Synthesis and Photophysical Properties of C₃-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. C₃-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 C₃-symmetric “privileged” ligands have been designed to advance the asymmetric synthesis and chiral recognition. Many octahedral complexes contain C₃-symmetric molecules.² In this context, limited numbers of C₃-symmetric molecules have been designed as compared with C₃-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 C₃-symmetric molecules³ 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 C₃-symmetric molecules and investigate their photophysical properties. Moreover, such C₃-symmetric systems are subject of interest as active materials for organic electronic devices such as solar cells or field-effect transistors⁴ 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.⁸

RESULTS AND DISCUSSION

For the first time, we report a unified approach to design a novel class of C₃-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 C₃-symmetric molecules, we intend to use Suzuki–Miyaura (SM) cross-coupling,⁹ Vilsmeier–Haack reaction,¹⁰ and Van Leusen oxazole synthesis¹¹ (Figure 1) as the key steps. To realize the strategy shown in Figure 1, we begin our journey with the trimerization¹² 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 tri-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 C₃-symmetric tri-bromo compound 2. Unfortunately, under those conditions, the starting material was recovered. Finally, we found that N-bromosuccinimide/acetonitrile/triethylsilyl chloride (NBS/MeCN/TMSCl) condition¹⁵ at room temperature gave the desired tri-brominated product 2 in 88% yield (Scheme 1).

Next, to install various heterocycles in C₃-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(Ph₃)₄ catalyst and K₂CO₃ or Na₂CO₃ 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 tri-thiophene derivative 3 was subjected to Vilsmeier–Haack reaction with POCl₃ in dimethylformamide (DMF) at

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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,
the tri-aldehyde 11 was treated with toluenesulfonylmethyl isocyanide (TosMIC)/K₂CO₃ 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 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/K₂CO₃ 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...
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 H₂SO₄ as a standard (quantum yield Φ = 0.55).

The decay curves of samples 6, 12, and 18 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.

### CONCLUSIONS

In summary, we have demonstrated a simple and useful strategy to synthesize star-shaped molecules containing multiple heterocycles via cycloitrimerization, 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 C₃-symmetric heterocycles. Here, we have used readily available starting materials such as thiophene, 2-formyl furan, and 2-acetyl furan to generate various C₃-symmetric molecules such as 4, 6, 12, 15, 18, and

### Table 1. TCSPC Data Analysis of C₃-Symmetric Compounds

| compounds | λₓ (nm) | λₓₓ (nm) | τ₁ (ns) | A₁ | τ₂ (ns) | A₂ | χ² | kₓ | kₓₓ |
|-----------|--------|--------|--------|----|--------|----|---|----|----|
| 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|    |    |
| 18        | 340    | 420    | 4.34   | 0.82| 19.22  | 0.18| 1 | 0.017|    |    |
| 20        | 340    | 410    | 9.74   | 0.81| 2.77   | 0.19| 1 | 0.033|    |    |

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

| compounds | quantum yield |
|-----------|---------------|
| 6         | 0.030         |
| 12        | 0.004         |
| 4         | 0.108         |
| 15        | 0.178         |
| 18        | 0.150         |
| 20        | 0.236         |
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 were dried over predried molecular sieves (4 Å). Column chromatography was performed with silica gel (100–200 mesh) using a mixture of petroleum ether and EtOAc as eluent. 

**Numerical Data.** Column chromatography was performed on 400 MHz and 100 or 500 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 spectrometry (HRMS) was performed with a Q-ToF mass spectrometer in the positive ESI mode. The IR spectra were recorded on Thermo Nicolet Avator 320 FT-IR and Nicolette impact 400 machine.

**Experimental Procedures.** 1,3,5-Tris(5-bromothiophen-2-yl)benzene (3). In a two-necked round-bottom flask, the trimerized thiophene (100 mg, 0.3 mmol) in MeCN (5 mL) was added portionwise NBS (174 mg, 0.8 mmol) at room temperature. The mixture was degassed with nitrogen for 20 min. Pd(PPh3)4 (5 mol %) was then added and the reaction was reweigh at room temperature for 2 h. After the completion of the reaction (TLC monitoring), the reaction mixture was brought to room temperature and red precipitate was formed and 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 (3 × 20 mL). The combined organic layer was washed with water and brine, dried over Na2SO4, and solvent was removed to give the crude product, which was purified by silica gel column chromatography using petroleum ether to afford the tri-bromo compound 3 (152 mg, 88%) as a colorless solid; Rf = 0.84 (petroleum ether); 1H NMR (500 MHz, CDCl3): δ 7.52 (s, 3H), 7.12 (d, J = 4 Hz, 3H), 7.07 (d, J = 4 Hz, 3H); 13C NMR (125 MHz, CDCl3): δ 144.4, 135.4, 131.1, 124.0, 118.1, 108.3, 107.5; HRMS (ESI, Q-ToF): calcd for C21H13O3S3 [M + H]+ 629.0022; found m/z 629.0021.

1,3,5-Tris(5-(thiophen-2-yl)furan-2-yl)benzene (4). To a mixture of a red precipitate formed and then stirred at room temperature for 2 h. After the completion of the reaction (thin-layer chromatography using petroleum ether), 2-yl)benzene (2). In a two-necked round-bottom flask, the trimerized thiophene (100 mg, 0.3 mmol) in MeCN (5 mL) was added portionwise NBS (174 mg, 0.8 mmol) at room temperature. The mixture was degassed with nitrogen for 20 min. Pd(PPh3)4 (5 mol %) was then added and the reaction was reweigh at room temperature for 2 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 water and brine, dried over Na2SO4, and solvent was removed to give the crude product, which was purified by silica gel column chromatography using petroleum ether to afford the tri-bromo compound 3 (152 mg, 88%) as a colorless solid; Rf = 0.84 (petroleum ether); 1H NMR (500 MHz, CDCl3): δ 7.52 (s, 3H), 7.12 (d, J = 4 Hz, 3H), 7.07 (d, J = 4 Hz, 3H); 13C NMR (125 MHz, CDCl3): δ 144.4, 135.4, 131.1, 124.0, 118.1, 108.3, 107.5; HRMS (ESI, Q-ToF): calcd for C21H13O3S3 [M + H]+ 629.0022; found m/z 629.0021.

1,3,5-Tris(5-furanylfuran-2-yl)benzene (6). Colorless solid; yield = 78% (43 mg, starting with 60 mg of tri-bromo compound 3); Rf = 0.64 (petroleum ether); 1H NMR (500 MHz, CDCl3): δ 7.52 (s, 3H), 7.12 (d, J = 4 Hz, 3H); 13C NMR (125 MHz, CDCl3): δ 144.4, 142.7, 135.8, 134.3, 129.1, 127.8, 125.9, 124.9, 122.1.
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 Na₂SO₄ and concentrated. The crude product was purified by silica gel column chromatography using (petroleum ether) to afford the tri-bromo furan 14 (122 mg, 65%) as a colorless solid; Rf = 0.89 (petroleum ether); mp: 86–90 °C (decomposed); ¹H NMR (500 MHz, CDCl₃): δ 7.72 (s, 3H), 7.39 (d, J = 3.4 Hz, 3H), 7.08 (d, J = 3.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 155.1, 131.1, 122.3, 117.7, 113.7, 108.6; HRMS (ESI, Q-ToF): calcld for C₁₈H₁₀O₃Br₃ [M + H]⁺ m/z 478.1034, found m/z 478.1033; IR (neat) νmax 2926, 1646, 1110, 781 cm⁻¹.

5,5′,5″-(Benzene-1,3,5-triy1)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 reaction mixture was stirred at 0 °C for 30 min. To this ice cold solution POCl₃ (5.4 mL, 57.92 mmol) was added dropwise where a few fumes were observed. The reaction 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 Na₂SO₄ 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; Rf = 0.58 (4:6 ethyl acetate/petroleum ether); mp: 190 °C; ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (125 MHz, CDCl₃): δ 177.6, 157.5, 152.7, 131.0, 123.5, 122.6, 109.5; HRMS (ESI, Q-ToF): calcld for C₁₈H₁₀O₃Br₃ [M + H]⁺ m/z 478.1036, found m/z 478.1035; IR (neat) νmax 2926, 1646, 1110, 781 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 K₂CO₃ (9.0 equiv) were added portion wise to the reaction mixture. The reaction 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 Na₂SO₄. 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); Rf = 0.63 (7:3 ethyl acetate/petroleum ether); mp: 172 °C (decomposed); ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): δ 150.2, 146.8, 143.5, 135.4, 129.6, 125.7, 124.8, 122.6, 121.7; HRMS (ESI, Q-ToF): calcld for C₂₇H₁₆N₃O₃ [M + H]⁺ m/z 399.0265, found m/z 399.0263; IR (neat) νmax 2927, 1672, 1038, 770 cm⁻¹.

1,3,5-Tris(5-oxazol-5-yl)fururan-2-yl)benzene (20). Pale yellow solid; yield = 58% (77 mg, starting from 100 mg of tri-aldehyde 19); Rf = 0.54 (6:4 ethyl acetate/petroleum ether); mp: 135–140 °C (decomposed); ¹H NMR (500 MHz, CDCl₃): δ 7.93 (s, 3H), 7.92 (s, 3H), 7.41 (d, J = 3.5 Hz, 3H), 6.79 (d, J = 3.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 153.6, 150.3, 143.9, 143.4, 131.4, 122.1, 118.9, 110.1, 108.3; HRMS (ESI, Q-ToF): calcld for C₂₇H₁₆N₃O₅ [M + H]⁺ m/z 478.1034, found m/z 478.1033; IR (neat) νmax 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 Eclipse 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. The lifetime values were obtained by fitting the fluorescence decays to multieponential functions by an iterative reconvolution technique using reduced χ² as the parameter for goodness of fit (χ² < 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 \( \tau_i \) denote the amplitude and lifetime, respectively, of the \( i \)th component of the decay.

**ASSOCIATED CONTENT**

3 Supporting Information

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

Copies of ¹H, ¹³C 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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