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Linear Heterocyclic Aromatic Fluorescence Compounds Having Various Donor−Acceptor Spacers Prepared by the Combination of Carbon−Carbon Bond and Carbon−Nitrogen Bond Cross-Coupling Reactions

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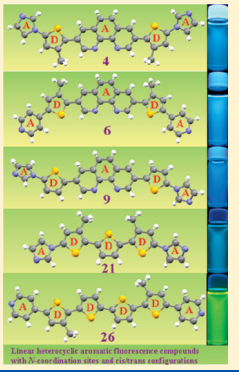
Supporting Information

ABSTRACT: A family of novel linear 1,10-phenanthroline-based (A−D−A−D−A) and oligothiophene-based (A−D−D−D−(D)−A) heterocyclic aromatic fluorescence compounds having *N*-containing imidazole and pyridine tails with effective π-conjugated systems, prepared by the combination of carbon−carbon (C−C) bond and carbon−nitrogen (C−N) bond cross-coupling reactions, is described. They have molecular lengths of more than 2.30 nm in the cases of **4**, **6**, **9**, and **26**, various D−A spacers, and certain *N*-coordination sites (phen, imidazole, and pyridine). X-ray single-crystal structures of 13 compounds reveal a variety of trans and cis configurations with different dihedral angles between adjacent aromatic heterocycles. Synthetic, computational, and spectral studies have been made to reveal the differences between cross-coupling approaches on the C−C bond and C−N bond formation as well as band gaps and energy levels and optical and electrochemical properties for related compounds. The influences of introducing a β-methyl group to the thiophene ring on reaction activity, solubility, and conformation of related compounds have also been discussed.



INTRODUCTION

Linear aromatic heterocyclic semiconducting compounds[1] bearing delocalized π-systems, versatile donor−acceptor (D−A) hybrid spacers, and certain coordination sites are expected to be valuable advanced functional materials on the applications of organic and polymeric light-emitting devices,[2] field-effect transistors,[3] photoconductive materials, and photovoltaic solar cells.[4] Transition-metal-catalyzed cross-coupling reactions supply versatile routes to the formation of C−C and C−N bonds, and their great developments have witnessed many types of named cross-coupling reactions such as Kumada−Tamao−Corriu, Suzuki−Miyaura, Migita−Kosugi, Negishi, Ullmann, Heck, and so on, and even the awarding of the 2010 Nobel Prize in Chemistry.[5]

The combination of C−C bond and C−N bond cross-coupling reactions is an effective strategy to extend heterocyclic aromatic systems.[1,6] The ones having 3,8-extended 1,10-phenanthroline (phen) segments have been widely used in the studies on optoelectronic materials and devices in the micrometer and nanometer sizes.[7] In addition, 2,5-extended thiophene and oligothiophene compounds, produced by C−C bond cross-coupling reactions, have been extensively used in molecular electronics because of their excellent optical and electronic properties.[8] However, further extended aromatic heterocycles by the combination of C−C and C−N bond cross-coupling reactions have not been documented up until now.

We have previously reported thiophene,[7a] oligothiophene,[7d] phenyl,[8b] or imidazole[8c] extended phen compounds at the 3 and 8 positions and their Ru^{II} species because of their high performance on the research of photoresponsive nanocomposite thin films and nanodevices. Following the idea of introducing specific organic D−A hybrid spacers and retaining certain coordination sites to promote direct electronic separation and transportation within the molecules, we further extend the thiophene-based phen compounds by building a new series of organic semiconducting compounds with various aromatic heterocycles and coordination sites and describe herein the syntheses and full characterizations of a family of novel linear phen-based heterocyclic aromatic fluorescence compounds (**1**−**6**, **8**−**13**, **15**, and **16**) with various D−A hybrid spacers by virtue of the combination of C−C bond and C−N bond cross-coupling reactions (Scheme 1). As a common feature of this family of compounds, they have dissimilar electron-withdrawing units bearing metal binding groups (phen/imidazole/pyridine) and electron-donating units (thiophene/Me-thiohene), delocalized π-systems, and photoresponsive thiophene moieties in their molecular structures. We have also described another unexpected 2-extended 3,8-dibromo phen compound (**18**) prepared from 1-(5-bromothiophene-2-yl)-1*H*-imidazole (**17**) via a suggested mechanism of double-molecular self-exchange between the MgBr groups

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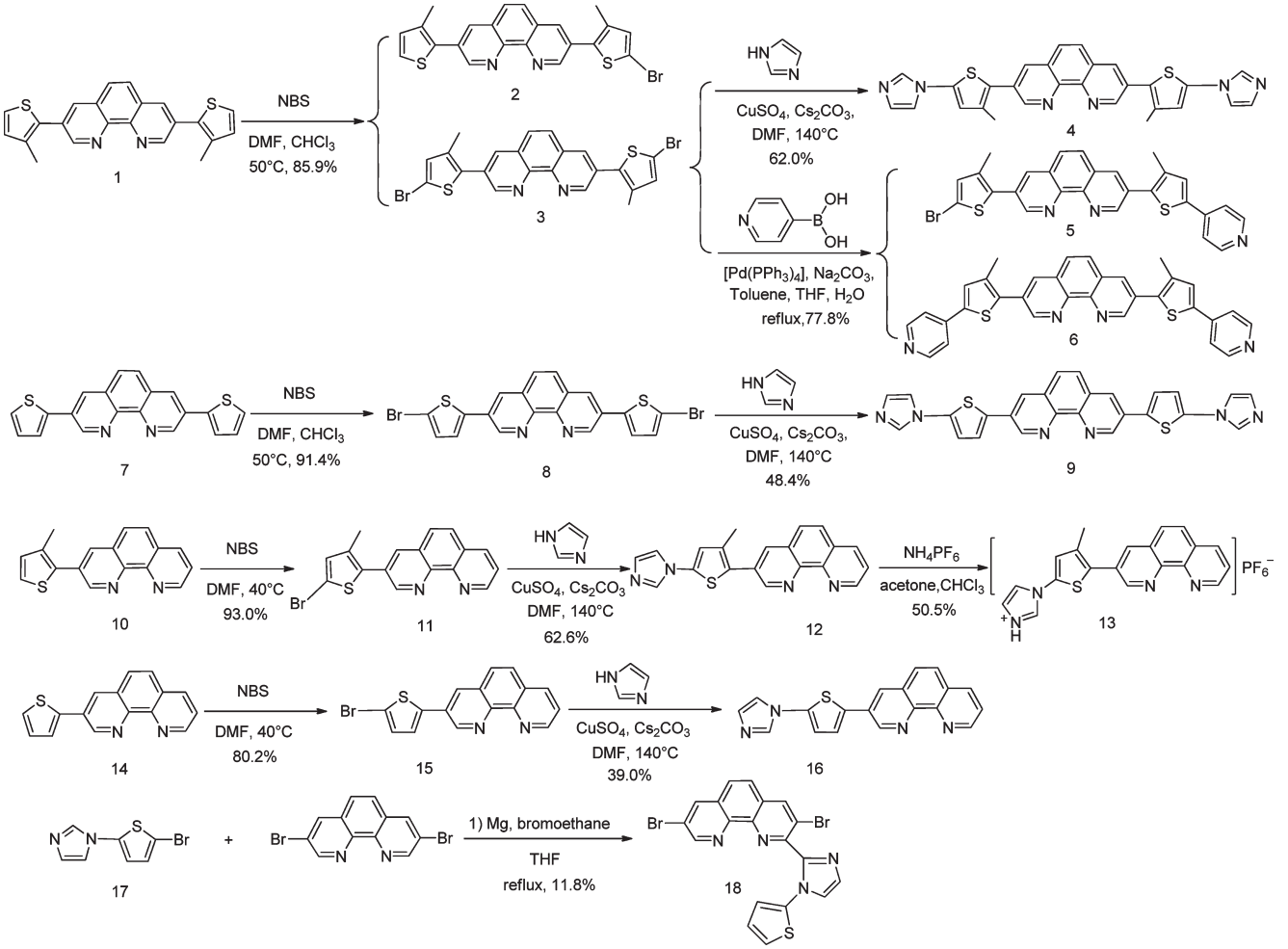
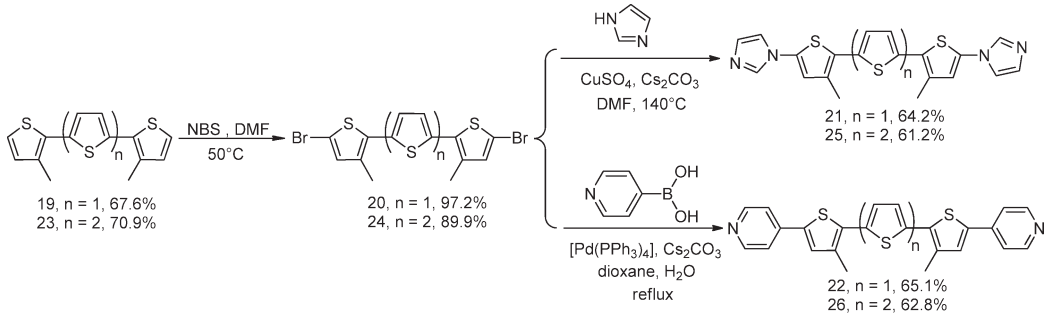
Scheme 1. Synthetic Route of 3- and 3,8-Extended 1,10-Phenanthroline-Based Heterocyclic Aromatic Fluorescence Compounds



Scheme 2. Synthetic Route of 2,5-Extended Oligothiophene-Based Heterocyclic Aromatic Fluorescence Compounds



of Grignard reagent. Moreover, partially methyl-substituted terthiophene and quathiophene derivatives **20**−**22** and **24**−**26** have been produced by the similar synthetic strategy of combining C−C bond and C−N bond cross-coupling reactions (Scheme 2). To the best of our knowledge, this is the first report on successful linear incorporation of thiophene (or β-methylthiophene) and imidazole (or pyridine) into phen molecule simultaneously and incorporation of imidazole into oligothiophene molecules.

RESULTS AND DISCUSSION

Our synthetic strategy was based upon the routes shown in Schemes 1 and 2, in which **7**, **14**, **19**, and **23** are known compounds. All the target compounds were prepared by transition-metal-catalyzed C−C bond and C−N bond cross-coupling reactions. The combination of different cross-coupling methods, such as Kumada−Corriu, Suzuki−Miyaura, and Ullmann reactions, have been carried out to optimize the experimental conditions in

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Table 1. Crystal Data and Structural Refinements for 13 Compounds 1−4, 6, 9, 13, 16−18, 21, 24, and 26

compd	1	2	3	4	6	9	13
emp formula	$C_{22}H_{16}N_2S_2$	$C_{24}H_{21}BrN_2O_2S_2$	$C_{23}H_{15}Br_2Cl_3N_2S_2$	$C_{59}H_{46}C_{16}N_{12}OS_4$	$C_{33}H_{23}Cl_3N_4S_2$	$C_{27}H_{17}Cl_3N_6S_2$	$C_{20}H_{15}F_6N_4PS$
form wt	372.49	513.46	649.66	1280.02	646.02	595.94	488.39
T (K)	291(2)	291(2)	291(2)	291(2)	291(2)	291(2)	291(2)
wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst size (mm)	0.16 × 0.19 × 0.20	0.10 × 0.10 × 0.12	0.10 × 0.12 × 0.12	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.11	0.10 × 0.12 × 0.12	0.12 × 0.12 × 0.10
cryst syst	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.856(6)	7.544(15)	8.034(14)	11.080(12)	7.3376(14)	8.461(19)	8.163(8)
b (Å)	16.164(12)	10.573(2)	10.950(19)	11.400 (12)	10.669(2)	11.516(3)	11.131(11)
c (Å)	13.794(10)	14.340(3)	14.898(3)	14.479(15)	20.154(4)	13.513(3)	11.562(11)
α (deg)	90	85.00(3)	94.525(2)	87.593(2)	77.835(3)	87.678(3)	88.605(14)
β (deg)	94.326(9)	85.59(2)	99.489(10)	71.357(10)	89.540(3)	86.804(2)	77.241(16)
γ (deg)	90	78.26(3)	103.592(2)	62.879(2)	77.556(3)	87.208(3)	78.707(15)
V (Å^3)	1747(2)	1113.5(4)	1247.0(4)	1530.7(3)	1504.9(5)	1312.1(5)	1004.6(17)
Z/D_{calcd} (g/cm^3)	4/1.416	2/1.531	2/1.730	1/1.389	2/1.426	2/1.508	2/1.615
F(000)	776	524	640	658	664	608	496
μ (mm^{-1})	0.313	2.058	3.755	0.468	0.474	0.539	0.312
max/min transmission	0.9516/0.9401	0.8207/0.7932	0.7052/0.6614	0.9546/0.9546	0.9541/0.9497	0.9481/0.9381	0.9694/0.9635
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
h_{min}/h_{max}	−8/9	−8/8	−9/8	−8/13	−8/7	−9/10	−9/4
k_{min}/k_{max}	−19/19	−12/12	−13/12	−11/13	−12/10	−13/7	−13/11
l_{min}/l_{max}	−11/16	−14/17	−17/16	−16/17	−23/23	−14/16	−13/13
data/param	3074/238	3842/337	4338/291	5309/372	5138/381	4551/343	3441/319
final R indices $[I > 2\sigma(I)]^a$	$R1$ = 0.0489, $wR2$ = 0.1159	$R1$ = 0.0865, $wR2$ = 0.2033	$R1$ = 0.0526, $wR2$ = 0.1380	$R1$ = 0.0768, $wR2$ = 0.1787	$R1$ = 0.0511, $wR2$ = 0.0753	$R1$ = 0.0677, $wR2$ = 0.2072	$R1$ = 0.0642 $wR2$ = 0.1702
R indices (all data)	$R1$ = 0.0383, $wR2$ = 0.1093	$R1$ = 0.1081, $wR2$ = 0.2189	$R1$ = 0.0854, $wR2$ = 0.1484	$R1$ = 0.1674, $wR2$ = 0.1981	$R1$ = 0.1506, $wR2$= 0.0877	$R1$ = 0.0903, $wR2$ = 0.2275	$R1$ = 0.1013 $wR2$ = 0.2068
S	1.078	0.925	0.927	1.008	0.835	1.076	1.080
max/min$\Delta\rho$ [e·Å^{-3}]	0.262/−0.318	0.445/−0.631	0.747/−0.504	1.073/−0.342	0.420/−0.413	0.521/−0.731	0.484/−0.663

compd	16	17	18	21	24	26
emp formula	$C_{19}H_{16}N_4O_2S$	$C_7H_5BrN_2S$	$C_{20}H_{11}Br_2Cl_3N_4S$	$C_{20}H_{16}N_4S_3$	$C_{18}H_{12}Br_2S_4$	$C_{28}H_{20}N_2S_4$
form wt	364.42	229.10	605.56	408.55	516.34	512.70
T (K)	291(2)	291(2)	291(2)	291(2)	291(2)	291(2)
wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst size (mm)	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.16 × 0.14 × 0.10	0.13 × 0.11 × 0.10	0.10 × 0.10 × 0.11
cryst syst	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	14.1891(13)	5.992(4)	8.116(16)	7.973(5)	6.9905(16)	11.211(5)
b (Å)	14.4246(14)	7.978(5)	11.169(2)	22.289(13)	10.659(3)	7.868(3)
c (Å)	17.7590(17)	9.542(7)	12.788(3)	10.729(6)	13.335(3)	16.060(7)
α (deg)	76.4170(10)	67.835(18)	96.786(3)	90	90	90
β (deg)	84.6550(10)	71.955(19)	98.909(2)	101.187	108.125(3)	120.036(5)
γ (deg)	76.2390(10)	77.75(2)	104.079(3)	90	90	90
V (Å^3)	3429.0(6)	399.3(5)	1095.7(4)	1870.6(19)	944.3(4)	1226.4(9)
Z/D_{calcd} (g/cm^3)	8/1.412	2/1.905	2/1.836	4/1.451	2/1.816	2/1.388
F(000)	1520	224	592	848	508	532
μ (mm^{-1})	0.211	5.337	4.177	0.409	4.732	0.408

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Table 1. Continued

compd	16	17	18	21	24	26
max/min transmission	0.9792/0.9751	0.6174/0.5668	0.6801/0.6341	0.9602/0.9374	0.6490/0.9374	0.9603/0.9565
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
h_{min}/h_{max}	−12/16	−6/7	−9/9	−9/9	−8/8	−13/7
k_{min}/k_{max}	−16/17	−9/8	−13/13	−26/21	−12/11	−9/9
l_{min}/l_{max}	−21/21	−11/11	−11/15	−12/11	−12/15	−18/19
data/param	11897/937	1383/101	3818/271	3297/246	1651/110	2152/155
final R indices $[I > 2\sigma(I)]^a$	$R1$ = 0.0493 w$R2$ = 0.0940	$R1$ = 0.0308, w$R2$ = 0.0750	$R1$ = 0.0780, w$R2$ = 0.2041	$R1$ = 0.0393 w$R2$ = 0.0913	$R1$ = 0.0331 w$R2$ = 0.0612	$R1$ = 0.0350 w$R2$ = 0.0638
R indices (all data)	$R1$ = 0.0968 w$R2$ = 0.1099	$R1$ = 0.0346, w$R2$= 0.0762	$R1$ = 0.1157, w$R2$= 0.2222	$R1$ = 0.0597 w$R2$ = 0.0999	$R1$ = 0.0596 w$R2$ = 0.0651	$R1$ = 0.0601 w$R2$ = 0.0697
S	0.872	1.008	1.122	0.952	0.874	0.857
max/min$\Delta\rho$ [e·Å^{-3}]	0.178/−0.236	0.530/−0.406	2.989/−1.504	0.183/−0.252	0.451/−0.409	0.147/−0.225

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

order to obtain linear aromatic heterocyclic compounds. As can be seen in Figures SI2−22 (Supporting Information), all the heterocyclic aromatic compounds have been characterized by ^{1}H, ^{13}C, and ^{1}H−^{1}H correlation spectroscopy (COSY) NMR and EI-TOF-MS spectra, and the results clearly demonstrate the formation of expected compounds. It is noted that the assignments of NMR peaks are further confirmed by ^{1}H−^{1}H COSY experiments, where the sequence of deshielding effects for electron-attractive groups are found to be pyridine > bromide > imidazole > thiophene.

Thiophene and β-methylthiophene extended phen compounds **1** and **10** were first prepared in good yields (82.3 and 91.3%) by the treatment of Grignard reagents obtained from corresponding phen-based bromides and magnesium turnings with a [$NiCl_2$-(dppp)] catalyst in dry THF, and then the bromination products were synthesized by controlling the molar ratio of *N*-bromosuccinimide and reactants in *N*,*N*′-dimethylformamide (DMF) at 50 °C. Nevertheless, the preparation of compound **8** was hindered by the low solubility of compound **7**. A mixture of chloroform and DMF was replaced to overcome this drawback and the resulting yield could reach as high as 91.4%.

As anticipated, pyridine-terminated compounds **5** and **6** could not be yielded by the above-mentioned experimental conditions due to their low reaction activity in the C−C bond formation. Instead, they were synthesized by a stronger cross-coupling reagent (4-pyridine boronic acid) and catalyzed by [$PdCl_2$(dppf)] or [$Pd(PPh_3)_4$]. In contrast, the coupling of the monobromo and dibromo compounds **3**, **8**, **11**, and **15** with excess imidazole under Ullmann coupling conditions gave the corresponding compounds **4**, **9**, **12**, and **16** in the presence of a base and anhydrous $CuSO_4$ catalysts in DMF solution. Furthermore, the resultant yields can be more or less improved by using Cs_2CO_3 instead of Na_2CO_3 as a base. On the basis of the above-mentioned synthetic experiences, pyridine-terminated oligothiophenes **22** and **26** were prepared directly from 4-pyridineboronic acid with satisfactory yields in the presence of [$Pd(PPh_3)_4$] and Cs_2CO_3 catalysts, as shown in Scheme 2.

In comparison with the thiophene-extended phen compounds, it is concluded that the introduction of a β-methyl group to the thiophene ring can effectively increase the solubility of resulting compounds in organic solvents, which facilitates the related C−C bond and C−N bond cross-coupling reactions and improves the yields of cross-coupling reactions. Meanwhile, the planarity and delocalized π-systems of corresponding compounds are not reduced, and a variety of trans and cis configurations between adjacet aromatic heterocycles have been observed, which will be discussed below.

X-ray single-crystal structural analyses for compounds **1**−**4**, **6**, **9**, **13**, and **16** (Tables 1 and SI1, Supporting Information) reveal that they have various heterocyclic aromatic backbones exhibiting diverse cis and trans molecular configurations as depicted in Figure 1. On one hand, they all have many *N*-donors in their molecular structures such as phen, imidazole, and pyridine units. On the other hand, compounds **4**, **6**, and **9** have the common alternate A−D−A−D−A heterocyclic aromatic system. On the basis of the two aforementioned aspects, it is possible for us to finely tune their optoelectronic properties by introducing a variety of metal ions by means of the formation of coordinative bonds. Because of the free rotatation of C−C and C−N single bonds between adjacent aromatic heterocycles, all phen-based molecules are not essentially coplanar with dissimilar dihedral angles (Table SI2, Supporting Information), especially for compound **9** having both imidazole tails (up to 47.1(3)°). The whole molecular lengths of linear compounds **4**, **6**, and **9** are 2.321, 2.301, and 2.303 nm, respectively. In the case of compound **13**, the proton is added to the nitrogen atom of imidazole ring.

According to retrosynthetic analysis, there is another possible way to produce compound **9**, where 1-(5-bromothiophene-2-yl)-1*H*-imidazole (**17**) and 3,8-dibromo-1,10-phenanthroline could be selected as the starting materials. However, the reaction between them was complicated, and an unexpected 2-extended 3,8-dibromo phen compound (**18**) was isolated in a low yield. X-ray single-crystal structural analysis on compound **18** exhibits the formation of a unique phen/imidazole/thiophene array (Figure 2). However, all the aromatic heterocycles in this case are not coplanar with the dihedral angles of 82.7(8) and 66.3(1)°. To the best of our knowledge, there is only one literature reference

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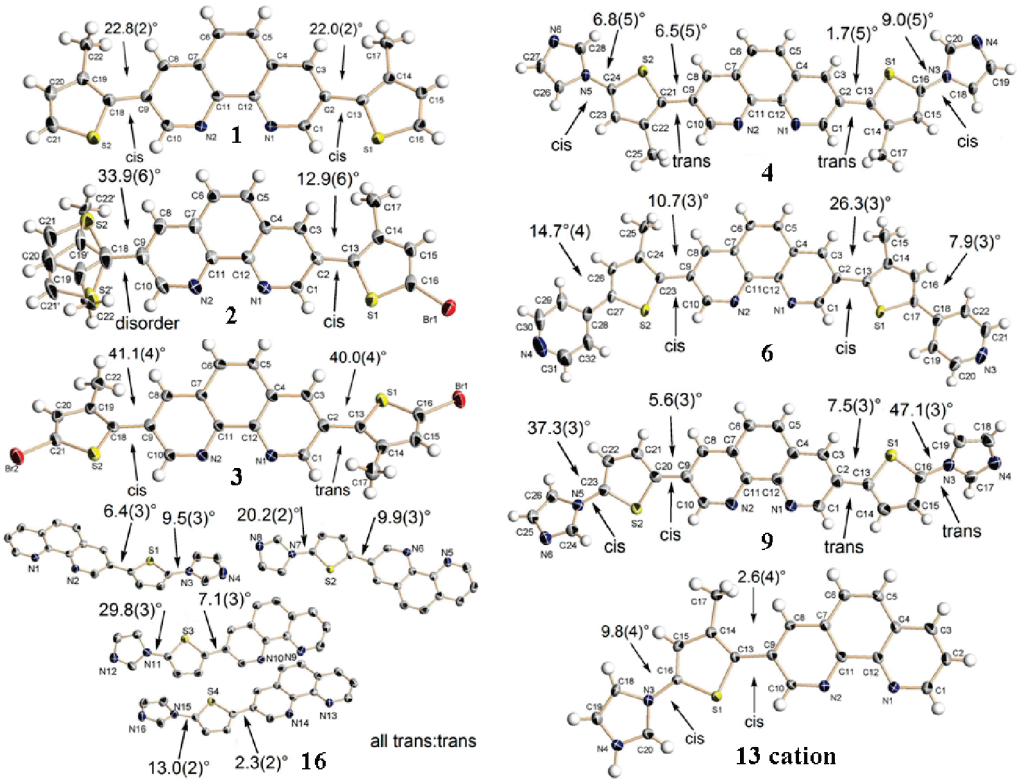

Figure 1. ORTEP diagrams (30% thermal probability ellipsoids) of the molecular structures of the cations **1**−**4**, **6**, **9**, and **13** and **16** showing the dihedral angles and relative configurations between adjacent aromatic heterocycles.

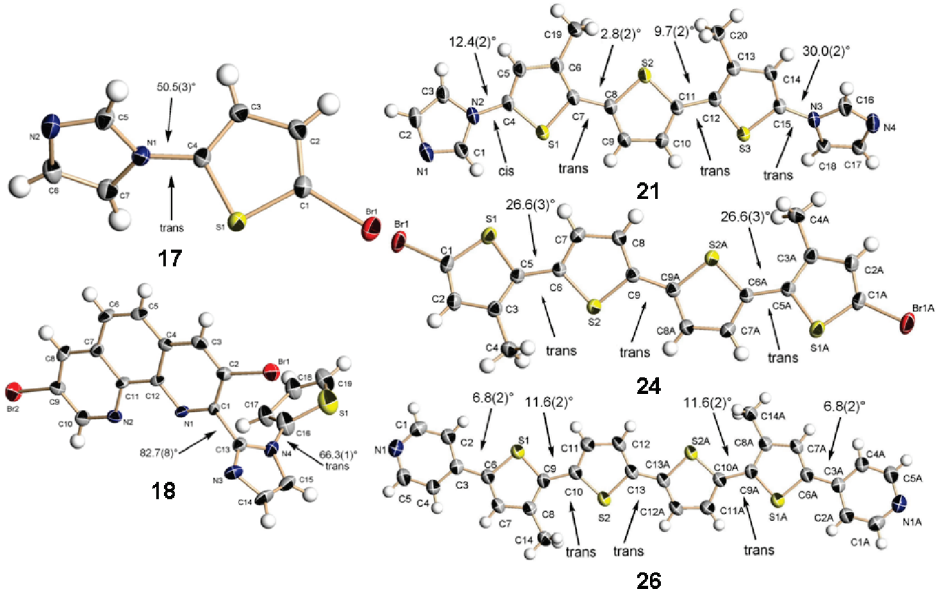

Figure 2. ORTEP diagrams (30% thermal probability ellipsoids) of the molecular structures of **17**, **18**, **21**, **24**, and **26** showing the dihedral angles and relative configurations between adjacent aromatic heterocycles.

about direct alkylation of 3,8-dibromo-1,10-phen with Grignard reagents at the 2 position.[9]

The possible mechanism for producing compound **18** is represented in Scheme 3. Compound **17** is initiated by bromoethane to prepare the corresponding Grignard reagent, which needs more extreme operating conditions compared with conventional Grignard reactions mainly due to the presence of an imidazole unit. Then the reaction of double-molecular self-exchange of MgBr groups was carried out simultaneously between the low-activity Grignard reagents because of the Schlenk equilibrium between several species. The resulting Grignard reagent is suggested to be more stable in this reaction. Finally, introduction

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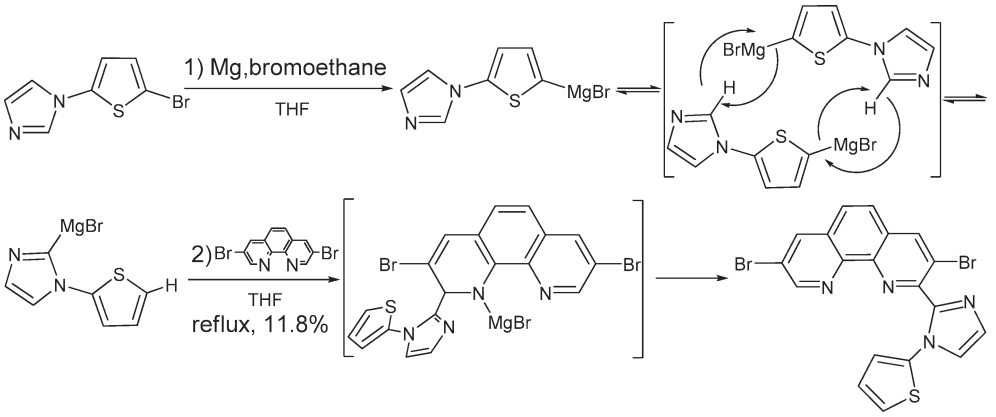
Scheme 3. Possible Mechanism for the Formation of Unexpected 2-Extended 3,8-Dibromo Phen Heterocyclic Aromatic Compound 18



of the Grignard reagent at the 2 position of 3,8-dibromo-phen yields the 2-substituted 3,8-dibromo-phen compound **18**. Actually, only three main products (3,8-dibromo-1,10-phen, **17** and **18**) have been observed by the TLC analysis in the absence of fluorescence active product **9**. As a contrast experiment, the same reaction is performed without addition of the $[Ni(dppp)Cl_2]$ catalyst; however, the same TLC analytical result can be observed. Additionally, 1-(5-bromothiophene-2-yl)-2-methyl-1*H*-imidazole has been tried as the starting material to block the possible double-molecular self-exchange between the MgBr groups of Grignard reagent, but the reaction is much more complicated and no expected product can be obtained via the TLC analysis.

In addition, we have successfully characterized the single-crystal structures of compounds **21**, **24**, and **26** in Scheme 2. Their molecular structures are illustrated in Figure 2, where the molecular lengths of A−D−D−D−A and A−D−D−D−D−A types of heterocyclic aromatic compounds **21** and **26** are 1.839 and 2.305 nm, respectively. In **21**, the central thiophene ring and its side β-methyl thiophene rings are almost coplanar, and the mean deviation from least-squares plane of all non-hydrogen atoms is 0.0569 Å. The two terminal imidazole rings have different dihedral angles with the above-metioned least-squares plane respect to the three thiophene rings 13.2(2) and 36.1(2)°. In **24**, there is a 2-fold rotational axis across the molecule, which makes the central two thiophene rings coplanar, and the dihedral angles between two central thiophene and two side β-methyl thiophene rings are the same as 26.6(3)°. In **26**, there is also a 2-fold rotational axis across the molecule, but all the non-hydrogen atoms are nearly coplanar with the mean deviation from the least-squares plane of 0.1168 Å.

The influence of the β-methyl group to the thiophene ring on the conformation and the dihedral angles of linear phen-based heterocyclic aromatic compounds is neglectable because both cis and trans configurations for the thiophene and β-methyl thiophene rings are accessible. For example, the side β-methyl thiophene rings show cis/trans, trans/trans, and cis/cis configurations relative to the central phen units in **3**, **4**, and **6**, respectively. Nevertheless, with regard to oligothiophene-based compounds, only the all-trans conformation is observed in **21**, **24**, and **26**, which is same as those pyridine-terminated monthiophene,[10a] bithiophene,[10b] and quathiophene[10c] compounds without any substituted groups in the thiophene rings.

As a common feature of organic compounds having delocalized π-system, typical offset $\pi-\pi$ stacking interactions are found in the solid-state structures of this family of linear phen-based and oligothiophene-based heterocyclic aromatic compounds with different D−A hybrid spacers, as illustrated in Figures SI1a−1j (Supporting Information). The centroid-to-centroid separations between different donor and acceptor aromatic heterocycles vary in the range 3.606−3.903 Å forming layer packing structures. However, there are no $\pi-\pi$ stacking interactions in the crystal packing of linear heterocyclic aromatic compounds **24** and **26**. In addition, versatile O−H···N, O−H···N, C−H···O, C−H···N, C−H···F, and N−H···F hydrogen-bonding interactions are observed to further stabilize the structures, as illustrated in Table SI3 (Supporting Information).

Density functional theory (DFT) computations are carried out with the Gaussian 03, Revision C.02 programs,[11] using the B3LYP method and 6-31G* basis set. The fixed atom coordinates of linear aromatic heterocyclic compounds **4**, **6**, **9**, **12**, **16**, **21**, **24**, and **26**, based on the structural parameters determined by the X-ray diffraction method, are used for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) gap (band gap) calculations (Table 2). The resultant HOMO−LUMO gaps for 3,8-extended D−A−D−A−D heterocyclic aromatic proconducting compounds **4**, **6**, and **9** are 3.64, 3.48, and 3.42 eV, respectively, while that for 3-extended phen compound **16** is as high as 3.74 eV. In contrast, the HOMO−LUMO gaps of oligothiophene-based heterocyclic aromatic compounds **21**, **24**, and **26** are much smaller at 3.45, 3.21, and 2.80 eV, respectively, which are analogous to their UV−vis absorption peaks.

The electrochemical behavior of five representative heterocyclic aromatic compounds **4**, **6**, **9**, **21**, and **26** has been examined by cyclic voltammetry (CV) in their 1.0×10^{-3} M CH_2Cl_2 solutions containing 0.1 M $TBAClO_4$ at a scanning rate of 100 $mV \cdot s^{-1}$, together with those of ferrocene for comparison. In our experiments, the CV diagrams are not good enough because this family of compounds is easily deposited on the Pt working electrode as red solid after the first cycle which will influence the further scans (Figure SI23, Supporting Information). Redetermination is only possible by carefully polishing the Pt working electrode again. In addition, the CV peaks are all indistinctive and irreversible. So we carried out differential pulse voltammetry (DPV) experiments to verify the first oxidation potentials (E_{ox}^0)

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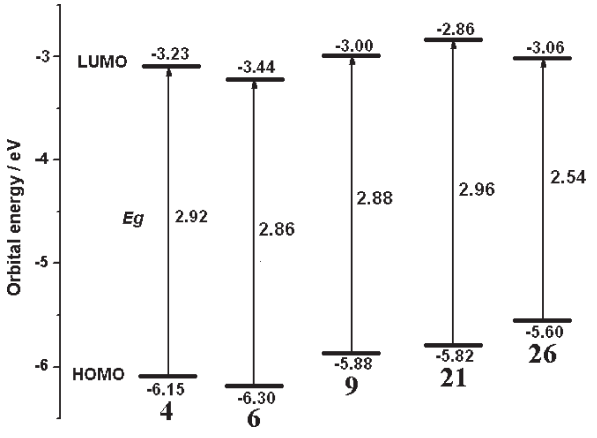
Table 2. UV−vis Absorption and Fluorescence Emission Data, Optical, And Calculated HOMO−LUMO Energy Gaps (*Eg*) Based on the Corresponding CIFs for Related Heterocyclic Aromatic Compounds

compd	UV−vis λ_{max} [nm (eV)]	ε (L·mol^{-1} cm^{-1})	*Eg*[a] (eV)	*Eg* (calcd[b]) (eV)	fluorescence λ_{max} (nm)
1	351 (3.53)	13100	3.02	3.78	415
2	355 (3.49)	12200	3.05	3.80	416
3	357 (3.47)	10900	3.01	3.71	419
4	369 (3.36)	11700	2.92	3.64	445
5	368 (3.37)	15900	2.89		440
6	381 (3.25)	17900	2.86	3.48	452
8	361 (3.43)	13700	2.94		422
9	371 (3.34)	23700	2.88	3.42	445
10	333 (3.72)	5640	3.19		439
11	337 (3.68)	5560	3.15		449
12	336 (3.69)	8140	3.09		434
15	335 (3.70)	12100	3.18		398
16	341 (3.64)	10800	3.09	3.74	425
17	263 (4.71)	9550	4.05	4.96	
18	277 (4.48)	21100	3.85	4.25	
20	348 (3.56)	38200	3.07		438
21	357 (3.47)	47700	2.96	3.45	460
22	399 (3.11)	45800	2.66		506
24	384 (3.23)	37700	2.79	3.21	482
25	389 (3.19)	57700	2.73		452
26	420 (2.95)	27750	2.54	2.80	533

[a] Optical band gap determined from the UV−vis absorptions in solution. [b] The geometries are calculated by B3LYP method and 6-31G* basis set.

Scheme 4. Energy Level (eV) Diagram of Representative Linear Heterocyclic Aromatic Compounds 4, 6, 9, 21, and 26 Estimated from Their Electronic Spectra and Electrochemistry Data, Where $E_{HOMO} = -(E_{ox}^{o} + 5.10)$ and $E_{LOMO} = E_{HOMO} + Eg$[a]



of **4**, **6**, **9**, **21**, and **26**. As can be seen in Figures SI23−SI28 (Supporting Information), the values of E_{ox}^{0} in the cases of aforementioned five compounds are determined to be 1.05 V for **4**, 1.20 V for **6**, 0.78 V for **9**, 0.72 V for **21**, and 0.50 V for **26** by their DPV experiments.

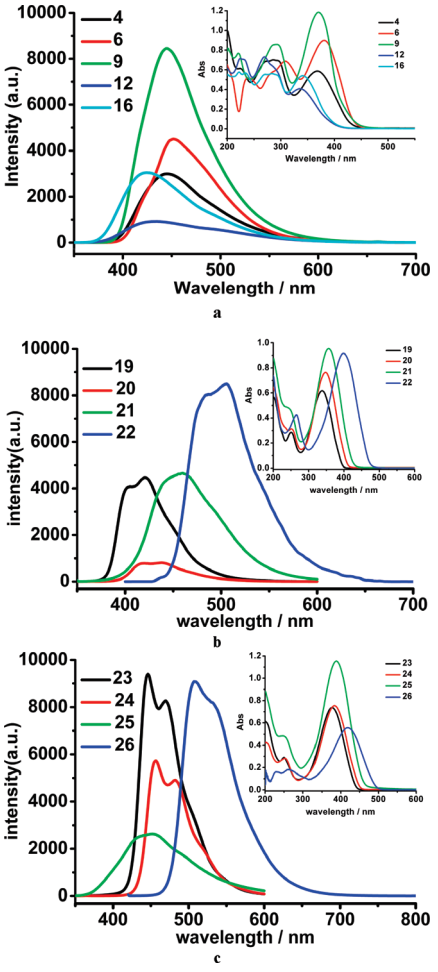


Figure 3. Fluorescence emission (excited at 350 nm) and UV−vis absorption spectra (inset) for heterocyclic aromatic compounds in their methanol solutions with the same concentration of 5.0×10^{-5} mol/L: (a) 3,8-extended phen compounds (**4**, **6**, and **9**) and 3-extended phen compounds (**12** and **16**); (b) terthiophene-based compounds **19**−**22**; (c) quathiophene-based compounds **23**−**26**.

By comparing the CV data of these linear heterocyclic aromatic compounds, it is found that the first oxidation of pyridine-terminated compounds requires a higher potential than that of imidazole-terminated ones, which can be reasonably accounted for by the higher electron-withdrawing nature of pyridine than imidazole. However, no cathodic reduction waves for this series of compounds can be observed in their CH_2Cl_2 solutions. Comparable CV results can be found for compounds with analogous molecular structures in literature.[12] For example, 2-pyridine- and 2-pyrimidine-terminated oligothiophene compounds reported by Yamamoto et al. show similar CV curves as well as first oxidation potentials in the range 0.75−0.88 V.[12a] Furthermore, our DPV results including the shapes of DPV curves and the values of first oxidation potentials are also consistent with those reported by Ma et al.[12b] On the basis of the above-mentioned electronic spectra and electrochemistry data, the energy level diagram of linear heterocyclic aromatic compounds **4**, **6**, **9**, **21**, and **26** can be estimated (Scheme 4) where pyridine-terminated quathiophene compound **26** gives the smallest band gaps of 2.54 eV.

As illustrated in the inset of Figure 3a, compounds **4**, **6**, **9**, **12**, and **16** show characteristic absorptions at 336−381 nm in their

electronic spectra, corresponding to the $\pi-\pi^*$ transitions between adjacent aromatic heterocycles. Among them, the maximum absorption wavelengths of linear phen-based heterocyclic aromatic compounds are obviously shifted to the lower energy bands from 351 nm in **1** to 369, 381, and 371 nm in **4**, **6**, and **9** when the number of aromatic heterocycles is increased, which are comparable with those in 3,8-phenyl extended phen and oligothiophene compounds from 357 to 413 nm.[13a] Similarly, the maximum absorption wavelengths of linear oligothiophene-based heterocyclic aromatic compounds are also shifted to the lower energy bands with the increase of delocalized π-system. Moreover, this family of linear heterocyclic aromatic compounds are fluorescence active, where the maximum absorption wavelengths of 1,10-phenanthroline-based linear heterocyclic aromatic compounds are obviously shifted to the lower energy bands from 415 nm in **1** to 445 nm in **4** and **9** and 452 nm in **6** when the number of aromatic heterocycles is increased. Similar bathochromic shifts have been found in the fluorescence emission spectra of linear oligothiophene-based compounds on going from 438 to 533 nm in the cases of three to six aromatic heterocycles.[13]

Fluorescence and electronic spectra of terthiophene and quathiophene derivatives **19**−**26** are depicted in parts b and c, respectively, of Figure 3. Similarly, the maximum absorption wavelengths of **19**−**26** are shifted to lower energy bands when the number of aromatic heterocycles is increased. Compared with the phen-based aromatic heterocyclic compounds showing blue fluorescence emissions, obvious red-shifts are observed for these oligophene-based compounds especially for pyridine-terminated terthiophene and quathiophene compounds **22** and **26**, where green fluorescence emissions are observed. The alteration of molecular rigidity, planarity, and electronic structures of oligothiophene-based compounds is suggested to be the main reason for the above-mentioned red-shifts in UV−vis absorption and fluorescence emission spectra.

CONCLUSIONS

In summary, a series of linear phen-based and oligothiophene-based heterocyclic aromatic fluorescence compounds with molecular lengths more than 2.30 nm (compounds **4**, **6**, **9**, and **26**), prepared by the combination of C−C bond and C−N bond cross-coupling reactions, has been described in this paper. They are believed to be good candidates for investigations on the optoelectronic nanomaterials and nanodevices. They all have delocalized π-systems and versatile D−A spacers with rigid backbones and high electron mobility as well as certain coordination sites in their molecular structures, i.e., the nitrogen atoms from the middle phen and the terminal imidazole and pyridine units. Synthetic, structural, computational, and spectral comparisons have been carried out for these mono- and bithiophene (β-methylthiophene)/imidazole/pyridine extended phen compounds and imidazole or pyridine extended oligothiophene compounds with different numbers of aromatic heterocycles and D−A spacers, in order to reveal the differences between cross-coupling approaches and experimental conditions on the C−C bond and C−N bond formation, molecular conformation, and dihedral angles between neighboring heterocycles, band gaps and energy levels, electronic, fluorescence and electrochemistry spectra of related compounds. Further studies are being undertaken on the coordination chemistry of this family of linear heterocyclic aromatic fluorescence compounds as well as the dye-sensitized solar cells, field-effect transistor,and light-emitting and photoresponsive properties of the corresponding coordination complexes, nanowires, nanocomposite films, and nanodevices.

EXPERIMENTAL SECTION

Materials and Measurements. All melting points were measured without any corrections. Heterocyclic aromatic compounds 3,8-di(thiophene-2,2′-yl)-1,10-phenanthroline (**7**),[7e] 3-(thiophene-2-yl)-1,10-phenanthroline (**14**),[7f] 3,3′′-dimethyl-2,2′:5′,2′′-terthiophene (**19**), and 3,3′′′-dimethyl-2,2′:5′,2′′:5′′,2′′′-quaterthiophene (**23**)[8a] were prepared from 3,8-dibromo-1,10-phenanthroline and 3-bromo-1,10-phenanthroline via literature methods.

Syntheses and Characterizations of Heterocyclic Aromatic Compounds 1−6, 8−13, and 15−26. *Compound* ***1***. Activated Mg turnings (3.55 g, 146.03 mmol) in 20 mL of anhydrous THF and a catalytic amount of iodine were added to a flame-dried 100 mL three-necked flask equipped with vigorous stirring at room temperature under argon atmosphere. Then a solution of 2-bromo-3-methylthiophene (8.5 mL, 75.50 mmol) in 10 mL of anhydrous THF was slowly dropped into the reaction mixture. Once the vigorous reaction had started, the rest of the 2-bromo-3-methylthiophene solution was added dropwise to keep the mixture refluxing over 20 min. The reaction mixture was allowed to proceed for 2 h at room temperature and cannulated into an ice-cooled solution of 3,8-dibromo-1,10-phenanthroline (10.05 g, 29.73 mmol) and [Ni(dppp)Cl_2] (0.46 g, 0.84 mmol) in dry THF (80 mL). After being stirred for 2 h at room temperature, the reaction mixture was refluxed for another 12 h and then cooled to room temperature. The reaction mixture was quenched with saturated NH_4Cl aqueous solution, extracted thoroughly with chloroform ($CHCl_3$) until no more products could be detected by TLC, washed with brine, and purified by column chromatography (silica gel, $CHCl_3$/petroleum ether 1:1). Light yellow solid product (9.11 g, 82.3%) was finally obtained after removal of solvent, and the product was dried in vacuo. The yellow single crystals of **1** suitable for X-ray diffraction measurement were obtained from ethyl acetate (EA) by slow evaporation in air at room temperature for 2 days. Mp: 215−216 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3061 (m), 1596 (m), 1540 (m), 1485 (m), 1439 (vs), 1377 (m), 1357 (m), 1281 (w), 1230 (w), 1103 (m), 1055 (m), 1026 (m), 904 (s), 770 (vs), 629 (w). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.36 (s, 2H, phen), 8.32 (d, 2H, J = 1.9 Hz, phen), 7.88 (s, 2H, phen), 7.38 (d, 2H, J = 5.1 Hz, thiophene-yl), 7.05 (d, 2H, J = 5.1 Hz, thiophene-yl), 2.47 (s, 6H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.5, 144.5, 135.3, 135.0, 133.7, 131.6, 130.3, 128.3, 127.0, 125.2, 15.0. EI-TOF-MS (m/z): calcd for $[C_{22}H_{16}N_2S_2]^+$ 372.5, found 372.0. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 351 (13120), 283 (18660), 256 (15800), 222 (17340) nm. Fluorescence emission in methanol, λ_{max} = 415 nm. Anal. Calcd for $C_{22}H_{16}N_2S_2$: C, 70.93; H, 4.33; N, 7.52. Found: C, 70.84; H, 4.26; N, 7.63.

Compounds ***2*** *and* ***3***. In the absence of light, NBS (1.72 g, 9.66 mmol) was dissolved in DMF (5 mL) and injected into a solution of **1** (1.80 g, 4.83 mmol) in DMF (20 mL) and $CHCl_3$ (10 mL) at 50 °C under argon atmosphere. The mixture was stirred for 5 h at this temperature and cooled to room temperature. To the mixture was added 50 mL of water, and the crude yellow solid was precipitated, filtered, and rinsed with a 50% ethanol/water solution. The desired compounds **2** and **3** were purified by silica gel column chromatography employing $CHCl_3$ solution to give yellow solid in yields of 0.16 g (7.3%) for **2** and 1.81 g (70.7%) for **3**, respectively. The light yellow single crystals of **2** and **3** suitable for X-ray diffraction determination were grown from $CHCl_3$ by slow evaporation in air at room temperature for 3 days. **2**. Mp: 120−121 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3060 (m), 2949 (w), 2920 (m), 1660 (m), 1604 (m), 1542 (m), 1477 (m), 1438 (vs), 1378 (s), 1059 (w), 906 (s), 831 (m), 734 (s), 715 (m).

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^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.36 (d, 1H, J = 2.0 Hz, phen), 9.28 (d, 1H, J = 2.1 Hz, phen), 8.32 (d, 1H, J = 2.1 Hz, phen), 8.25 (d, 1H, J = 2.8 Hz, phen), 7.87 (dd, 1H, J = 9.1 Hz, J = 8.8 Hz, phen), 7.38 (d, 1H, J = 5.1 Hz, thiophene-yl), 7.05 (d, 1H, J = 5.1 Hz, thiophene-yl), 7.0 (s, 1H, thiophene-yl), 2.46 (s, 3H, Me), 2.40 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.4, 150.1, 144.3, 143.9, 136.0, 135.5, 135.2, 135.1, 134.1, 133.4, 131.6, 130.6, 129.3, 128.5, 128.3, 127.3, 127.0, 125.4, 112.2, 15.1, 14.9. EI-TOF-MS (m/z): calcd for $[C_{22}H_{15}BrN_2S_2]^+$ 451.4, found 451.9; 449.9. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 355 (12200), 284 (15700), 260 (14280), 223 (14680) nm. Fluorescence emission in methanol, λ_{max} = 416 nm. Anal. Calcd for $C_{22}H_{15}BrN_2S_2$ (**2**): C, 58.54; H, 3.35; N, 6.21. Found: C, 58.63; H, 3,37; N, 6.18. **3**. Mp: 127−128 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3058 (m), 2948 (w), 2920 (m), 1655 (m), 1604 (m), 1560 (w), 1478 (m), 1438 (vs), 1378 (s), 1063 (m), 907 (s), 826 (s), 783 (w), 732 (s), 718 (w). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.33 (s, 2H, phen), 8.30 (d, 2H, J = 1.6 Hz, phen), 7.91 (s, 2H, phen), 7.04 (s, 2H, thiophene-yl), 2.43 (s, 6H, Me). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.2, 144.7, 135.9, 135.2, 134.9, 134.1, 129.3, 128.3, 127.2, 112.1, 15.0. EI-TOF-MS (m/z): calcd for $[C_{22}H_{14}Br_2N_2S_2]^+$ 530.3, found 529.9. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 357 (10920), 285 (12780), 265 (12440), 223 (12520) nm. Anal. Calcd for $C_{22}H_{14}Br_2N_2S_2$ (**3**): C, 49.83; H, 2.66; N, 5.28. Found: C, 49.81; H, 2,87; N, 5.26. Fluorescence emission in methanol, λ_{max} = 419 nm.

Compound ***4***. A solution containing **3** (1.01 g, 1.90 mmol), imidazole (5.20 g, 76.38 mmol), Cs_2CO_3 (3.68 g, 11.29 mmol), and anhydrous $CuSO_4$ (16 mg, 0.10 mmol) in DMF (30 mL) was heated to 140 °C for 72 h under argon atmosphere. The reaction mixture was then cooled to room temperature, and the solid was removed by filtration and rinsed thoroughly with $CHCl_3$ until no more products could be detected by TLC. The filtrate was concentrated using a rotary evaporator to give a brown oil, and the residue was dissolved in $CHCl_3$ (200 mL) and washed thoroughly with brine to remove excess imidazole which could be detected by TLC (iodine fuming). The organic layer was dried by anhydrous $MgSO_4$ and filtered. The solvent was removed at reduced pressure. The desired compound **4** was finally separated by silica gel column chromatography using chloroform as an eluent affording yellow solid in a yield of 0.59 g (62.0%). X-ray quality yellow crystals of **4** were grown by slow diffusion techniques in an H-shaped tube containing $CHCl_3$ and CH_3OH solution in one arm and ethyl ether solution in the other arm for one week. Mp: >300 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 2922 (w), 1644 (m), 1569 (s), 1503 (vs), 1429 (m), 1315 (w), 1236 (m), 1107 (s), 1043 (vs), 902 (w), 820 (m), 732 (m), 655 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.31 (d, 2H, J = 1.5 Hz, phen), 8.29 (d, 2H, J = 1.5 Hz, phen), 7.89 (s, 2H, phen), 7.84 (s, 2H, imidazolyl), 7.26 (s, 2H, imidazolyl), 7.21 (s, 2H, imidazolyl), 6.96 (s, 2H, thiophene-yl), 2.46 (s, 6H, Me). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.3, 143.8, 137.2, 135.6, 134.1, 133.6, 129.5, 128.5, 128.1, 127.3, 126.2, 121.5, 118.7, 14.3. EI-TOF-MS (m/z): calcd for $[C_{28}H_{20}N_6S_2]^+$ 504.6, found 504.1. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 369 (11720), 287 (14000), 224 (12260), 200 (19960) nm. Fluorescence emission in methanol, λ_{max} = 445 nm. Anal. Calcd for $C_{28}H_{20}N_6S_2$: C, 66.64; H, 3.99; N, 16.65. Found: C, 66.52; H, 3.75; N, 16.77.

Compounds ***5*** *and* ***6***. A degassed three-necked flask containing **3** (1.00 g, 1.89 mmol), 4-pyridineboronic acid (1.02 g, 8.30 mmol), $[Pd(PPh_3)_4]$ (0.10 g, 0.09 mmol), and Na_2CO_3 (4.00 g, 37.74 mmol) was dissolved in a degassed mixture of toluene (40.0 mL), THF (10.0 mL), and H_2O (10.0 mL). The mixture was stirred and refluxed under argon for 48 h. After the mixture was cooled to room temperature, $CHCl_3$ (100 mL) was added, and the organic phase was washed with brine, separated, and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure, and the solid residue was purified by silica gel column chromatography ($CHCl_3/CH_3OH$ = 40:1) to provide the desired monosubstituted product **5** as light yellow solid and disubstituted product **6** as brown solid in yields of 0.55 g (55.6%) and 0.22 g (22.2%), respectively. The yellow single crystals of **6** suitable for X-ray diffraction determination were grown from a solution of $CHCl_3$ by slow evaporation in air at room temperature for 5 days. **5**. Mp: 289−291 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 1595 (vs), 1437 (m), 1112 (w), 900 (m), 818 (m), 731 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.35 (d, J = 2.0 Hz, 1H, phen), 9.27 (d, J = 2.0 Hz, 1H, phen), 8.64 (d, J = 4.3 Hz, 2H, pyridinyl), 8.34 (d, J = 2.2 Hz, 1H, phen), 8.25 (d, J = 2.2 Hz, 1H, phen), 7.89 (d, J = 1.3 Hz, 2H, phen), 7.55 (d, J = 5.7 Hz, 2H, pyridinyl), 7.48 (s, 1H, thiophene-yl), 7.02 (s, 1H, thiophene-yl), 2.50 (s, 3H, Me), 2.41 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4, 150.3, 150.3, 144.9, 144.8, 141.0, 140.3, 136.7, 136.0, 135.7, 135.2, 135.0, 134.1, 129.7, 129.7, 129.4, 128.4, 128.3, 127.2, 127.2, 119.6, 112.2, 15.3, 15.0. EI-TOF-MS (m/z): calcd for $[C_{27}H_{18}BrN_3S_2]^+$ 528.5, found 526.9, 449 $[M - Br]^+$. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 374 (15920), 285 (12880), 229 (12280) nm. Fluorescence emission in methanol, λ_{max} = 440 nm. Anal. Calcd for $C_{27}H_{18}BrN_3S_2$ (**5**): C, 61.36; H, 3.43; N, 7.95. Found: C, 61.22; H, 3.35; N, 8.12. **6**. Mp: >300 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3026 (m), 1539 (vs), 1422 (m), 1377 (m), 1094 (m), 813 (m), 735 (w). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.37 (d, J = 2.1 Hz, 2H, phen), 8.68−8.59 (m, 4H, pyridinyl), 8.36 (d, J = 2.1 Hz, 2H, phen), 7.91 (s, 2H, phen), 7.59−7.51 (m, 4H, pyridinyl), 7.48 (s, 2H, thiophene-yl), 2.51 (s, 6H, Me). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5, 150.3, 144.9, 141.0, 140.4, 136.8, 135.7, 135.0, 129.7, 128.4, 127.3, 119.6, 15.3. EI-TOF-MS (m/z): calcd for $[C_{32}H_{22}N_4S_2]^+$ 526.7, found 525.9. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 381 (17960), 308 (13740), 239 (10380) nm. Fluorescence emission in methanol, λ_{max} = 452 nm. Anal. Calcd for $C_{32}H_{22}N_4S_2$ (**6**): C, 72.98; H, 4.21; N, 10.64. Found: C, 72.76; H, 4.08; N, 10.77.

Compound ***8***. In the absence of light, NBS (2.11 g, 11.86 mmol) was dissolved in DMF (10 mL) and injected into a solution of 3,8-di(thiophene-2′,2″-yl)-1,10-phenanthroline **7** (2.0 g, 5.81 mmol) in DMF (30 mL) and $CHCl_3$ (10 mL) at 50 °C under argon atmosphere. The mixture was stirred for 5 h at this temperature, and the resulting slurry was cooled to 0 °C and filtered. The solid was rinsed with distilled water and air-dried to afford **8** (2.67 g, 91.4%) as a yellow solid. No further purification was conducted, and the solid was used directly for the next synthetic step. Mp: 251−253 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 2973 (w), 2930 (m), 2353 (w), 1645 (m), 1605 (m), 1554 (w), 1474 (w), 1440 (vs), 1425 (s), 1047 (m), 969 (w), 901 (w), 788 (m), 743 (w). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.37 (s, 2H, phen), 8.27 (s, 2H, phen), 7.84 (s, 2H, phen), 7.35 (d, 2H, J = 3.8 Hz, thiophene-yl), 7.16 (d, 2H, J = 3.7 Hz, thiophene-yl). EI-TOF-MS (m/z): calcd for $[C_{20}H_{10}Br_2N_2S_2]^+$ 502.2, found 503.9, 501.8. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 372 (13660), 361 (13700), 295 (10100) nm. Fluorescence emission in methanol, λ_{max} = 422 nm. Anal. Calcd for $C_{20}H_{10}Br_2N_2S_2$ (**8**): C, 47.83; H, 2.01; N, 5.58. Found: C, 47.73; H, 2.08; N, 5.64.

Compound ***9***. The synthetic procedure for preparation of compound **4** was followed using **8** (1.28 g, 2.55 mmol), imidazole (5.20 g, 76.34 mmol), Cs_2CO_3 (3.33 g, 10.21 mmol), and anhydrous $CuSO_4$ (20 mg, 0.13 mmol) in DMF (30 mL). The desired compound **9** was purified by sil-gel column chromatography employing a binary gradient formed from $CHCl_3$ (solution A) and 3.3% CH_3OH in $CHCl_3$ (solution B). The chromatographic run started with the solution of A, followed by a gradient increase of solution B from 50% to 100%. After the byproduct eluted out, compound **9** was isolated as yellow solid in a yield of 0.59 g (48.4%). X-ray quality yellow crystals of **9** were grown by slow diffusion techniques in an H-shaped tube containing the $CHCl_3$ solution in one arm and the ethyl ether solution in the other arm for one week. Mp: >300 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3407 (br s), 1644 (m), 1563 (s), 1503 (vs), 1428 (w), 1304 (w), 1232 (w), 1107 (m), 1077 (m), 1049 (m), 1035 (m), 902 (w), 802 (m), 730 (m), 654 (m).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.43 (d, 2H, J = 1.5 Hz, phen), 8.35 (d, 2H, J = 2.0 Hz, phen), 7.89 (s, 2H, phen), 7.87 (s, 2H, imidazolyl), 7.49 (d, 2H, J = 3.8 Hz, thiophene-yl), 7.30 (s, 2H, imidazolyl), 7.24 (s, 2H, imidazolyl), 7.12 (d, 2H, J = 3.7 Hz, thiophene-yl). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 147.8, 145.2, 139.7, 136.8, 136.3, 131.6, 130.7, 128.8, 128.6, 127.4, 124.1, 119.9, 119.8. EI-TOF-MS (m/z): calcd for $[C_{26}H_{16}N_6S_2]^+$ 476.6, found 476.1. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 371 (23700), 292 (17140), 221 (15360), 201 (16380) nm. Fluorescence emission in methanol, λ_{max} = 445 nm. Anal. Calcd for $[C_{26}H_{16}N_6S_2]$: C, 65.53; H, 3.38; N, 17.63. Found: C, 65.37; H, 3.31; N, 17.75.

Compound ***10***. Similar to the preparation of **1**, a Grignard reagent was generated in situ from 2-bromo-3-methylthiophene (3.3 mL, 28.2 mmol) in dry THF (5 mL) and activated Mg turnings (0.96 g, 39.49 mmol) in dry THF (10 mL). This mixture was then cannulated into a solution of 3-bromo-1,10-phenanthroline (5.80 g, 22.39 mmol) and $[Ni(dppp)Cl_2]$ (0.15 g, 0.28 mmol) in dry THF (50 mL). Compound **10** was separated by silica gel column chromatography using $CHCl_3$/petroleum ether as a gradient eluent and subsequent recrystallization from $CHCl_3$ affording light yellow solid in a yield of 5.61 g (91.3%). Mp: 141−144 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3400(br s), 2971 (m), 1649 (m), 1503 (w), 1426 (s), 1091 (s), 1049 (s), 907 (m), 833 (m), 734 (s), 711 (m). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.33 (d, 1H, J = 2.0 Hz, phen), 9.24 (m, 1H, phen), 8.30 (dd, 2H, J = 5.0 Hz, J = 2.8 Hz, phen), 7.85 (s, 2H, phen), 7.67(dd, 1H, J = 8.0 Hz, J = 4.4 Hz, phen), 7.37 (d, 1H, J = 5.1 Hz, thiophene-yl), 7.04 (d, 1H, J = 5.1 Hz, thiophene-yl), 2.45 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.4, 150.2, 146.0, 144.6, 135.9, 135.1, 134.8, 133.6, 131.5, 130.2, 128.5, 128.2, 127.0, 126.4, 125.1, 122.9, 15.0. EI-TOF-MS (m/z): calcd for $[C_{17}H_{12}N_2S]^+$ 276.4, found 276.0. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 333 (5640), 265 (13060), 225 (13860) nm. Fluorescence emission in methanol, λ_{max} = 439 nm. Anal. Calcd for $C_{17}H_{12}N_2S$: C, 73.88; H, 4.38; N, 10.14. Found: C, 73.64; H, 4.21; N, 10.05.

Compound ***11***. In the absence of light, a solution of NBS (2.80 g, 15.73 mmol) in DMF (10 mL) was injected into a solution of compound **10** (4.30 g, 15.58 mmol) in DMF (30 mL) at 40 °C under argon atmosphere. The mixture was stirred for 5 h at this temperature, and the resulting solution was cooled to 0 °C, poured into an aqueous NaCl solution (100 mL), and extracted with $CHCl_3$ (3 × 50 mL). The solvent was removed in vacuo using a rotary evaporator, and the residue was purified by silica-gel column chromatography using $CHCl_3$/petroleum ether as a gradient eluent affording yellow solid yield of 5.0 g (90.3%). Melting point: 186−187 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 2947 (m), 1666 (m), 1614 (w), 1586 (m), 1555 (w), 1501 (m), 1449 (s), 1424 (vs), 1373 (w), 1339 (w), 1102 (w), 1068 (w), 978 (w), 891 (s), 867 (m), 831 (s), 820 (s), 732 (vs), 657 (w) 528 (w). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.23 (d, 1H, J = 2.1 Hz, phen), 9.19 (dd, 1H, J = 4.3 Hz, J = 1.5 Hz, phen), 8.23 (dd, 1H, J = 8.1 Hz, J = 1.5 Hz, phen), 8.17 (d, 1H, J = 2.2 Hz, phen), 7.78 (m, 2H, phen), 7.63 (dd, 1H, J = 8.1 Hz, J = 4.3 Hz, phen), 6.96 (s, 1H, thiophene-yl), 2.36 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.6, 150.1, 146.1, 145.0, 136.2, 136.0, 135.4, 135.0, 134.2, 129.3, 128.9, 128.3, 127.4, 126.5, 123.3, 112.1, 15.0. EI-TOF-MS (m/z): calcd for $[C_{17}H_{11}BrN_2S]^+$ 355.3, found 353.9; 355.9. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 337(5560), 268 (12600), 231 (12440) nm. Fluorescence emission in methanol, λ_{max} = 449 nm. Anal. Calcd for $C_{17}H_{11}BrN_2S$: C, 57.48; H, 3.12; N, 7.89. Found: C, 57.29; H, 3.24; N, 8.02.

Compounds ***12*** *and* ***13***. The synthetic procedure for preparation of compound **4** was followed using **11** (0.73 g, 2.05 mmol), imidazole (1.40 g, 20.56 mmol), Cs_2CO_3 (1.34 g, 4.10 mmol), and anhydrous $CuSO_4$ (16.0 mg, 0.10 mmol) in DMF (20 mL). Compound **12** was separated by silica gel column chromatography using chloroform/petroleum ether as a gradient eluent affording pale yellow solid in a yield of 0.44 g (62.6%). Product **13** was obtained by the reaction of compound **12** (0.01 g, 0.03 mmol) in $CHCl_3$ (10 mL) with a saturated solution of NH_4PF_6 dissolved in a mixture of acetone and deionized water. The green yellow crystals suitable for X-ray diffraction determination were gained by slow evaporation of the filtrate for 6 days at room temperature (7.2 mg, 50.5%). **12**. Mp: 250−252 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3066 (m), 1616 (w), 1571 (m), 1494 (s), 1390 (m), 1346 (w), 1240 (m), 1101 (w), 1047 (m), 888 (m), 836 (m), 822 (w), 734 (vs), 710 (w), 658 (m), 622 (w). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.29 (s, 1H, phen), 9.20 (d, 1H, J = 2.9 Hz, phen), 8.25 (s, 2H, phen), 7.82 (s, 2H, phen +1H, imidazolyl), 7.64 (dd, J = 7.8 Hz, J = 4.2 Hz, 1H, phen), 7.25 (s, 1H, imidazolyl), 7.21 (s, 1H, imidazolyl), 6.93 (s, 1H, thiophene-yl), 2.42 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.6, 150.0, 146.0, 145.0, 138.0, 136.6, 136.0, 135.0, 134.4, 130.5, 129.6, 128.9, 128.8, 128.1, 127.4, 126.2, 123.2, 122.4, 119.7, 15.2. EI-TOF-MS (m/z): calcd for $[C_{20}H_{14}N_4S]^+$ 342.4, found 342.0. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 336 (8140), 270 (14620), 225 (14280) nm. Fluorescence emission in methanol, λ_{max} = 434 nm. Anal. Calcd for $C_{20}H_{14}N_4S$: C, 70.15; H, 4.12; N, 16.36. Found: C, 70.07; H, 4.04; N, 16.45. The ^{1}H NMR data of **13** could not be obtained since it is nearly insoluble in common solvents. Main FT-IR absorptions (KBr pellets, cm^{-1}): 1621 (w), 1595 (w), 1570 (m), 1511 (m), 1456 (m), 1301 (w), 1112 (m), 1040 (m), 841 (vs), 748 (w), 724 (m), 621 (w), 558 (s). Anal. Calcd for $C_{20}H_{15}N_4SF_6P$: C, 49.18; H, 3.10; N, 11.47. Found: C, 49.07; H, 3.02; N, 11.54.

Compound ***15***. The synthetic procedure for preparation of compound **11** was followed using 3-(thiophene-2-yl)-1,10-phenanthroline **14** (2.30 g, 8.77 mmol), NBS (1.60 g, 8.98 mmol), and DMF (25 mL). Compound **15** was separated by silica gel column chromatography using chloroform/petroleum ether as a gradient eluent affording brown solid in a yield of 2.40 g (80.2%). Mp: 173−175 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3048 (m), 1654 (m), 1590 (m), 1500 (m), 1450 (s), 1428 (s), 1333 (w), 1099 (m), 966 (w), 893 (w), 866 (m), 827 (m), 728 (s), 631 (w). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.35 (d, 1H, J = 1.7 Hz, phen), 9.21 (d, 1H, J = 3.2 Hz, phen), 8.25 (m, 2H, phen), 7.80 (dd, 2H, J = 12.2, 8.8 Hz, phen), 7.65 (dd, 1H, J = 8.0, 4.3 Hz, phen), 7.32 (d, 1H, J = 3.8 Hz, thiophene-yl), 7.14 (d, 1H, J = 3.8 Hz, thiophene-yl). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.5, 147.4, 145.8, 145.1, 145.0, 141.8, 136.3, 131.4, 128.9, 128.7, 128.5, 127.4, 126.4, 125.3, 123.1, 113.6. EI-TOF-MS (m/z): Calcd. for $[C_{16}H_9BrN_2S]^+$ 341.2, found 339.9; 341.9. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 335 (12120), 283 (13640), 268 (13500), 232 (14920) nm. Fluorescence emission in methanol, λ_{max} = 398 nm. Anal. Calcd for $C_{16}H_9BrN_2S$: C, 56.32; H, 2.66; N, 8.21. Found: C, 56.14; H, 2.58; N, 8.39.

Compound ***16***. The synthetic procedure for preparation of compound **4** was followed using **15** (1.12 g, 3.28 mmol), imidazole (2.20 g, 32.31 mmol), Cs_2CO_3 (2.13 g, 6.55 mmol), and anhydrous $CuSO_4$ (26.0 mg, 0.16 mmol) in DMF (30 mL). Compound **16** was purified by silica gel column chromatography using chloroform/petroleum ether as a gradient eluent affording 0.42 g (39.0%) yellowish-brown solid. The light yellow single crystals of **16** suitable for X-ray diffraction determination were grown from a solution of $CHCl_3$ by slow evaporation in air at room temperature for one week. Mp: >300 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3407(br s), 1656 (m), 1591 (w), 1559 (s), 1509 (m), 1495 (vs), 1424 (m), 1350 (w), 1305 (m), 1236 (w), 1102 (m), 1078 (s), 918 (w), 899 (m), 865 (w), 827 (m), 726 (m), 650 (m). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.41 (s, 1H, phen), 9.22 (d, 1H, J = 3.1 Hz, phen), 8.33 (s, 1H, phen), 8.27 (d, 1H, J = 7.9 Hz, phen), 7.84 (dd, 3H, J = 12.4, 8.7 Hz, phen, imidazolyl), 7.66 (dd, 1H, J = 7.8, 4.2 Hz, phen), 7.47 (d, 1H, J = 3.6 Hz, thiophene-yl), 7.29 (s, 1H, imidazolyl), 7.23 (s, 1H, imidazolyl), 7.10 (d, 1H, J = 3.5 Hz, thiophene-yl). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 150.6, 147.3, 146.0, 145.4, 139.5, 136.7, 136.3, 136.0, 131.4, 130.6, 128,7, 128.5, 128.3, 127.5, 126.2, 123.9, 123.1, 119.8, 119.6. EI-TOF-MS (m/z): calcdfor $[C_{19}H_{12}N_4S]^+$ 328.4, found 328.0; UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 341 (10780), 283 (11220), 271 (11060), 222 (11520) nm. Anal. Calcd for $[C_{19}H_{12}N_4S]$: C, 69.49; H, 3.68; N, 17.06. Found: C, 69.32; H, 3.61; N, 17.19.

Compound ***17***. The synthetic procedure for preparation of compound **4** was followed using 2,5-dibromothiophene (6.00 g, 24.80 mmol), imidazole (5.80 g, 25.32 mmol), K_2CO_3 (3.43 g, 24.80 mmol), and anhydrous CuI (0.12 g, 0.62 mmol) in DMF (30 mL). The crude compound was purified by sil-gel column chromatography (EA/petroleum ether = 1:3) to provide the desired monosubstituted product **17** as light yellow solid in a yield of 4.16 g (73.2%) and disubstituted byproduct 2,5-di(1*H*-imidazol-1-yl)thiophene as a tight beige solid in a yield of 0.14 g (2.6%). The colorless single crystals of **17** suitable for X-ray diffraction determination were grown from a solution of EA by slow evaporation in air at room temperature for 3 days. Mp: 186−187 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3103 (m), 1655 (m), 1560 (s), 1483 (m), 1445 (m), 1355 (w), 1330 (w), 1300 (m), 1243 (s), 1197 (m), 1101 (m), 1053 (m), 1037 (m), 969 (m), 905 (m), 833 (m), 793 (s), 738 (m), 654 (m), 614 (w), 559 (w), 510 (m). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.74 (s, 1H, imidazolyl), 7.18 (s, 1H, imidazolyl), 7.15 (s, 1H, imidazolyl), 6.99 (d, 1H, J = 4.0 Hz, thiophene-yl), 6.80 (d, 1H, J = 4.0 Hz, thiophene-yl). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 139.1, 136.9, 130.5, 129.0, 120.1, 119.8, 108.9. EI-TOF-MS (m/z): calcd for $[C_7H_5BrN_2S]$ 229.1, found 227.9. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 264 (9550) and 223 (9600) nm. Anal. Calcd for $C_7H_5BrN_2S$: C, 36.70; H, 2.20; N, 12.23. Found: C, 36.58; H, 2.06; N, 12.34.

Compound ***18***. Activated Mg turnings (0.40 g, 15.15 mmol) in 20 mL of anhydrous THF and a catalytic amount of bromoethane (0.10 mL, 1.3 mmol) were added to a flame-dried 100 mL three-necked flask equipped with vigorous stirring at room temperature under argon atmosphere. The temperature of the mixture increased about 2 °C after addition of bromoethane, and then a solution of **17** (1.50 g, 6.55 mmol) in 10 mL of anhydrous THF was dropped into the reaction mixture. The color of the solution became violet once the reaction had started. The mixture was kept refluxing over 30 min, allowed to proceed for 2 h at room temperature, and then cannulated into an ice-cooled solution of 3,8-dibromo-1,10-phenanthroline (1.00 g, 2.96 mmol) in dry THF (30 mL). After being stirred for 2 h at room temperature, the reaction mixture was refluxed for another 12 h, cooled to room temperature, quenched with saturated NH_4Cl aqueous solution, extracted thoroughly with chloroform ($CHCl_3$), and washed with brine. The desired compound **18** was purified by sil-gel column chromatography employing a binary gradient formed from $CHCl_3$ (solution A) and 5% CH_3OH in $CHCl_3$ (solution B). The chromatographic run started with the solution of A, followed by a gradient increase of solution B from 50% to 100%. After unreacted materials were eluted out, compound **18** was isolated as pale yellow solid in a yield of 0.59 g (11.8%). The pale yellow single crystals of **18** suitable for X-ray diffraction measurement were obtained from $CHCl_3$ by slow evaporation in air at room temperature for 5 days. Mp: >300 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3102 (s), 2922 (w), 1615 (w), 1590 (w), 1550 (m), 1525 (m), 1494 (w), 1456 (s), 1426 (m), 1391 (s), 1292 (s), 1256 (s), 1211 (m), 1125 (m), 1100 (s), 1059 (w), 904 (vs), 846 (w), 824 (m), 797 (s), 773 (s), 752 (s), 707 (m), 683 (vs), 544 (w). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.18 (s, 1H, phen), 8.49 (s, 1H, phen), 8.40 (s, 1H, phen), 7.77 (s, 2H, phen), 7.37 (s, 1H, imidazolyl), 7.32 (s, 1H, imidazolyl), 7.01 (s, 2H, thiophene-yl), 6.73 (s, 1H, thiophene-yl). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.9, 144.1, 144.0, 139.8, 137.6, 130.0, 129.8, 128.1, 127.7, 127.6, 126.5, 125.7, 123.8, 123.6, 122.9, 121.6, 120.6. EI-TOF-MS (m/z): calcd for $[C_{19}H_{10}Br_2N_4S]$ 486.18, found 485.8 and 406.9. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 351 (1350), 334 (2950), 244 (52650), 209 (21150) nm. Anal. Calcd for $C_{19}H_{10}Br_2N_4S$: C, 46.94; H, 2.07; N, 11.52. Found: C, 46.49; H, 1.96; N, 11.73.

Compound ***20***. The synthetic procedure for preparation of compound **8** was followed by treatment of **19** (2.11 g, 7.63 mmol) with NBS (2.64 g, 15.41 mmol) in DMF (30 mL). The mixture was stirred for 3 h at 50 °C, and the resulting slurry was cooled to 0 °C and filtered. The solid was rinsed with distilled water and air-dried to afford compound **20** (3.22 g, 97.2%) as a pale yellow solid. No further purification was conducted, and **20** was used directly for the next synthetic step. Mp: 137−138 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3408 (s), 2914 (w), 1643 (m), 1502 (w), 1423 (m), 1251 (w), 824 (m), 783 (s), 619 (m). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.03 (s, 2H, thiophene-yl), 6.88 (s, 2H, thiophene-yl), 2.37 (s, 6H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.4, 134.7, 134.0, 132.1, 126.9, 110.3, 15.3. EI-TOF-MS (m/z): calcd for $[C_{14}H_{10}Br_2S_3]^+$ 434.2, found 433.7. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 348 (38150) and 252 (15650) nm. Fluorescence emission in methanol, λ_{max} = 438 and 420 nm. Anal. Calcd for $C_{14}H_{10}Br_2S_3$: C, 38.72; H, 2.32. Found: C, 38.68; H, 2.29.

Compound ***21***. The synthetic procedure for preparation of compound **4** was followed in DMF (20 mL) using **20** (0.43 g, 1 mmol), imidazole (1.36 g, 19.98 mmol), anhydrous $CuSO_4$ (8.0 mg, 0.05 mmol), and Cs_2CO_3 (0.65 g, 2.00 mmol) as the starting materials. The mixture was heated to 140 °C for 40 h under argon atmosphere. The crude compound was purified by silica gel column chromatography (EA/PE = 1:1) to provide the desired product **21** as yellow solid in a yield of 0.26 g (64.2%). The yellow single crystals of **21** suitable for X-ray diffraction determination were grown from a solution of chloroform by slow evaporation in air at room temperature for 7 days. Melting point: 198−199 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3411 (s), 3082 (w), 2945 (w), 1647 (m), 1566 (s), 1527 (s), 1485 (s), 1309 (m), 1113 (m), 1041 (s), 900 (w), 778 (m), 649 (m), 496 (w). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.77 (s, 2H, imidazolyl), 7.20 (d, J = 10.1 Hz, 4H, imidazolyl), 7.10 (s, 2H, thiophene-yl), 6.83 (s, 2H, thiophene-yl), 2.43 (s, 6H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 136.6, 136.3, 135.4, 133.4, 130.4, 126.6, 126.4, 122.4, 119.7, 15.7. EI-TOF-MS (m/z): calcd for $[C_{20}H_{16}N_4S_3]^+$ 408.6, found 407.9. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 357 (47700) and 245 (23850) nm. Fluorescence emission in methanol, λ_{max} = 460 nm. Anal. Calcd for $C_{20}H_{16}N_4S_3$: C, 58.79; H, 3.95; N, 13.71. Found: C, 58.70; H, 3.91; N, 13.82.

Compound ***22***. The synthetic procedure for preparation of compound **6** was followed using **20** (0.22 g, 0.50 mmol), pyridin-4-ylboronic acid (0.15 g, 1.22 mmol), $[Pd(PPh_3)_4]$ (34.7 mg, 0.03 mmol), Cs_2CO_3 (0.27 g, 0.83 mmol), dioxane (20 mL), and H_2O (2 mL). The reaction mixture was stirred at 100 °C for 48 h under argon. The crude compound was purified by silica gel column chromatography employing an EA solution to provide the desired product **22** as red solid in a yield of 65.1%. Mp: 230−231 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3411 (s), 3042 (w), 1655 (w), 1591 (s), 1410 (m), 1062 (m), 811 (s), 641 (w), 620 (w). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.59 (d, J = 4.3 Hz, 4H, Py), 7.46 (d, J = 5.4 Hz, 4H, Py), 7.34 (s, 2H, thiophene-yl), 7.20 (s, 2H, thiophene-yl), 2.48 (s, 6H, Me). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 150.0, 141.2, 138.0, 136.2, 135.5, 133.0, 129.9, 126.4, 119.4, 15.8. EI-TOF-MS (m/z): calcd for $[C_{24}H_{18}N_2S_3]^+$ 430.6, found 430.1. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 399 (45800) and 266 (21150) nm. Anal. Calcd for $C_{24}H_{18}N_2S_3$: C, 66.94; H, 4.21; N, 6.51. Found: C, 66.85; H, 4.11; N, 6.65.

Compound ***24***. The synthetic procedure for preparation of compound **20** was followed using **23** (2.00 g, 5.58 mmol) and NBS (1.99 g, 11.16 mmol) in DMF (30 mL). The solid was rinsed with distilled water and air-dried to afford **24** (2.59 g, 89.9%) as a yellow solid. No further purification was conducted, and **24** was used directly for the next synthetic step. The light brown single crystals of **24** suitable for X-ray diffraction determination were grown from a solution of chloroform by slow evaporation in air at room temperature for 2 days. Mp: 195−196 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3411 (s), 2945 (w), 2356 (w),1647 (m), 1556 (s), 1527 (s), 1485 (s), 1309 (m), 1232 (m), 1113 (m), 1041 (s), 900 (w), 805 (m), 778 (m), 649 (m). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.11 (s, 2H, thiophene-yl), 6.98 (s, 2H, thiophene-yl), 6.86 (s, 2H, thiophene-yl), 2.37 (s, 6H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 136.9, 134.7, 134.5, 134.0, 126.5, 124.0, 110.2,

15.4. EI-TOF-MS (m/z): calcd for $[C_{18}H_{12}Br_2S_4]^+$ 516.4, found 515.7. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 384 (37700) and 252 (14050) nm. Fluorescence emission in methanol, λ_{max} = 482 and 457 nm. Anal. Calcd for $C_{18}H_{12}Br_2S_4$: C, 41.87; H, 2.34. Found: C, 41.81; H, 3.81.

Compound ***25***. The synthetic procedure for preparation of compound **21** was followed using **24** (0.63 g, 1.23 mmol), imidazole (1.59 g, 23.38 mmol), anhydrous $CuSO_4$ (9.6 mg, 0.06 mmol), and Cs_2CO_3 (0.80 g, 2.46 mmol) in DMF (20 mL). The mixture was heated to 140 °C for 40 h under argon atmosphere. The crude compound was purified by silica gel column chromatography (EA/CH_3OH = 30:1) to provide the brown product **25** in a yield of 0.36 g (61.2%). Mp: 227−228 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3411 (s), 2354 (w), 1650 (m), 1556 (m), 1517 (s), 1309 (m), 1248 (w), 1045 (s), 1028 (w), 790 (w), 653 (w). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.78 (s, 2H, imidazolyl), 7.19 (d, J = 8.3 Hz, 4H, imidazolyl), 7.16 (s, 2H, thiophene-yl), 7.06 (d, J = 2.3 Hz, 2H, thiophene-yl), 6.82 (s, 2H, thiophene-yl), 2.43 (s, 6H, Me). EI-TOF-MS (m/z): calcd for $[C_{24}H_{18}N_4S_4]^+$ 490.7, found 489.8. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 389 (57700) and 248 (24300) nm. Fluorescence emission in methanol, λ_{max} = 452 and 435 nm. Anal. Calcd for $C_{24}H_{18}N_4S_4$: C, 58.75; H, 3.70; N, 11.42. Found: C, 58.68; H, 3.60; N, 11.54.

Compound ***26***. The synthetic procedure for preparation of compound **22** was followed using **25** (0.13 g, 0.25 mmol), pyridin-4-ylboronic acid (76.8 mg, 0.63 mmol), $[Pd(PPh_3)_4]$ (17.4 mg, 0.015 mmol), Cs_2CO_3 (0.27 g, 0.81 mmol), dioxane (20 mL), and H_2O (2 mL). The reaction mixture was stirred at 100 °C for 48 h under argon. The crude compound was purified by silica gel column chromatography employing EA solution to provide the desired product **26** as light red solid in a yield of 0.081 g (62.8%). The red single crystals of **26** suitable for X-ray diffraction determination were grown from a solution of chloroform by slow evaporation in air at room temperature for 5 days. Mp: 269−270 °C. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3421 (s), 3064 (w), 1643 (w), 1592 (s), 1413 (m), 1265 (m), 1095 (m), 1054 (s), 823 (s), 651 (s). ^1H NMR (500 MHz, $CDCl_3$) δ: 8.59 (d, J = 4.9 Hz, 4H, Py), 7.44 (d, J = 5.1 Hz, 4H, Py), 7.33 (s, 2H, thiophene-yl), 7.19 (d, J = 3.6 Hz, 2H, thiophene-yl), 7.14 (d, J = 3.7 Hz, 2H, thiophene-yl), 2.48 (s, 6H, Me). EI-TOF-MS (m/z): calcd for $[C_{28}H_{20}N_2S_4]^+$ 512.7, found 511.9. UV−vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 420 (27750), 261 (9150), and 229 (8100) nm. Fluorescence emission in methanol, λ_{max} = 533 and 507 nm. Anal. Calcd for $C_{28}H_{20}N_2S_4$: C, 65.59; H, 3.93; N, 5.46. Found: C, 65.50; H, 3.86; N, 5.58.

X-ray Data Collection and Structural Determination. Single-crystal samples of **1**−**4**, **6**, **9**, **13**, **16**−**18**, **21**, **24**, and **26** were glue-covered and mounted on glass fibers and then used for data collection. Crystallographic data of **2** were collected on a Rigaku Mercury CCD area-detector, while the other seven samples were collected on a Bruker SMART 1K CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). In the cases of **2**, the original data files generated by Crystalclear were transformed to SHELXTL97 format by TEXSAN program.[14,15] The crystal systems were determined by laue symmetry, and the space groups were assigned on the basis of systematic absences using XPREP. Absorption corrections were performed to all data and the structures were solved by direct methods and refined by full-matrix least-squares method on F_{obs}^2 by using the SHELXTL-PC software package.[16] All non-H atoms were anisotropically refined, and all hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The summary of the crystal data, experimental details, and refinement results for 13 compounds (**1**−**4**, **6**, **9**, **13**, **16**−**18**, **21**, **24**, and **26**) is listed in Table 1, whereas bond distances and angles related to the metal centers are given in Table SI1 Supporting Information. In addition, the dihedral angles between adjacent heterocycles for compounds **1**−**4**, **6**, **9**, **13**, **16**−**18**, **21**, **24**, and **26** are illustrated in Table SI3 (Supporting Information) and hydrogen-bonding parameters are tabulated in Table SI4 (Supporting Information).

■ ASSOCIATED CONTENT

Supporting Information. Tables of selected bond lengths and angles and intermolecular hydrogen bonds; figures of $\pi-\pi$ stacking interactions; ^1H, ^{13}C, $^1H-^1H$ COSY NMR and EI-TOF-MS spectra and cyclic voltammetry diagrams for related compounds. CCDC nos. 777364−777371 for **1**−**4**, **6**, **9**, **13**, **16** and 805872−805876 for **17**, **18**, **21**, **24**, and **26**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173–205. (b) Mishra, A.; Ma, C. Q.; Bauerle, P. *Chem. Rev.* **2009**, *109*, 1141–1276. (c) Cheng, Y. J.; Yang, S. H.; Hsu, C. S. *Chem. Rev.* **2009**, *109*, 5868–5923. (d) Chen, J. W.; Cao, Y. *Acc. Chem. Res.* **2009**, *42*, 1709–1718. (e) Wu, W.; Liu, Y.; Zhu, D. *Chem. Soc. Rev.* **2010**, *39*, 1489–1502.

(2) Selected examples: (a) Grushin, V. V.; Herron, N.; LeCloux, D. D.; Marshall, W. J.; Petrov, V. A.; Wang, Y. *Chem. Commun.* **2001**, *16*, 1494–1495. (b) Kim, C.; Forrest, S. R. *Adv. Mater.* **2003**, *6*, 541–545. (c) Fang, Q.; Xu, B.; Jiang, B.; Fu, H.; Chen, X.; Cao, A. *Chem. Commun.* **2005**, *13*, 1788. (d) Du, C.; Ye, S.; Chen, J.; Guo, Y.; Liu, Y.; Lu, K.; Liu, Y.; Qi, T.; Gao, X.; Shuai, Z.; Yu, G. *Chem.—Eur. J.* **2009**, *33*, 8275–8282. (e) Hamwi, S.; Meyer, J.; Kroeger, M.; Winkler, T.; Witte, M.; Riedl, T.; Kahn, A.; Kowalsky, W. *Adv. Func. Mater.* **2010**, *11*, 1762–1766.

(3) Selected examples: (a) Yoon, M. H.; Facchetti, A.; Stern, C. E.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 5792–5801. (b) Qi, T.; Guo, Y.; Liu, Y.; Xi, H.; Zhang, H.; Gao, X.; Liu, Y.; Lu, K.; Du, C.; Yu, G.; Zhu, D. *Chem. Commun.* **2008**, *46*, 6227–6229. (c) Jung, Y.; Kline, R. J.; Fischer, D. A.; Lin, E. K.; Heeney, M.; McCulloch, I.; DeLongchamp, D. M. *Adv. Func. Mater.* **2008**, *5*, 742–750. (d) Kim, D. H.; Lee, B. L.; Moon, H.; Kang, H. M.; Jeong, E. J.; Park, J. I.; Han, K. M.; Lee, S.; Yoo, B. W.; Koo, B. W.; Kim, J. Y.; Lee, W. H.; Cho, K.; Becerril, H. A.; Bao, Z. *J. Am. Chem. Soc.* **2009**, *131*, 6124–6132. (e) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Deliomeroglu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5586–5608. (f) DiBenedetto, S. A.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *Adv. Mater.* **2009**, *21*, 1407–1433.

(4) Selected examples: (a) Hattori, S.; Wada, Y.; Yanagida, S.; Fukuzumi, S. *J. Am. Chem. Soc.* **2005**, *26*, 9648–9654. (b) Hou, J. H.; Tan, Z. A.; Yan, Y.; He, Y. J.; Yang, C. H.; Li, Y. F. *J. Am. Chem. Soc.* **2006**, *128*, 4911–4916. (c) Wong, W. Y.; Wang, X. Z.; He, Z.; Chan, K. K.; Djurisic, A. B.; Cheung, K. Y.; Yip, C. T.; Ng, A. M. C.; Xi, Y. Y.; Mak, C. S. K.; Chan, W. K. *J. Am. Chem. Soc.* **2007**, *129*, 14372–14380. (d) Mitsopoulou, C. A.; Veroni, I.; Philippopoulos, A. I.; Falaras, P. *J. Photochem. Photobiol. A* **2007**, *1*, 6–12. (e) Westenhoff, S.; Howard, I. A.; Hodgkiss, J. M.; Kirov, K. R.; Bronstein, H. A.; Williams, C. K.; Greenham, N. C.; Friend, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 13653–13658. (f) Yin, J. F.; Chen, J. G.; Lu, Z. Z.; Ho, K. C.;

Lin, H. C.; Lu, K. L. *Chem. Mater.* **2010**, *22*, 4392–4399. (g) Sun, Y.; Onicha, A. C.; Myahkostupov, M.; Castellano, F. N. *App. Mater. Inter.* **2010**, *2*, 2039–2045.

(5) (a) Negishi, E. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley: New York, 2002. (b) Mitchell, T. N. *Metal-catalyzed Cross-coupling Reactions*; Wiley-VCH: Weinheim, 2004. (c) Martin, R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3844–3845. (d) Tobisu, M.; Shimasaki, T.; Chatani, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 4866–4869. (e) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771–1780. (f) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483. (g) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1469. (h) Frisch, A. C.; Beller, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 674–688.

(6) (a) Fichou, D. *Handbook of Oligo- and Polythiophenes*; Wiley-VCH: Weinheim, 1999. (b) Ma, D. W.; Cai, Q. *Acc. Chem. Res.* **2008**, *41*, 1450–1460. (c) Zhang, H.; Cai, Q.; Ma, D. W. *J. Org. Chem.* **2005**, *70*, 5164–5173. (d) Siddle, J. S.; Batsanov, A. S.; Bryce, M. R. *Eur. J. Org. Chem.* **2008**, *16*, 2746–2750. (e) Carroll, R. L.; Gorman, C. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 4378–4400. (f) Kisselev, R.; Thelakkat, M. *Chem. Commun.* **2002**, 1530–1531. (g) Lu, J. P.; Xia, P. F.; Lo, P. K.; Tao, Y.; Wong, M. S. *Chem. Mater.* **2006**, *18*, 6194–6203. (h) Ge, Z.; Hayakawa, T.; Ando, S.; Ueda, M.; Akiike, T.; Miyamoto, H.; Kajita, T.; Kakimoto, M. A. *Chem. Lett.* **2008**, *37*, 262–263.

(7) (a) Araki, K.; Endo, H.; Masuda, G.; Ogawa, T. *Chem.—Eur. J.* **2004**, *10*, 3331–3340. (b) Chen, X. Y.; Yang, X.; Holliday, B. J. *J. Am. Chem. Soc.* **2008**, *130*, 1546–1547. (c) Zeng, X.; Tavasli, M.; Perepichka, I. F.; Batsanov, A. S.; Bryce, M. R.; Chiang, C. J.; Rothe, C.; Monkman, A. P. *Chem.—Eur. J.* **2008**, *14*, 933–943. (d) Huang, W.; Tanaka, H.; Ogawa, T. *J. Phys. Chem. C* **2008**, *112*, 11513–11526. (e) Huang, W.; Wang, L.; Tanaka, H.; Ogawa, T. *Eur. J. Inorg. Chem.* **2009**, 1321–1330.

(8) (a) Chaloner, P. A.; Gunatunga, S. R.; Hitchcock, P. B. *J. Chem. Soc., Perkin Trans. 2* **1997**, *8*, 1597–1604. (b) Huang, W.; Masuda, G.; Maeda, S.; Tanaka, H.; Ogawa, T. *Chem.—Eur. J.* **2006**, *12*, 607–619. (c) Huang, W.; Masuda, G.; Maeda, S.; Tanaka, H.; Hino, T.; Ogawa, T. *Inorg. Chem.* **2008**, *47*, 468–480. (d) Wang, L.; You, W.; Huang, W.; Wang, C.; You, X. Z. *Inorg. Chem.* **2009**, *48*, 4295–4305. (e) Huang, W.; Tanaka, H.; Ogawa, T. *Adv. Mater.* **2010**, *22*, 2753–2758. (f) Wang, L.; Tao, T.; Fu, S. J.; Wang, C.; Huang, W.; You, X. Z. *CrystEngComm.* **2011**, *13*, 747–749.

(9) Anzai, K.; Fukumoto, H.; Yamamoto, T. *Chem. Lett.* **2004**, *33*, 252–253.

(10) (a) Yue, W.; Tian, H. K.; Hu, N. H.; Geng, Y. H.; Wang, F. S. *Cryst. Growth Des.* **2008**, *8*, 2352–2358. (b) Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Schmitt, C. X. *Polyhedron* **2006**, *25*, 1844–1863. (c) Albers, W. M. *Tetrahedron* **1995**, *51*, 3895–3904.

(11) Gaussian 03, Revision C.02. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A.; Clifford, G. S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill P, M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford, CT, 2004.

(12) (a) Kumagai, A.; Fukumoto, H.; Yamamoto, T. *J. Phys. Chem. B* **2007**, *111*, 8020–8026. (b) Ma, C. Q.; Pisula, W.; Weber, C.; Feng, X. L.; Mullen, K.; Bauerle, P. *Chem.—Eur. J.* **2011**, *17*, 1507–1518. (c) Shinamura, S.; Miyazaki, E.; Takimiya, K. *J. Org. Chem.* **2010**, *75*, 1228–1234. (d) Leventis, N.; Rawashdeh, A. M. M.; Elder, I. A.; Yang, J. H.; Dass, A.; Sotiriou-Leventis, C. *Chem. Mater.* **2004**, *16*, 1493–1506. (e) Colle, M. D.; Cova, C.; Distefano, G.; Jones, D.; Modelli, A.; Comisso, N. *J. Phys. Chem. A* **1999**, *103*, 2828–2835. (f) Hapiot, P.; Demanze, F.; Yassar, A.; Garnier, F. *J. Phys. Chem.* **1996**, *100*, 8397–8401. (g) Kuzuhara, D.; Mack, J.; Yamada, H.; Okujima, T.; Ono, N.; Kobayashi, N. *Chem.—Eur. J.* **2009**, *15*, 10060–10069. (h) Balandier, J. Y.; Quist, F.; Amato, C.; Bouzakraoui, S.; Cornil, J.; Sergeyev, S.; Geerts, Y. *Tetrahedron* **2010**, *66*, 9560–9572.

(13) (a) Chen, C. Y.; Lu, H. C.; Wu, C. G.; Chen, J. G.; Ho, K. C. *Adv. Funct. Mater.* **2007**, *17*, 29–36. (b) Wu, C. G.; Lu, H. C.; Chen, L. N.; Lin, Y. C. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1586. (c) Promarak, V.; Punkvuang, A.; Sudyoadsuk, T.; Jungsuttiwong, S.; Saengsuwan, S.; Keawin, T.; Sirithip, K. *Tetrahedron* **2007**, *63*, 8881–8890. (d) Svoboda, J.; Stenclova, P.; Uhlik, F.; Zednik, J.; Vohlidal, J. *Tetrahedron* **2011**, *67*, 75–79.

(14) Molecular Structure Corp. & Rigaku Corp. *CRYSTALCLEAR* Version 1.3. MSC, The Woodlands, TX, and Rigaku, Toyko, 2001.

(15) Molecular Structure Corp. & Rigaku Corp. *TEXSAN* Version 1.11. MSC, The Woodlands, TX, and Rigaku, Toyko, 2000.

(16) Sheldrick, G.-M. *SHELXTL* (Version 6.10). Software Reference Manual; Bruker AXS, Inc.: Madison, WI, 2000.