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Synthesis and Photophysical Properties of C_3-Symmetric Star-Shaped Molecules Containing Heterocycles Such as Furan, Thiophene, and Oxazole

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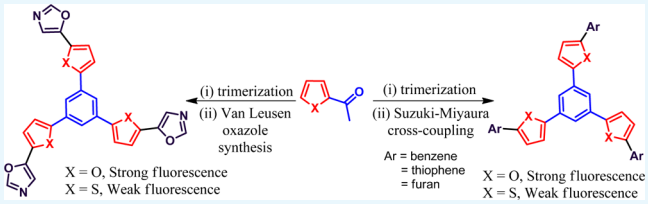
Supporting Information

ABSTRACT: We report simple strategies to synthesize star-shaped molecules containing different heterocycles integrated with a number of variations. Here, cyclotrimerization, Vilsmeier–Haack reaction, Suzuki–Miyaura cross-coupling, and Van Leusen oxazole synthesis have been used as key steps to introduce diverse five-membered heterocycles such as furan, thiophene, and oxazole. More importantly, readily available starting materials such as thiophene, 2-formyl furan, and 2-acetyl furan were utilized. Also, the fluorescent behavior of these π-conjugated systems was studied. C_3-Symmetric molecules containing furan moieties show a stronger fluorescence than thiophene-containing star-shaped compounds.



INTRODUCTION

Symmetry plays an important role in science, art, and architecture.[1] In chemistry, symmetry improves the selectivity by reducing the number of different reaction paths, thereby minimizing the competing alternatives. A large number of C_2-symmetric "privileged" ligands have been designed to advance the asymmetric synthesis and chiral recognition. Many octahedral complexes contain C_3-symmetric molecules.[2] In this context, limited numbers of C_3-symmetric molecules have been designed as compared with C_2-symmetric molecules. Initially, the synthesis of star-shaped molecules was focused due to their esthetic nature. Recently, their optical, electronic, and symmetry properties found widespread applications. Our goal in star-shaped C_3-symmetric molecules[3] is to design π-conjugated systems containing heteroatoms such as nitrogen, oxygen, and sulfur. In this regard, we intend to incorporate thiophene, furan, and oxazole moieties in C_3-symmetric molecules and investigate their photophysical properties. Moreover, such C_3-symmetric systems are subject of interest as active materials for organic electronic devices such as solar cells or field-effect transistors[4] and as core units for discotic liquid crystals.[5] More importantly, conjugated star-shaped molecules have been used in electroluminescent devices,[6] organic light-emitting diodes,[7] and photovoltaics.[4d,8]

RESULTS AND DISCUSSION

For the first time, we report a unified approach to design a novel class of C_3-symmetric star-shaped molecules embedded with thiophene, furan, and oxazole rings on a benzene core substituted at the 1, 3, and 5 positions. To incorporate different heterocycles in the C_3-symmetric molecules, we intend to use Suzuki–Miyaura (SM) cross-coupling,[9] Vilsmeier–Haack reaction,[10] and Van Leusen oxazole synthesis[11] (Figure 1) as the key steps. To realize the strategy shown in Figure 1, we begin our journey with the trimerization[12] of 2-acetyl-4-bromo thiophene (**1**) by using the known trimerization conditions.[13] However, we did not get the desired product **2**. Therefore, we changed the route to prepare the tri-bromo compound **2**. Here, the trimerized product tris-thiophene **3** (65%) was prepared from 2-acetyl thiophene (**5**) by using the literature procedure.[14] Later, we attempted different reaction conditions to introduce bromine atoms to obtain the C_3-symmetric tri-bromo compound **2**. Unfortunately, under those conditions, the starting material was recovered. Finally, we found that N-bromosuccinimide/acetonitrile/trimethylsilyl chloride (NBS/MeCN/TMSCl) condition[15] at room temperature gave the desired tri-brominated product **2** in 88% yield (Scheme 1).

Next, to install various heterocycles in C_3-symmetric molecules, we performed the SM cross-coupling reaction by treating the tri-bromo compound **2** with 5-formylfuran-2-yl boronic acid using $Pd(PPh_3)_4$ catalyst and K_2CO_3 or Na_2CO_3 as a base in tetrahydrofuran, toluene, and water (1:1:1) under reflux conditions. However, we could not get the desired tri-aldehyde. To test the reactivity of **2**, it was treated with phenylboronic acid (**7**) and 2-furanylboronic acid (**8**) under SM reaction conditions to deliver the corresponding cross-coupling products **4** and **6** in 84 and 78% yields, respectively (Scheme 2).

Then, to introduce other heterocycles at the second position of the thiophene moiety in a star-shaped molecule **2** (or **3**), the tri-aldehyde derivative **11** preparation was required. Therefore, the tris-thiophene derivative **3** was subjected to Vilsmeier–Haack reaction with $POCl_3$ in dimethylformamide (DMF) at

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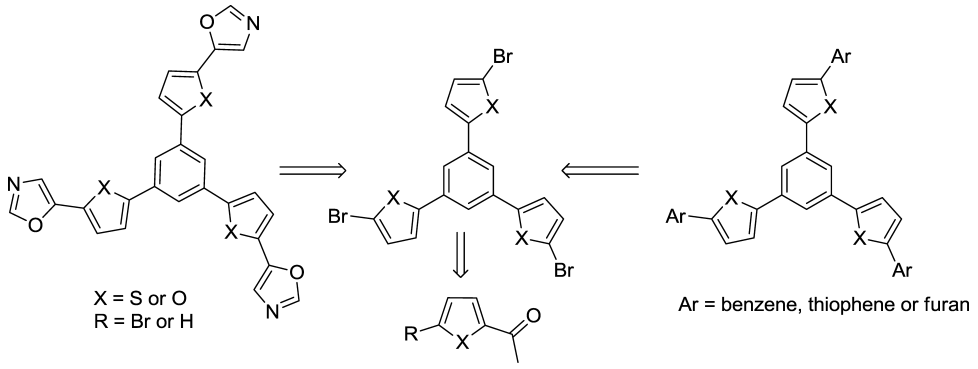
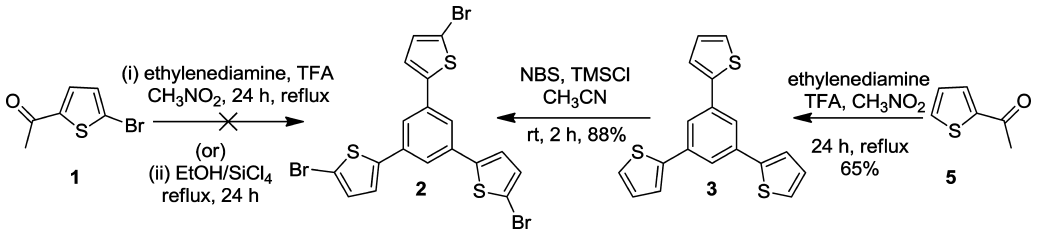
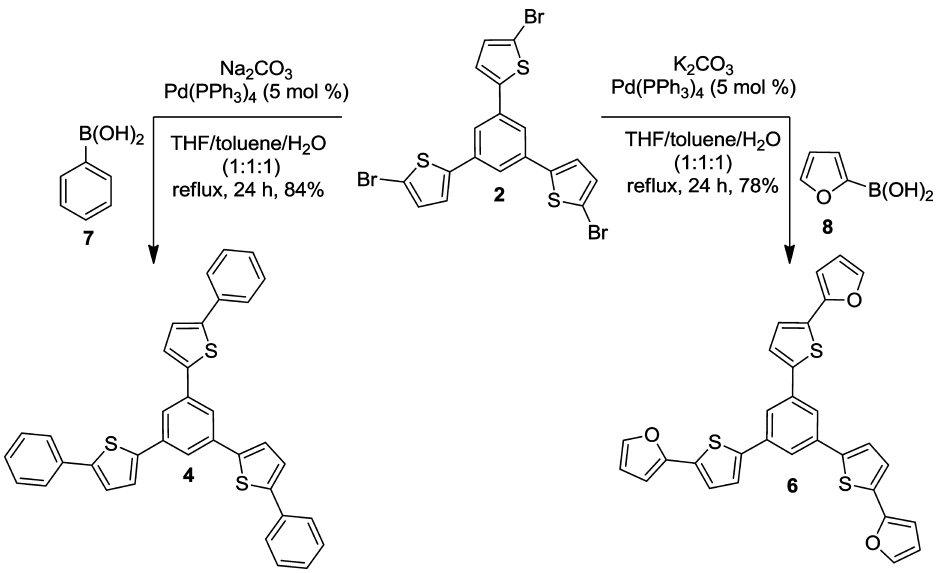


Figure 1. Retrosynthetic route to different heterocyclic rings containing C_3-symmetric derivatives.

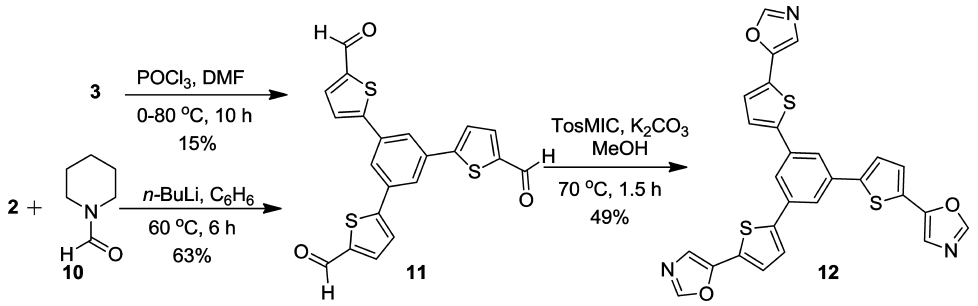
Scheme 1. Preparation of Tri-bromo Thiophene Derivative 2



Scheme 2. Synthesis of Compounds 4 and 6 via SM Cross-Coupling Reaction



Scheme 3. Synthesis of Oxazole Ring Containing Star-Shaped Derivative 12



0−80 °C for 10 h delivered the tri-aldehyde **11** in 15%. To improve the yield of **11**, tri-bromo compound **2** was treated with *n*-BuLi and then reacted with *N*-formylpiperidiene (**10**) in dry benzene at 60 °C to deliver the tri-aldehyde **11** (63%) with an improved yield. After obtaining compound **11**, our next task was to prepare the tris-oxazole derivative **12**. For this purpose,

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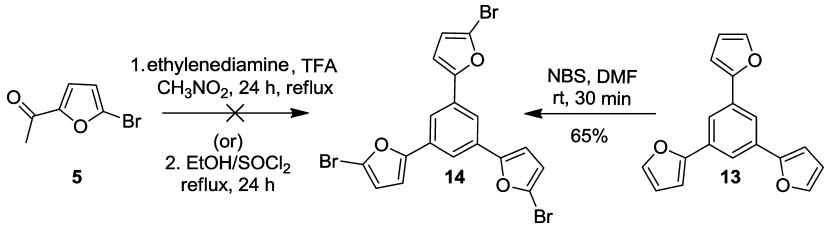
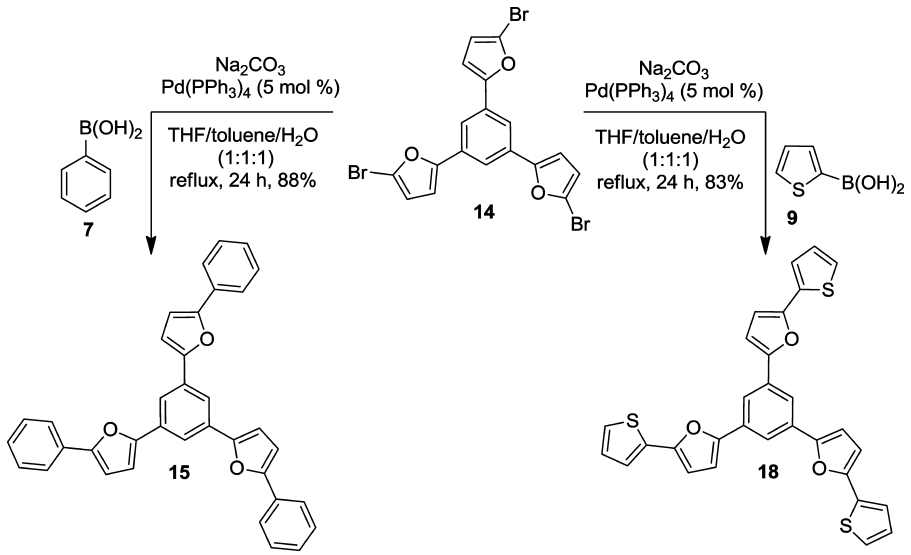
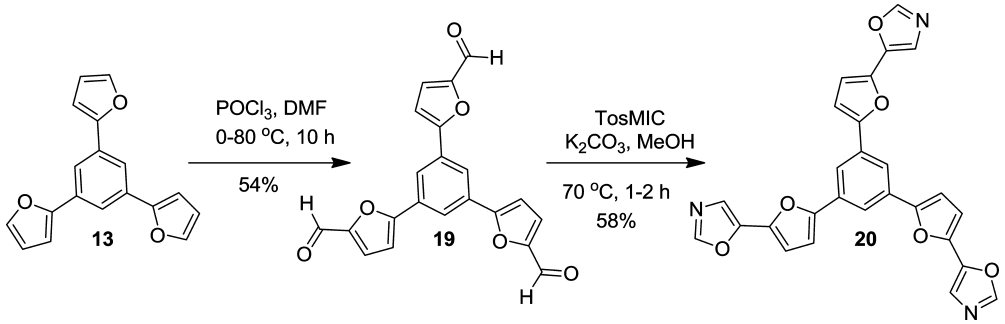
Scheme 4. Synthesis of Star-Shaped Tri-bromo Derivative 14



Scheme 5. Synthesis of C_3-Symmetric Derivatives 15 and 18 via SM Cross-Coupling Reaction



Scheme 6. Synthesis of Star-Shaped Tris-Oxazole Compound 20



the tri-aldehyde **11** was treated with toluenesulfonylmethyl isocyanide (TosMIC)/K_2CO_3 in methanol under reflux conditions to deliver the tris-oxazole **12** in 49% yield (Scheme 3).

Different conditions to synthesize tri-bromo compound **14** via trimerization of the 2-acetyl-4-bromo furan (**5**) was not successful. Alternatively, the known[14c,16] trimerized compound **13** was subjected to bromination with NBS/TMSCl in MeCN at room temperature and later at 50 °C. Unfortunately, these conditions could not generate the desired tri-bromo compound **14**. After experimenting with several conditions, we found that the target tri-bromo compound **14** could be obtained in 65% yield by the treatment of **13** with NBS in DMF at room temperature (Scheme 4).

Later, we performed the SM reaction with 5-formylfuran-2-yl boronic acid under standard coupling reaction conditions (Scheme 5). However, we could not get the desired product. In this regard, compound **14** was treated with phenylboronic acid (**7**) and 2-thienylboronic acid (**9**) under SM reaction conditions to give the cross-coupling products **15** and **18** in 88 and 83% yields, respectively.

Finally, the tri-aldehyde **19** (54%) was obtained through Vilsmeier−Haack reaction of **13**. Then, the aldehyde groups were transformed to oxazole rings by Van Leusen oxazole synthesis. In this context, the tri-aldehyde **19** was treated with TosMIC/K_2CO_3 in the presence of methanol under reflux condition to generate the star-shaped tris-oxazole derivative **20** in 58% yield (Scheme 6).

FLUORESCENCE STUDIES OF STAR-SHAPED DERIVATIVES 4, 6, 12, 15, 18, AND 20

Steady-state and time-resolved fluorescence measurements (Figure 2) were performed in dilute solutions contained in standard quartz cuvettes. The superimposability of the excitation and absorption spectra of the samples suggests a

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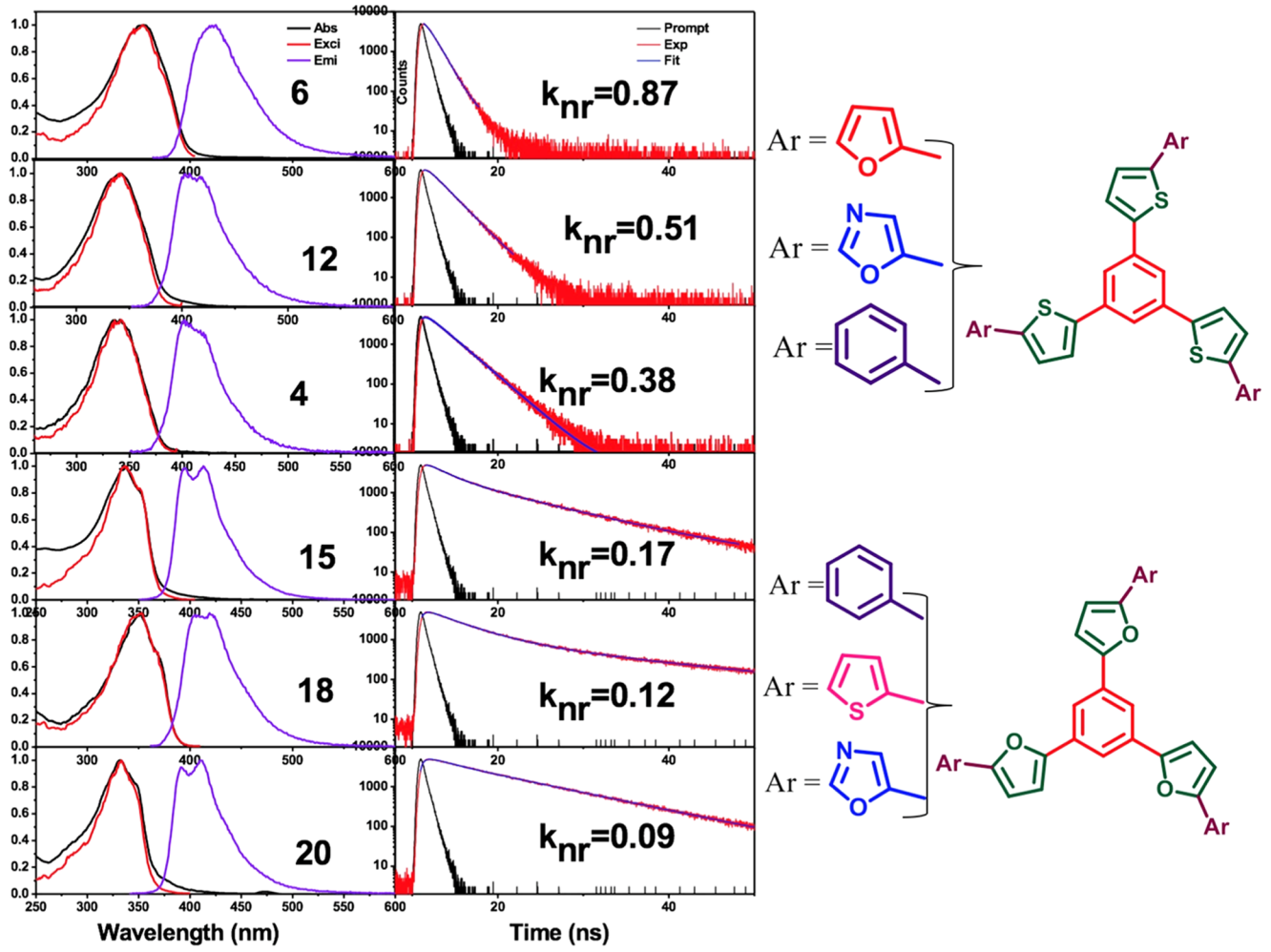

Figure 2. Left panel shows the steady-state emission (purple), excitation (red), and absorption (black) spectra of the samples. Right panel shows the time-correlated single-photon counting (TCSPC) data. λ_{ex} = 340 nm, λ_{em} = respective fluorescence maxima as given in Table 1.

Table 1. TCSPC Data Analysis of C_3-Symmetric Compounds

compounds	λ_{ex} (nm)	λ_{em} (nm)	τ_1 (ns)	A_1	τ_2 (ns)	A_2	χ^2	k_R	k_{NR}
6	340	425	1.12	1			1.14	0.026	0.87
12	340	408	1.96	1			1.14	0.001	0.51
4	340	402	2.36	1			1.06	0.055	0.38
15	340	415	2.4	0.59	8.63	0.41	1	0.035	0.17
18	340	420	4.34	0.82	19.22	0.18	1.09	0.017	0.12
20	340	410	9.74	0.81	2.77	0.19	1.11	0.033	0.09

high degree of purity of the compounds prepared. The emission spectrum for each compound is obtained, with excitation at the wavelength of the absorption maximum. The quantum yields were measured using quinine sulfate dissolved in 0.5 M H_2SO_4 as a standard (quantum yield Φ = 0.55).

The decay curves of samples **6**, **4**, and **12** show a single exponential nature, whereas those of samples **15**, **20**, and **18** show biexponential nature (Tables 1 and 2). All of the compounds show similar absorption spectra, with the onset of absorption near about 275 nm suggesting a similar band gap in these compounds. The synthesized products **6**, **4**, **12**, **15**, **20**, and **18** exhibit fluorescence behaviour in dichloromethane solvent.

Table 2. Calculated Quantum Yields of the Star-Shaped Compounds from Photophysical Studies

compounds	**6**	**12**	**4**	**15**	**18**	**20**
quantum yield	0.030	0.004	0.108	0.178	0.150	0.236

CONCLUSIONS

In summary, we have demonstrated a simple and useful strategy to synthesize star-shaped molecules containing multiple heterocycles via cyclotrimerization, Vilsmeier–Haack, SM cross-coupling reaction, and Van Leusen oxazole synthesis as key steps under operationally simple reaction conditions. The knowledge gained to prepare the key building blocks **3** and **14** will pave the way to complex C_3-symmetric heterocycles. Here, we have used readily available starting materials such as thiophene, 2-formyl furan, and 2-acetyl furan to generate various C_3-symmetric molecules such as **4**, **6**, **12**, **15**, **18**, and

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20. Compounds in which the inner ring has a furan moiety are better substrates as fluorophore than those containing thiophene in the inner ring. The effect of the third moiety on the fluorescent nature is significant as well, but the trends are reversed between furans and thiophene moieties.

EXPERIMENTAL SECTION

General Information. Some of the reactions were performed under nitrogen or argon atmosphere using well-dried reaction flask. All of the starting materials and reagents were obtained from commercial suppliers and used without purification. All of the solvents dried used as reaction media over predried molecular sieves (4 Å). Column chromatography was performed with silicagel (100−200 mesh) using a mixture of petroleum ether and EtOAc as eluent. ^{1}H and ^{13}C NMR spectral data were recorded on 400 MHz and 100 or 500 MHz and 125 MHz spectrometers using tetramethylsilane as the internal standard and chloroform-*d* as the solvent. The NMR data are in the order of chemical shifts, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), and coupling constants (*J*), given in Hertz (Hz). The mass spectral data were recorded on a Q-ToF micromass spectrometer. A high-resolution mass spectroscopy (HRMS) was performed with a ToF mass spectrometer in the positive ESI mode. The IR spectra were recorded on Thermo Nicolete Avater 320 FT-IR and Nicolete impact 400 machine.

Experimental Procedures. *1,3,5-Tris(5-bromothiophen-2-yl)benzene (**2**).*[17] In a two-necked round-bottom flask, the trimerized thiophene **2** (100 mg, 0.3 mmol) in MeCN (5 mL) was added portionwise NBS (174 mg, 0.8 mmol) at room temperature. Then, TMSCl (0.1 equiv) was added to this reaction mixture under inert atmosphere and the mixture was then stirred at room temperature for 2 h. After the completion of the reaction (thin-layer chromatography (TLC) monitoring), the reaction mixture was extracted with EtOAc (2 × 15 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, and the solvent removed to give the crude product, which was purified by silica gel column chromatography using (petroleum ether) to afford the tribromo compound **3** (152 mg, 88%) as a colorless solid; R_f = 0.84 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (s, 3H), 7.12 (d, J = 4 Hz, 3H), 7.07 (d, J = 4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.5, 135.4, 131.1, 124.4, 122.3, 112.6.

General Procedure for the Suzuki−Miyaura Cross-Coupling Reaction of 4, 6, 15, and 18. To a solution of tribromo derivatives **3** and **14** in toluene/tetrahydrofuran/water (1:1:1, each 10 mL), Na_2CO_3 or K_2CO_3 (9.0 equiv) and boronic acid (3.0 equiv) were added at room temperature. The mixture was degassed with nitrogen for 20 min. $Pd(PPh_3)_4$ (5 mol %) was then added and the reaction was reflux for 24 h. At the conclusion of the reaction (TLC monitoring), the reaction mixture was cooled to room temperature and washed with both water and brine. The organic layer was extracted with EtOAc (3 × 20 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography using appropriate mixture of EtOAc-petroleum ether to obtain the Suzuki−Miyaura cross-coupling product.

*1,3,5-Tris(5-phenylthiophen-2-yl)benzene (**4**).*[12] Colorless solid; yield = 84% (20 mg, starting with 25 mg of tri-bromo compound **3**); R_f = 0.64 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (s, 3H), 7.67 (d, J = 7.3 Hz, 6H), 7.43−7.40 (m, 9H), 7.35 (d, J = 3.7 Hz, 3H), 7.31 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 142.7, 135.8, 134.3, 129.1, 127.8, 125.9, 124.9, 124.2, 122.1.

*1,3,5-Tris(5-(furan-2-yl)thiophene-2-yl)benzene (**6**).* Colorless solid; yield = 78% (43 mg, starting with 60 mg of tri-bromo compound **3**); R_f = 0.64 (petroleum ether); mp: 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 3H), 7.43 (d, J = 0.8 Hz, 3H), 7.34 (d, J = 4 Hz, 3H), 7.25 (d, J = 4 Hz, 3H), 6.55 (d, J = 3.2 Hz, 3H), 6.47 (dd, J = 3.2, 1.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.3, 142.0, 141.9, 135.6, 133.7, 124.6, 123.6, 121.9, 112.0 105.6; HRMS (ESI, Q-ToF): calcd for $C_{30}H_{19}O_3S_3$ $[M + H]^+$ m/z 523.0491, found m/z 523.0497; IR (neat) $\tilde{\nu}_{max}$ 3855, 2361, 1044, 736 cm^{-1}.

*1,3,5-Tris(5-phenylfuran-2-yl)benzene (**15**).* Colorless solid; yield = 88% (25 mg, starting from 30 mg of tri-bromo compound **14**); R_f = 0.54 (petroleum ether); mp: 228−230 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (s, 3H), 7.81 (dd, J = 3.0, 1.5 Hz, 6H), 7.45 (t, J = 7.5 Hz, 6H), 7.31 (t, J = 7.5 Hz, 3H), 6.91 (d, J = 3.5 Hz, 3H), 6.81 (d, J = 3.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9, 153.0, 131.9, 130.8, 128.9, 127.7, 124.0, 118.1, 108.3, 107.5; HRMS (ESI, Q-ToF): calcd for $C_{36}H_{24}O_3Na$ $[M + Na]^+$ m/z 527.1618, found m/z 527.1610; IR (neat) $\tilde{\nu}_{max}$ 3020, 1216, 760, 669 cm^{-1}.

*1,3,5-Tris(5-(thiophen-2-yl)furan-2-yl)benzene (**18**).* Colorless solid; yield = 83% (34 mg, starting from 40 mg of tri-bromo compound **14**); R_f = 0.65 (petroleum ether); mp: 236−238 °C decomposed; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 3H), 7.39 (dd, J = 8.6, 1.0 Hz, 3H), 7.28 (dd, J = 5.0, 1.0 Hz, 3H), 7.09 (q, J = 3.6 Hz, 3H), 6.85 (d, J = 3.5 Hz, 3H), 6.64 (d, J = 3.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.5,149.5, 133.8, 131.6, 127.9, 124.6, 123.0, 118.0, 108.3, 107.5; HRMS (ESI, Q-ToF): calcd for $C_{30}H_{19}O_3S_3$ $[M + H]^+$ m/z 523.0491, found m/z 523.0496; IR (neat) $\tilde{\nu}_{max}$ 3423, 1654, 1032, 771 cm^{-1}.

*5,5′5″-(Benzene-1,3,5-triyl)tris(thiophen-2-carbaldehyde) (**11**).* In a dry two-necked round-bottom flask, compound **3** (500 mg, 0.89 mmol) was dissolved in dry benzene under nitrogen atmosphere and then the reaction mixture was stirred at 0 °C for 30 min. *n*-BuLi (1.83 mL, 1.6 M in Hexane, 2.937 mmol) was the added dropwise to the reaction mixture. After 30 min, the reaction mixture was heated at 60 °C for 3 h. Later, the reaction mixture was cooled to 0 °C and *N*-formylpipyridine **10** was added slowly in a dropwise manner. Next, the reaction mixture was brought to room temperature and red colour precipitate was formed and *N*-formylpipyridine was added dropwise to the reaction mixture at 0 °C and slowly warming the reaction mixture to room temperature led to the formation of a red precipitate. This reaction mixture was acidified with HCl (1.3 M) and the stirring was continued for 6 h. After the completion of the reaction (TLC monitoring), the reaction mixture was extracted with EtOAc (3 × 20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by silica gel column chromatography using (30% EtOAc−petroleum ether) to afford the compound (234 mg, 63%) as a red solid; R_f = 0.33 (4:6 ethyl acetate/petroleum ether); mp: 160−162 °C (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 3H), 7.92 (s, 3H), 7.81 (d, J = 4 Hz, 3H), 7.53 (d, J = 3.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.9, 151.7, 143.8, 137.3, 135.4, 125.5, 125; HRMS (ESI, Q-ToF): calcd for $C_{21}H_{13}O_3S_3$ $[M + H]^+$ m/z 409.0021, found m/z 409.0022; IR (neat) $\tilde{\nu}_{max}$ 2928, 1658, 1045, 771 cm^{-1}.

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*1,3,5-Tris(5-bromofuran-2-yl)benzene (**14**).* To a solution of trimerized furan **13** (100 mg, 0.36 mmol) in dry DMF (5 mL) was added NBS (219 mg, 1.23 mmol) portionwise at room temperature. The mixture was stirred at room temperature for 30 min. After the completion of the reaction (TLC monitoring), the reaction mixture was extracted with EtOAc (2 × 15 mL). The organic layer was washed with water, dried over Na_2SO_4, and concentrated. The crude compound was purified by silica gel column chromatography using (petroleum ether) to afford the tri-bromo furan **14** (122 mg, 65%) as a colorless solid; R_f = 0.89 (petroleum ether); mp: 86−90 °C (decomposed); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (s, 3H), 6.73 (d, J = 3.4 Hz, 3H), 6.42 (d, J = 3.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.1, 131.1, 122.3, 117.7, 113.7, 108.6; HRMS (ESI, Q-ToF): calcd for $C_{18}H_{10}O_3Br_3$ $[M + H]^+$ m/z 510.8180, found m/z 510.8195; IR (neat) $\tilde{\nu}_{max}$ 2920, 1656, 1049, 773 cm^{-1}.

*5,5′5″-(Benzene-1,3,5-triyl)tris(furan-2-carbaldehyde) (**19**).* In a two-neck round-bottom flask, compound **13** (400 mg, 1.44 mmol) was dissolved in dry DMF (6.7 mL, 86.8 mmol) and the resulting mixture was stirred at 0 °C for 30 min. To this ice cold solution $POCl_3$ (5.4 mL, 57.92 mmol) was added dropwise during which fumes were observed. The stirring was continued until the fumes ceased and then the reaction mixture was heated at 80 °C for 10 h. After the completion of the reaction (TLC monitoring), the reaction mixture was poured into crushed ice and quenched with sodium acetate and then extracted with EtOAc (3 × 20 mL). Combined organic layer was washed with brine, dried over Na_2SO_4, and the solvent removed to give the residue, which was purified by silica gel column chromatography using (30% EtOAc−petroleum ether) to obtain the tri-aldehyde product **19** (280 mg, 54%) as a pale red solid; R_f = 0.58 (4:6 ethyl acetate/petroleum ether); mp: 190 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.73 (s, 3H), 8.23 (s, 3H), 7.39 (d, J = 3.7 Hz, 3H), 7.08 (d, J = 3.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.6, 157.5, 152.7, 131.0, 123.5, 122.6, 109.5; HRMS (ESI, Q-ToF): calcd for $C_{21}H_{12}O_6K$ $[M + K]^+$ m/z 399.0265, found m/z 399.0263; IR (neat) $\tilde{\nu}_{max}$ 2927, 1672, 1038, 770 cm^{-1}.

General Procedure for Oxazole Formation of 12 and 20. In a two neck round bottom flask the tri-aldehyde derivatives such as **11** and **19** were dissolved separately in dry methanol (10 mL). Later, TosMIC (4.0 equiv) and, K_2CO_3 (9.0 equiv) were added portion wise to the reaction mixture. This reaction mixture was heated at 70 °C for 1 h. After the completion of the reaction (TLC monitoring), the mixture was cooled to room temperature and methanol was removed under reduced pressure. The reaction mixture was extracted with EtOAc (3 × 15 mL). Combined organic layer was washed with both water and brine and dried with Na_2SO_4. The solvent was removed on a rotavapor and the crude products were purified by silica gel column chromatography using the appropriate mixtures of EtOAc−petroleum ether to afford the tri-oxazole products.

*1,3,5-Tris(5-(oxazol-5-yl)thiophen-2-yl)benzene (**12**).* Red solid; yield = 49% (25 mg, starting from 40 mg of tri-aldehyde **11**); R_f = 0.63 (7:3 ethyl acetate/petroleum ether); mp: 172 °C (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 3H), 7.72 (s, 3H), 7.38 (d, J = 4 Hz, 3H), 7.33 (d, J = 4 Hz, 3H), 7.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 146.8, 143.5, 135.4, 129.6, 125.7, 124.8, 122.6, 121.7; HRMS (ESI, Q-ToF): calcd for $C_{27}H_{16}O_3S_3$ $[M + H]^+$ m/z 526.0348, found m/z 526.0348; IR (neat) $\tilde{\nu}_{max}$ 2925, 1646, 1097, 757 cm^{-1}.

*1,3,5-Tris (5-(oxazol-5-yl)furan-2-yl)benzene (**20**).* Pale yellow solid; yield = 58% (77 mg, starting from 100 mg of tri-aldehyde **19**); R_f = 0.54 (6:4 ethyl acetate/petroleum ether); mp: 135−140 °C (decomposed); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 3H), 7.92 (s, 3H), 7.41 (s, 3H), 6.91 (d, J = 3.5 Hz, 3H), 6.79 (d, J = 3.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.6, 150.3, 143.9, 143.4, 131.4, 122.1, 118.9, 110.1, 108.3; HRMS (ESI, Q-ToF): calcd for $C_{27}H_{16}N_3O_3$ $[M + H]^+$ m/z 478.1034, found m/z 478.1033; IR (neat) $\tilde{\nu}_{max}$ 2926, 1646, 1110, 781 cm^{-1}.

Steady-State and Time-Resolved Fluorescence. Absorption and fluorescence spectra were recorded on a Jasco V530 spectrophotometer and a Varian Cary Eclispe fluorimeter, respectively. Bandwidths of 5 nm were used on the excitation and emission sides for fluorescence measurements. The samples were excited at 340 nm. The TCSPC measurements were performed on an IBH Fluorocube time-resolved fluorescence spectrophotometer. A Nanoled emitting at 340 nm was used to excite the samples. The instrument response function was 800 ps. Further details about the instrument are available elsewhere.[18] The lifetime values were obtained by fitting the fluorescence decays to multiexponential functions[19] by an iterative reconvolution technique using reduced χ^2 as the parameter for goodness of fit (χ^2 < 1.2 for a good fit). The fitting function is as follows

$$I(t) - I(0) \sum_i A_i \, e^{-t/\tau_i}$$

where $I(t)$ and $I(0)$ denote the fluorescence intensities at time t and time 0 after excitation, respectively. A_i and τ_i denote the amplitude and lifetime, respectively, of the ith component of the decay.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00941.

Copies of ^{1}H, ^{13}C NMR spectra for all of the new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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