02–8.05 (d, 2H), 8.51 (s, 1H), 8.80 (s, 1H); HRMS (EI): *m/z* $[M]^+$ calcd for $C_{31}H_{20}O_2S_3$, 520.0625; found, 520.0629.

*4.4.7. 7-(4-Methoxyphenyl)benzo[1,2-b;4,3-b′]dithiophene-2-carbaldehyde (**11**)*

A 2.5 M solution of *n*-BuLi in hexane (0.44 mL, 1.1 mmol, 1.1 equiv) was added dropwise under stirring to a solution of 2-(4-methoxyphenyl)benzo[1,2-*b*;4,3-*b*′]dithiophene **1** (296 mg, 1 mmol), in dry THF (25 mL) at −78 °C. The solution was stirred for 5 min at −78 °C and 15 min at room temperature. The resulting blue solution was cooled at −78 °C and treated with dry DMF (0.1 mL, 1.3 mmol). After 2 h at −78 °C, the solution was warmed to room temperature, and quenched with a saturated aqueous solution of NH_4Cl (5 mL). The THF was removed under reduced pressure, the crude material was taken up with dichloromethane (40 mL), and washed with a saturated aqueous solution of NH_4Cl until pH 5 (2×10 mL). The organic phases were dried over Na_2SO_4, the solvent was removed under reduced pressure, and the crude material was purified by flash column chromatography on silica gel with hexane/dichloromethane (1:1) as eluent to provide yellow solid, 96% yield, mp 198–200 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 6.99 (m, 1H), 7.01 (m, 1H), 7.70 (m, 1H), 7.73 (m, 1H), 7.77 (d, 1H), 7.85 (s, 1H), 7.91 (d, 1H), 8.39 (s, 1H), 10.17 (s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 55.5, 114.6, 116.1, 118.6, 122.7, 126.6, 127.9, 131.8, 133.5, 136.3, 137.3, 140.8, 143.0, 146.8, 184.2; HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{12}O_2S_2$, 324.0279; found, 324.0282.

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Supplementary data

Thin film fluorescence of **1**, **3**, and **7**, NMR, and IR spectra of compounds **1–10b** were provided. This material is available free of charge via the Internet. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2007.12.029.

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