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Facile Synthesis of Alternating Benzene–Pyrrole Oligomers by Cyclization of Propargylic Dithioacetals and Imines and Their Fluorescent Properties

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Alternating benzene–heteroaryl oligomers possess fascinating optoelectronic properties and a wide range of applications. This article presents the facile synthesis of benzene–pyrrole oligomers with diverse functional groups and the elongated alternating heterocycle–benzene–pyrrole oligoaryls. The syntheses are based on a one-pot, three-step reaction of propargylic dithioacetals and imines. The subtle influence of functional groups, such as ether, ester, hydroxy, and dithiacetal groups on the peripheral benzene rings, on the reaction, has been explored and the reaction conditions were finely changed accordingly to achieve reasonable yields. The elongation could be accomplished by using a similar procedure. The fluorescent properties of original and elongated alternating benzene–pyrrole oligomers were determined. Theoretical calculations preliminarily reveal that the fluorescent intensity is closely related to the molecular geometry and to the HOMO/LUMO energy difference in the ground state.

Introduction

Oligoaryls possess fascinating optoelectronic properties that have been explored in the applications of photovoltaic cells, light-emitting diodes (LEDs), field-effect transistors (FETs), electrochromic devices, chemical sensors, and microelectronic actuators, among others.[1] The optoelectronic properties of the oligoaryls can be enhanced and tuned to satisfy the requirements of various applications by incorporating five-membered heteroaromatic moieties.[2] However, although typical representative thiophene-containing oligoaryls have been extensively investigated,[3] the furan[4] or pyrrole[5] analogues have been only sporadically explored, mainly due to the limited synthetic methodologies available and because of the incompatibility of the desired functionalities of key intermediates in the synthesis.

There are various traditional approaches available for the synthesis of conjugated oligoaryls incorporating five-membered heteroaromatic rings. Cyclization of heteroatom compounds with pre-formed 1,4-diketones[6] and cross-coupling reactions catalyzed by transition metals[7] are two principal methodologies used in the construction of oligoaryl backbones. In recent years, Luh reported an exquisite one-pot method for the synthesis of oligoaryls containing 2,3,5-trisubstituted furans by treating propargylic dithioacetals with arenecarbaldehydes.[8] This strategy provides a versatile route for the synthesis of alternating teraryls with furan rings.[9] Additional functions, such as alkyl chains, can be introduced at the C-3 position of the furan ring to enhance the solubility and hence simplify the procedures used to obtain the oligomers. The synthesis is usually mild, and various functionalities, such as carbon–carbon double and triple bounds, and even ester groups, can be tolerated. Thus, elongation of the conjugation lengths of the oligoaryls can be achieved by means of the Suzuki[7b] or Stille[7c] coupling reactions, or by a convergent synthesis.[9b]

The pyrrol moiety, as an equivalent of furan and thiophene, can also be incorporated into oligoaryls through the traditional Paal–Knorr cyclization of amines with 1,4-diketones, which can be pre-formed through a necessary multistep preparation.[10] Luh's one-pot annulation protocol is applicable and allows access of benzene–pyrrole oligomers with a limited substituent scope by using imines instead of arenecarbaldehydes.[9] Our initial study suggested that this strategy could not be easily adopted in the synthesis of benzene–pyrrole oligoaryls with diverse functionalities or in the subsequent convergent synthesis of elongated analogues. In this article, we report a facile, one-pot synthesis of these oligoaryls through the annulation of propargylic dithioacetals with imines by modifying the reaction conditions. Moreover, the functional groups on the peripheral benzene rings could be utilized further for the construction of elongated oligoaryls with two or more five-membered heteroaromatic ring units in a convergent synthetic protocol.

Results and Discussion

The cyclization of propargylic dithioacetals and imines to give alternating benzene–furan or benzene–pyrrole oli-

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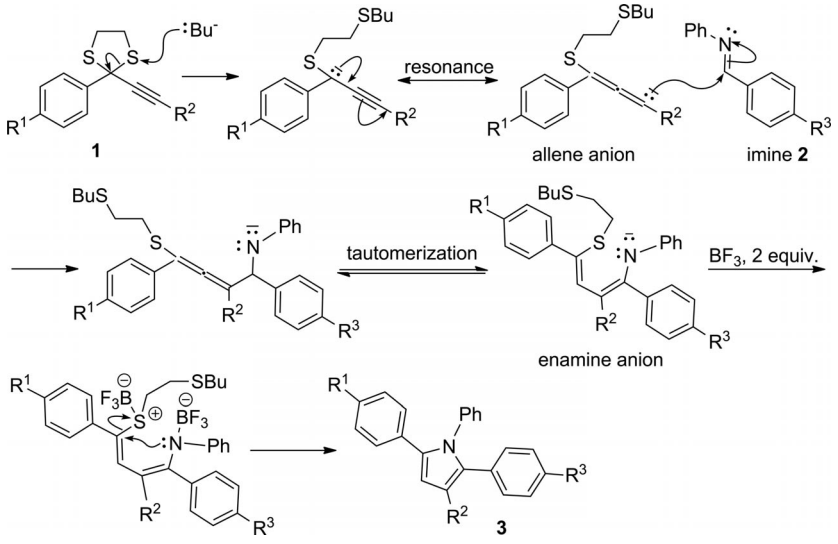
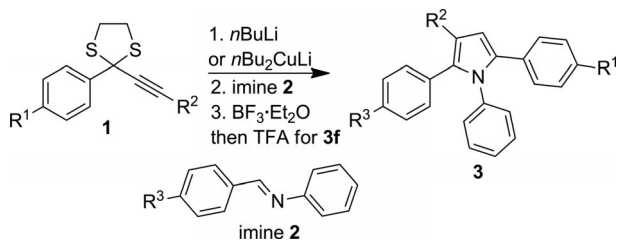


Scheme 1. Mechanistic illustration of the one-pot, three-step synthesis of alternating benzene–pyrrole oligoaryls.

goaryls by applying Luh's protocol was proposed to be accomplished through a one-pot, three-step reaction mechanism.[9a] Propargylic dithioacetal **1** reacts with butyllithium to form a lithiated allene intermediate that reacts with phenylenimine **2** and subsequently undergoes acid-catalyzed ring-closure to afforded the desired product **3** (Scheme 1). Two key processes that can reasonably be assumed to be involved in the mechanism are the resonance of the propargylic anion to the allene anion in the first step, and the tautomerization of the allene anion to the conjugated enamine anion in the second step. The Lewis acid catalyzed ring closure in the last step is believed to be carried out through the association of BF_3 with the alkyl sulfide, which increases its leaving ability and facilitates the ring closure.

Application of Luh's protocol worked smoothly for the cyclization for furan oligomers and for several cases of pyrrole oligomers without functionalities.[9] With respect to the synthesis of pyrrole oligomers capable of convergent elongation and further functionalization, necessary functionalities such as ethers, esters, hydroxy, and even dithiacetal groups need to be present in the corresponding benzene rings prior the cyclization reaction. Thus, we initialized the one-pot, three-step synthesis of pyrrole oligomers bearing the desired functionalities according to Luh's protocol as shown in Scheme 2.

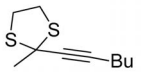


Scheme 2. Cyclization of propargylic dithioacetals and imines in a one-pot, three-step procedure.

Unfortunately, no cyclization product was formed in any of the cases when the reaction was performed at room temperature under the catalysis of $BF_3{\cdot}Et_2O$ in the third step of the reported procedure. Prolonging the reaction time did not benefit the cyclization. This failure may be attributed to the different contribution of electronic effects from the *N*-butyl group in Luh's case[9a] and the *N*-phenyl group in our case to the nucleophilicity of the enamine nitrogen atom. Clearly, the *N*-phenyl group decreases the nucleophilicity of the enamine nitrogen atom to a certain extent because of the increased delocalization compared to the *N*-butyl group, which reduces its ability to attack the olefinic carbon atom bearing the alkylsulfur group. However, the reaction was found to proceed (indicated by ^1H NMR analysis of the crude mixture) when heated at reflux for 6 h and then stirred at room temperature overnight for the last step. Indeed, these reaction conditions worked very well to produce **3a**, **3b** and **3g** with appreciable yields, as shown in Table 1; however, initially, the other expected products could not be obtained in reasonable yields.

Attempts were then made to increase the yields in the other cases. It was found that the reaction of propargylic dithioacetal **1b** with *n*-butyllithium in the presence of hexamethylphosphoramide (HMPA) was readily accomplished, and the yield of **3c** increased from 14% to 53% (Table 1). The promotion by HMPA is presumably attributed to its ability to stabilize the lithium counter ion,[11] because the presence of an electron-withdrawing methoxycarbonyl group at the *para* position of the phenyl dithioacetal renders the lithium counter ion unstable in the medium. Thus, lithium stabilization with HMPA was needed in the first step, leading the smooth addition of the allene anion to the imine in the second step. However, the addition of HMPA did not affect the reaction in the remaining cases. In the cases of **3d** and **3e**, because of the presence of the methoxymethyl group at the *para* position, the dithioacetal becomes more reactive to the nucleophile; it was therefore thought that the

Table 1. Summary of the product yields and their fluorescent properties.

Ditholane R^1	Ditholane R^2	Imine R^3	Reagents	Product	Yield [%]	λ_{max}[a] [nm]	λ_{em}[a] [nm]	Φ_f[b] [%]	log ε
H	Ph	$COOCH_3$	nBuLi/BF_3·OEt_2	**3a**	43	343	444	64	4.11
H	Ph	CH_3	nBuLi/BF_3·OEt_2	**3b**	65	300	393	3	4.27
$COOCH_3$	nBu	H	nBuLi/HMPA/BF_3·OEt_2	**3c**	53	345	428	88	4.33
CH_2OCH_3	nBu	H	$n$$Bu_2$CuLi/$BF_3$·$OEt_2$	**3d**	63	307	378	2	4.26
CH_2OCH_3	nBu	CH_3	$n$$Bu_2$CuLi/$BF_3$·$OEt_2$	**3e**	64	307	385	2	4.32
CH_2OH	nBu	H	nBuLi/BF_3·OEt_2/TFA	**3f**	48	309	384	2	4.32
H	Ph		$n$$Bu_2$CuLi/$BF_3$·$OEt_2$	**3g**	43	310	–	–	4.30
3g		H	nBuLi/BF_3·OEt_2	**5**	52	330	423	7	4.42
4		H	nBuLi/BF_3·OEt_2	**6**	49	360	435	39	4.47
H	Ph	**7**	nBuLi/BF_3·OEt_2	**8**	44	361	443	50	4.65

[a] Measured in EtOAc solution. [b] The quantum yield was determined in EtOAc by employing coumarin-1 (Φ_f = 0.99 in EtOAc)[13] as the reference.

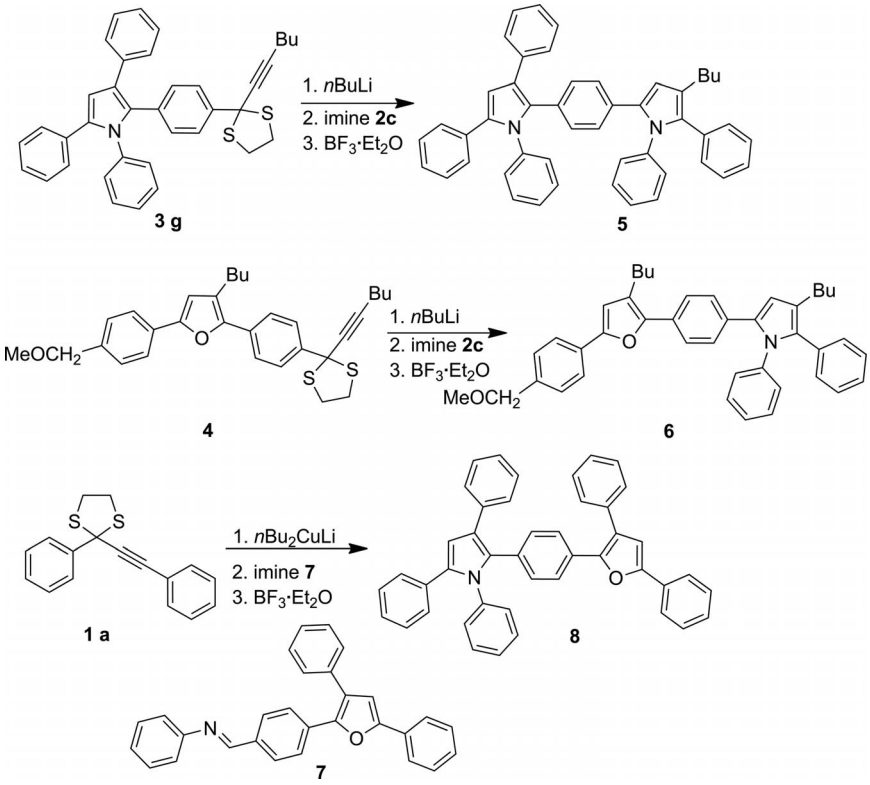
use of a weaker nucleophile from another alkanide source may be helpful. Thus, the yield of **3d** was increased from 36 to 63% when $n$$Bu_2$CuLi was used instead of nBuLi; whereas, for **3e**, the yield was increased from 32 to 64%. Interestingly, using either $n$$Bu_2$CuLi or nBuLi as the nucleophile source had no significant effect, and **3a** or **3b** were produced in similar yields.

When the reaction conditions (i.e., stirring at reflux for 6 h and then room temperature overnight in the last step) were adopted for the synthesis of the hydroxy-bearing product **3f**, no product was found. However, the crude NMR spectra clearly indicated the presence of an acyclic product in the reaction medium, indicating that the one-pot, three-step reaction stopped at the second stage. Hence, trifluoroacetic acid (TFA) was finally added, and the reaction medium was heated to reflux for a further 4 h; this led to ring closure and the formation of **3f** with a yield of up to 48%. A reasonable explanation for this result is that TFA, which is a stronger acid than BF_3·OEt_2, may improve the leaving ability of the thiolate group in the ring-closure step. It is worth mentioning that BF_3·OEt_2 cannot be omitted from the reaction, possibly because of its ability to promote the resonance of the propargylic to the allene anion, which then attacks the imine carbon atom in the second step. This phenomenon implies that BF_3·OEt_2 functions in the second step in all cases. However, for **3f**, a stronger acid catalysis is needed in the last step because of the presence of the hydroxy group.

With the facile synthesis of oligomers bearing functional groups established, the use of these functionalities to achieve elongation was attempted. In a similar manner, the pyrrole-bearing dithioacetal **3g** and the furan-bearing propargylic dithioacetal **4**[8a] were separately treated with nBuLi, then treated with the imines **2c** and subsequently submitted to BF_3·Et_2O-catalyzed ring closure with stirring first under reflux and then at room temperature overnight; the desired products **5** and **6** were thus obtained in 52 and 49% yield, respectively. Moreover, the propargylic dithioacetal **1a** could be employed in the reaction with the furan-bearing imine **7**,[12] by a similar procedure, to obtain **8** in 44% yield. Interestingly, substituents either on the propargylic dithioacetal side or on the imine side did not reduce the yield of the reaction. The syntheses of these compounds and their fluorescent properties are summarized in Scheme 3 and Table 1.

All the synthesized benzene–pyrrole oligoaryls fluoresce, but with significant differences; the maximum absorption wavelengths (λ_{max}), maximum emission wavelengths (λ_{em}), and the fluorescence quantum yields (Φ_f) of these oligomers are listed in Table 1. As expected, introducing an electron-withdrawing group (in the cases of **3a** and **3c**) or expanding the conjugated system (in the cases of **5**, **6** and **8**) could significantly bathochromically shift the maximum absorption and emission wavelengths. All compounds exhibited strong absorption (in all cases, log $\varepsilon > 4$), whereas only **3a**, **3c**, **6**, and **8** showed strong emission in the visible region in EtOAc solution, with fluorescence quantum yields of 64, 88, 39, and 50%, respectively. Other oligoaryls produced fluorescence quantum yields of less than 10%. Compounds **3a** and **3c** showed much stronger fluorescence, which clearly arose from the contribution of the conjugated carbonyl group to the delocalized system, regardless of whether the group was located on the propargylic dithioacetal side or the imine side of the starting material.

The fluorescent properties of oligoaryls, such as sexithiophene[14] and alternating benzene–furan oligomers,[2c] has been reported to be related to their structures and geometries. In our case, to preliminarily explore the origin of the differences in fluorescence of the synthesized compounds, theoretical calculations were performed by using Gaussian 03 at the B3LYP/6-31+G(d) basis set level for the elongated systems **5**, **6** and **8** in the ground state; the optimized geometries are illustrated in Figure 1. Incontrovertibly, all compounds displayed imperfect coplanar states with nonplanar twists; the dihedral angles between the two heterocycles separated by the middle benzene ring in **5**, **6** and **8** were 89.2°, 13.2° and 74.7°, respectively. With respect to the conformations, **5** and **8** have a similar dihedral angle, which is much larger than that of **6**; however, the maximum absorptions of **6** and **8** are similar, both being bathochromically shifted by approximately 30 nm compared with that of **5**. This result implies that the extent of conjugation is not a critical factor. The imbalance in the electronegativity of these compounds may contribute to the difference, be-



Scheme 3. Synthetic routes of pyrrole oligomers **5**, **6** and **8**.

cause compound **5** consists of only pyrrole rings, whereas compounds **6** and **8** contain both pyrrole and furan rings. Furan is a stronger electron-donating group than pyrrole;[15] thus, a partial movement of electron density through the middle benzene ring favors a bathochromic shift of the maximum absorptions in the systems of **6** and **8**. The energy differences between the HOMO and LUMO orbitals for compounds **5**, **6**, and **8** in the ground state were estimated to be 4.11, 3.65 and 3.56 eV, respectively. These differences result in the corresponding fluorescent quantum yields of 7, 39, and 50% for **5**, **6** and **8**, respectively. Because the fluorescent quantum yield of a conjugated system is reported to be related to the coplanarity and energy gaps not only in the ground state but also in excited state,[16] at present it is difficult to obtain a quantitative structure–effect relationship. Nonetheless, we were still able to preliminarily determine that smaller twist angles and narrower HOMO/LUMO energy gaps benefit the fluorescence quantum yield. Further investigations aimed at determining the correlation between the excited-state energy and fluorescence is underway.

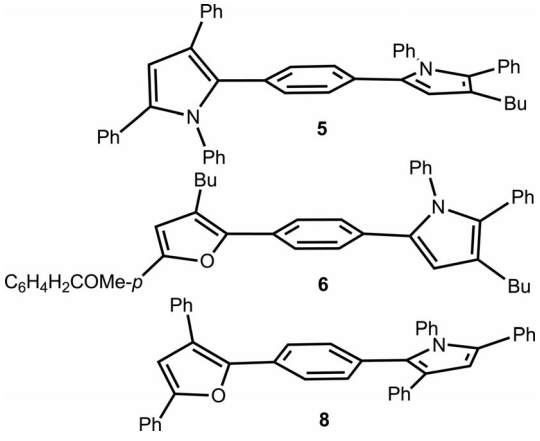


Figure 1. Geometries of oligomers **5**, **6** and **8**, calculated at the B3LYP/6-31G* level.

Conclusions

This work presents the development of the propargylic dithioacetal/imine cyclization strategy for the facile synthesis of 2,3,5-trisubstituted pyrroles bearing ether, ester, hydroxy, and dithiacetal groups on the peripheral benzene rings. The substituents on the peripheral benzene rings of propargylic dithioacetal can impart subtle changes to the electron distribution, leading to the requirement for modified reaction conditions to make the reactions proceed with a reasonable yield. Nevertheless, a simple guideline can still be derived from the listed examples: (1) allene anion formation with attack of organolithium is workable in the first step, with the exception of compounds such as **3d** and **3e**, for which the use of lithium dialkylcuprate is more suitable because of the presence of the methoxymethyl group in the propargylic dithioacetal; (2) the electron-withdrawing group methoxycarbonyl slightly decreases the electron density of the resulting allene anion, therefore stabilization of the lith-

ium cation is needed and addition of HMPA is helpful; (3) for hydroxy-bearing propargylic dithioacetal, at least 1 equiv. of TFA is needed in the ring-closure step. This guideline is suitable for the one-pot, three-step synthesis of pyrrole oligomers bearing functional groups, which are necessary for the synthesis of elongated derivatives. Moreover, the synthetic protocol is applicable to the convergent synthesis of elongated alternating heterocycle–benzene–furan oligomers regardless of which heterocycle is attached (e.g., for the synthesis of **5** and **8**). Theoretical calculations preliminarily suggest that the fluorescence intensity is closely related to the molecular geometry and to the HOMO/LUMO energy difference.

Experimental Section

General: Mass spectra were measured with a Finnigan Trace MS spectrometer. NMR spectra were recorded in $CDCl_3$ with a Bruker 400 MHz spectrometer and resonances are given in ppm (δ) relative to TMS. UV/Vis absorption spectra were measured with a Shimadzu UV-1601PC UV/Vis spectrophotometer. Emission spectra were recorded with an Aminco-Bowman Series 2 luminescence spectrometer.

Methyl 4-(1,3,5-Triphenyl-1*H*-pyrrol-2-yl)benzoate (3a): Under nitrogen, to a solution of 2-phenyl-2-(2-phenylethynyl)-1,3-dithiolane (**1a**; 0.3 g, 1 mmol) in THF (60 mL) cooled to –78 °C, was added, dropwise, *n*BuLi (2.5 M in hexane, 0.5 mL, 1.2 mmol). The mixture was stirred at –78 °C for 1 h, and then a solution of methyl 4-(benzylideneamino)benzoate (**2a**; 0.3 g, 1.2 mmol) in THF (20 mL) was introduced. The mixture was stirred at –78 °C for 0.5 h, and $BF_3{\cdot}OEt_2$ (0.3 mL, 2.3 mmol) was then added. The mixture was stirred at reflux for 1 h, then cooled to room temperature overnight, and quenched with saturated aqueous NH_4Cl. The organic layer was dried with $MgSO_4$, and the solvent was removed in vacuo to give a residue that was purified by chromatography on silica gel (hexane/ethyl acetate, 20:1) to give **3a** as white crystals (0.18 g, 43%); m.p. 134–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, OCH_3), 6.69 (s, 1 H, Pyrrole-H), 6.97–7.25 (m, 17 H, Ar-H), 7.78 (d, J = 8.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.0 (CH_3), 110.5, 124.6, 125.8, 126.6, 127.4, 128.0, 128.1, 128.2, 128.4, 128.6, 129.0, 130.7, 131.2, 132.6, 135.6, 135.8, 137.4, 138.5 (Ar-C), 166.9 (C=O) ppm. HRMS: calcd. for $C_{30}H_{23}NO_2$ 429.1729; found 429.1727. $C_{30}H_{23}NO_2$ (429.1): calcd. C 83.89, H 5.40, N 3.26; found C 83.78, H 5.31, N 3.44.

1,3,5-Triphenyl-2-(*p*-tolyl)-1*H*-pyrrole (3b): In a procedure similar to that for the preparation of **3a**, 2-phenyl-2-(2-phenylethynyl)-1,3-dithiolane (**1a**; 0.85 g, 3 mmol) in THF (150 mL), *n*BuLi (2.5 M in hexane, 1.4 mL, 3.6 mmol), and *N*-(4-methylbenzylidene)aniline (**2b**; 0.58 g, 3 mmol) were used to produce **3b** as pale-yellow crystals (0.75 g, 65%); m.p. 172–173 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, CH_3), 6.70 (s, 1 H, Pyrrole-H), 6.92–7.25 (m, 19 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (CH_3), 109.9, 123.3, 125.4, 126.3, 127.0, 127.9, 128.0, 128.1, 128.4, 128.5, 128.6, 129.1, 129.6, 131.3, 132.3, 133.0, 134.7, 136.3, 136.6, 138.9 (Ar-C) ppm. HRMS: calcd. for $C_{29}H_{23}N$ 385.1830; found 385.1834. $C_{29}H_{23}N$ (385.1): calcd. C 90.35, H 6.01, N 3.63; found C 90.08, H 6.09, N 3.74.

Methyl 4-(4-Butyl-1,5-diphenyl-1*H*-pyrrol-2-yl)benzoate (3c): In a procedure similar to that for the preparation of **3a**, 2-(1-hexyn-1-yl)-2-(4-methoxycarbonylphenyl)-1,3-dithiolane (**1b**; 0.96 g, 3 mmol) in THF (20 mL), *n*BuLi (2.5 M in hexane, 1.4 mL, 3.6 mmol), HPMA (0.64 g, 3.6 mmol) in the first step, and *N*-benzylideneaniline (**2c**; 0.65 g, 3.6 mmol) were used to afford **3c** as white crystals (0.65 g, 53%); m.p. 105–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.3 Hz, 3 H, *n*Bu CH_3), 1.34–1.39 (m, 2 H, *n*Bu CH_2), 1.59–1.63 (m, 2 H, *n*Bu CH_2), 2.50 (t, J = 7.6 Hz, 2 H, *n*Bu CH_2), 3.86 (s, 3 H, OCH_3), 6.53 (s, 1 H, Pyrrole-H), 6.92–7.19 (m, 12 H, Ar-H), 7.81 (dd, J_1 = 8.3, J_2 = 2.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (*n*Bu CH_3), 22.7, 25.9, 33.5, 51.9 (OCH_3), 111.6, 124.0, 126.7, 127.0, 127.6, 127.7, 128.6, 128.7, 129.2, 130.8, 132.5, 132.6, 134.0, 137.7, 138.9 (Ar-C), 167.0 (C=O) ppm. HRMS: calcd. for $C_{28}H_{27}NO_2$ 409.2042; found 409.2045.

3-Butyl-5-[4-(methoxymethyl)phenyl]-1,2-diphenyl-1*H*-pyrrole (3d): In a procedure similar to that for the preparation of **3a**, a solution of 2-(1-hexyn-1-yl)-2-(4-methoxymethylphenyl)-1,3-dithiolane (**1c**; 0.92 g, 3 mmol) in THF (20 mL), a solution of nBu$_2$CuLi [prepared from *n*BuLi (3.5 mmol) and CuI (0.34 g, 1.8 mmol) in THF (100 mL)], and *N*-benzylideneaniline (**2c**; 0.65 g, 3.6 mmol) were used to give **3d** as white crystals (0.75 g, 63%); m.p. 105–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.3 Hz, 3 H, *n*Bu CH_3), 1.34–1.39 (m, 2 H, *n*Bu CH_2), 1.59–1.63 (m, 2 H, *n*Bu CH_2), 2.51 (t, J = 7.7 Hz, 2 H, *n*Bu CH_2), 3.37 (s, 3 H, OCH_3), 4.37 (s, 2 H, OCH_2), 6.41 (s, 1 H, Pyrrole-H), 7.20–6.92 (m, 14 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (*n*Bu CH_3), 22.7, 26.0, 33.6, 58.2 (OCH_3), 74.5 (OCH_2), 110.3, 123.5, 126.4, 126.6, 127.4, 127.6, 128.3, 128.4, 128.8, 130.8, 132.5, 132.7, 132.8, 133.6, 135.6, 139.1 (Ar-C) ppm. HRMS: calcd. for $C_{28}H_{29}NO$ 395.2249; found 395.2245. $C_{28}H_{29}NO$ (395.2): calcd. C 85.02, H 7.39, N 3.54; found C 85.09, H 7.53, N 3.50.

3-Butyl-5-[4-(methoxymethyl)phenyl]-1-phenyl-2-(*p*-tolyl)-1*H*-pyrrole (3e): In a procedure similar to that for the preparation of **3d**, a solution of 2-(1-hexyn-1-yl)-2-(4-methoxymethylphenyl)-1,3-dithiolane (**1c**; 0.92 g, 3 mmol) in THF (100 mL), a solution of nBu$_2$CuLi [prepared from of *n*BuLi (3.5 mmol) and CuI (0.34 g, 1.8 mmol) in THF (100 mL)], and *N*-benzylideneaniline (**2c**; 0.70 g, 3.6 mmol) were used to give **3e** as white crystals (0.79 g, 64%); m.p. 149–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.3 Hz, 3 H, *n*Bu CH_3), 1.37–1.39 (m, 2 H, *n*Bu CH_2), 1.61–1.63 (m, 2 H, *n*Bu CH_2), 2.28 (s, 3 H, Ar-CH_3), 2.49 (t, J = 7.7 Hz, 2 H, *n*Bu CH_2), 3.36 (s, 3 H, OCH_3), 4.37 (s, 2 H, OCH_2), 6.40 (s, 1 H, Pyrrole-H), 6.92–6.94 (m, 4 H, Ar-H), 6.99–7.05 (m, 4 H, Ar-H), 7.10–7.15 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (*n*Bu CH_3), 21.2, 22.8 (CH_3), 26.1, 33.6, 58.2 (OCH_3), 74.6 (OCH_2), 110.3, 123.3, 126.5, 127.4, 128.2, 128.3, 128.4, 128.9, 129.8, 130.7, 132.6, 132.8, 133.4, 135.6, 136.0, 139.2 (Ar-C) ppm. HRMS: calcd. for $C_{29}H_{31}NO$ 409.2406; found 409.2408. $C_{29}H_{31}NO$ (409.2): calcd. C 85.04, H 7.63, N 3.42; found C 84.86, H 7.58, N 3.39.

4-Butyl-1-phenyl-5-(*p*-tolyl)-2-[(4-hydroxymethyl)phenyl]-1*H*-pyrrole (3f): In a procedure similar to that for the preparation of **3a**, a solution of 2-(1-hexyn-1-yl)-2-(4-hydroxymethylphenyl)-1,3-dithiolane (**1d**; 0.88 g, 3 mmol) in THF (150 mL), a solution of *n*BuLi (2.5 M in hexane, 2.9 mL, 7.2 mmol), and a solution of *N*-benzylideneaniline (**2c**; 0.65 g, 3.6 mmol) in THF (40 mL) were used. After the reaction, the solvent was removed in vacuo to give a residue, which was dissolved in THF (50 mL), and TFA (0.75 mL) was added. The mixture was heated at reflux overnight, then quenched with saturated aqueous $NaHCO_3$. The separated organic layer was washed with saturated aqueous $NaHCO_3$ (3× 25 mL) and brine (25 mL) and then dried with $MgSO_4$. The solvent was removed in vacuo to give a residue that was purified by chromatography on

silica gel (hexane/ethyl acetate, 20:1) to give **3f** as white crystals (0.55 g, 48%); m.p. 153–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.3 Hz, 3 H, *n*Bu CH_3), 1.34–1.40 (m, 2 H, *n*Bu CH_2), 1.58–1.64 (m, 2 H, *n*Bu CH_2), 2.51 (t, J = 7.7 Hz, 2 H, *n*Bu CH_2), 4.60 (s, 2 H, OCH_2), 6.42 (s, 1 H, Pyrrole-H), 6.93–6.94 (m, 2 H, Ar-H), 7.03–7.07 (m, 4 H, Ar-H), 7.14–7.20 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (*n*Bu CH_3), 22.7, 26.0, 33.6, 65.2 (CH_2OH), 110.4, 123.6, 126.4, 126.6, 127.6, 128.5, 128.8, 130.8, 132.6, 132.8, 133.5, 138.3, 139.2 (Ar-C) ppm. HRMS: calcd. for $C_{27}H_{27}NO$ 381.2093; found 381.2100. $C_{27}H_{27}NO$ (381.2): calcd. C 85.00, H 7.13, N 3.67; found C 84.74, H 7.13, N 3.83.

2-{4-[2-(Hex-1-yn-1-yl)-1,3-dithiolan-2-yl]phenyl}-1,3,5-triphenyl-1*H*-pyrrole (3g): In a procedure similar that for to the preparation of **3a**, a solution of 2-phenyl-2-(2-phenylethynyl)-1,3-dithiolane (**1a**; 1.02 g, 3.6 mmol) in THF (100 mL), a solution of *n*BuLi (2.5 M in hexane, 1.4 mL, 3.5 mmol), and the imine **2d** (1.10 g, 3 mmol) were used to give **3g** (0.72 g, 43%); m.p. 134–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.3 Hz, 3 H, *n*Bu CH_3), 1.39–1.44 (m, 2 H, *n*Bu CH_2), 1.50–1.56 (m, 2 H, *n*Bu CH_2), 2.33 (t, J = 7.1 Hz, 2 H, *n*Bu CH_2), 3.62–3.69 (m, 4 H, Dithiolane-H), 6.69 (s, 1 H, Pyrrole-H), 6.96–7.00 (m, 4 H, Ar-H), 7.25–7.10 (m, 13 H, Ar-H), 7.70 (d, J = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6 (*n*Bu CH_3), 18.9, 22.1, 30.7, 41.2, 62.1, 82.3, 88.2 (Alkyne-C), 110.2, 123.9, 125.5, 126.4, 127.2, 127.3, 127.9, 128.2, 128.3, 128.5, 128.6, 129.0, 131.0, 131.5, 132.5, 132.9, 135.0, 136.0, 137.6, 138.7 (Ar-C) ppm. HRMS: calcd. for $C_{37}H_{34}NS_2$ 555.2054; found 555.2054. $C_{37}H_{33}NS_2$ (555.2): calcd. C 79.96, H 5.98, N 2.52; found C 79.84, H 6.15, N 2.62.

3-Butyl-1,2-diphenyl-5-[4-(1,3,5-triphenyl-1*H*-pyrrol-2-yl)phenyl]-1*H*-pyrrole (5): In a procedure similar to that for the preparation of **3a**, a solution of propargylic dithioacetal (**3g**; 0.6 g, 1.1 mmol) in THF (100 mL), a solution of *n*BuLi (2.5 M in hexane, 0.5 mL, 1.25 mmol), and *N*-benzylideneaniline (**2c**; 0.29 g, 1.6 mmol) were used. After the usual workup, the residue was recrystallized from dichloromathene to give **5** (0.37 g, 52%); m.p. 250–251 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.3 Hz, 2 H, *n*Bu CH_3), 1.33–1.39 (m, 2 H, *n*Bu CH_2), 1.57–1.62 (m, 2 H, *n*Bu CH_2), 2.48 (t, J = 7.6 Hz, 2 H, *n*Bu CH_2), 6.39 (s, 1 H, Pyrrole-H), 6.68 (s, 1 H, Pyrrole-H), 6.81–7.23 (m, 29 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8 (CH_3), 22.6, 25.9, 33.5, 109.9, 110.7, 123.5, 125.3, 126.2, 126.3, 126.4, 126.9, 127.4, 127.8, 127.8, 127.9, 128.1, 128.3, 128.4, 128.7, 129.0, 130.8, 131.8, 132.1, 136.1, 138.8, 139.0 (Ar-C) ppm. HRMS: calcd. for $C_{48}H_{40}N_2$: 644.3191; found 644.3185. $C_{48}H_{40}N_2$ (644.3): calcd. C 89.40, H 6.25, N 4.34; found C 89.12, H 6.28, N 4.35.

3-Butyl-5-(4-{3-butyl-5-[4-(methoxymethyl)phenyl]furan-2-yl}phenyl)-1,2-diphenyl-1*H*-pyrrole (6): In a procedure similar to that for the preparation of **5**, a solution of the propargylic dithioacetal **4** (0.5 g, 1 mmol) in THF (50 mL), *n*BuLi (2.5 M in hexane, 0.5 mL, 1.25 mmol), and *N*-benzylideneaniline (**2c**; 0.26 g, 1.4 mmol) were used to give **5** (0.29 g, 49%); m.p. 155–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89–0.96 (m, 6 H, 2 *n*Bu CH_3), 1.36–1.45 (m, 4 H, 2 *n*Bu CH_2), 1.60–1.68 (m, 4 H, 2 *n*Bu CH_2), 2.52 (t, J = 7.6 Hz, 2 H, *n*Bu CH_2), 2.65 (t, J = 7.6 Hz, 2 H, *n*Bu CH_2), 3.39 (s, 3 H, OCH_3), 4.46 (s, 2 H, OCH_2), 6.48 (s, 1 H, Pyrrole-H), 6.62 (s, 1 H, Furan-H), 6.98 (d, J = 6.0 Hz, 2 H, Ar-H), 7.06 (dd, J = 7.6, J = 1.6 Hz, 2 H, Ar-H), 7.10–7.20 (m, 8 H, Ar-H), 7.33 (d, J = 8.0 Hz, 2 H, Ar-H), 7.49 (d, J = 8.4 Hz, 2 H, Ar-H), 7.66 (d, J = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (*n*Bu CH_3), 14.0, 22.6, 22.7, 25.8, 26.0, 32.0, 33.6, 58.0 (OCH_3), 74.5 (OCH_2), 109.3, 110.5, 123.6, 123.7, 124.0, 124.8, 126.5, 126.7, 127.6, 128.1, 128.3, 128.5, 128.9, 129.2, 130.2, 130.9, 131.6, 132.8, 133.5, 137.0, 139.2, 147.8, 151.6 (Ar-C) ppm. HRMS: calcd. for $C_{42}H_{43}NO_2$ 593.3294; found 593.3281. $C_{42}H_{43}NO_2$ (593.3): calcd. C 84.95, H 7.30, N 2.36; found C 84.67, H 7.28, N 2.35.

2-[4-(3,5-Diphenylfuran-2-yl)phenyl]-1,3,5-triphenyl-1*H*-pyrrole (8): In a procedure similar to that for the preparation of **5**, a solution of the propargylic dithioacetal **1a** (0.85 g, 3 mmol) in THF (100 mL), *n*BuLi (2.5 M in hexane, 1.35 mL, 3.3 mmol), and the imine **7** (0.6 g, 1.5 mmol) were used to give **8** (0.39 g, 44%); m.p. 119–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.70 (s, 1 H, Pyrrole-H), 6.78 (s, 1 H, Furan-H), 7.01–6.93 (m, 4 H, Ar-H), 7.41–7.12 (m, 23 H, Ar-H), 7.73 (d, J = 7.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.6, 110.2, 123.8, 124.7, 125.3, 125.6, 126.4, 127.2, 127.3, 127.5, 127.9, 128.2, 128.3, 128.5, 128.6, 128.6, 128.7, 129.1, 129.3, 130.4, 131.3, 131.6, 132.8, 134.2, 135.0, 136.1, 138.8, 147.5, 152.5 ppm. HRMS: calcd. for $C_{44}H_{31}NO$ 589.2406; found 589.2416. $C_{44}H_{31}NO$ (589.2): calcd. C 89.61, H 5.30, N 2.38; found C 89.31, H 5.34, N 2.47.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra for all new compounds.

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[12] In a manner similar to that used in the synthesis of **2c**, aniline (0.33 g, 3.6 mmol) was allowed to react with furancarbaldehyde (0.58 g, 1.8 mmol) in benzene (25 mL) to give imine **7** (0.56 g, 80%) as a yellow solid; m.p. 142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (s, 1 H, Pyrrole-H), 7.20–7.22 (m, 3 H, Ar-H), 7.39–7.48 (m, 10 H, Ar-H), 7.71 (d, J = 8.4 Hz, 2 H, Ar-H), 7.78–7.85 (m, 4 H, Ar-H), 8.43 (s, 1 H, Imine-H) ppm.

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