

Supplementary Information

Fabrication of complex hierarchical heterostructures with controlled luminescence via seeded self-assembly

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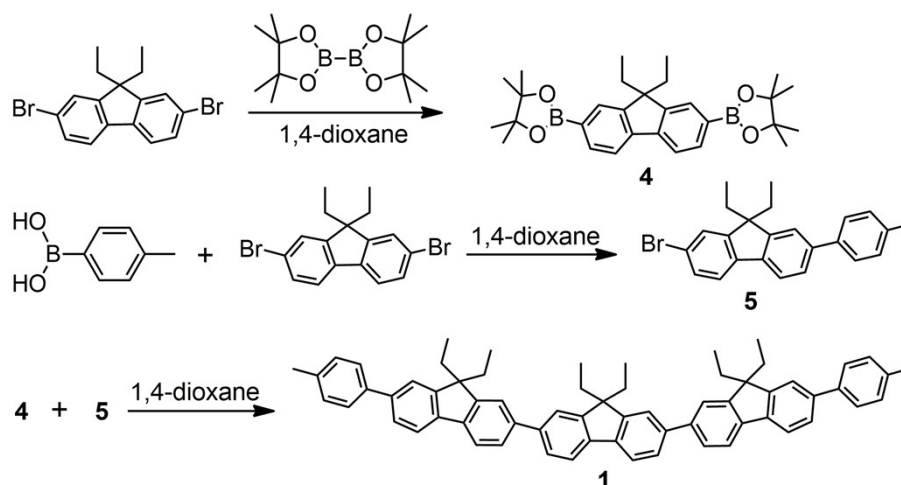
Supplementary Information

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1. Synthesis of molecules 1-3.

Synthesis of molecule 1.



Scheme 1. Synthesis of molecule 1.

2,2'-(9,9-diethyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4). A mixture of 2,7-dibromo-9,9-diethyl-9H-fluorene (2.30 g, 6 mmol), potassium acetate (1.76 g, 18 mmol), bis(pinacolato)diboron (6.10 g, 24 mmol), and Pd(dppf)Cl₂ (220 mg, 0.3 mmol) in deoxygenated 1,4-dioxane (50 mL) was heated to 80 °C and stirred overnight under Ar. The solvent was evaporated under vacuum. The residue was poured into water (100 mL) and extracted with ethyl acetate (3 * 100 mL). The combined organic layer was washed with brine (saturated), dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by column chromatography on the silica gel (petroleum: ethyl acetate = 30:1 as the eluent). Recrystallization in methanol affords 2.60 g (5.5 mmol, 92% yield) white crystals.

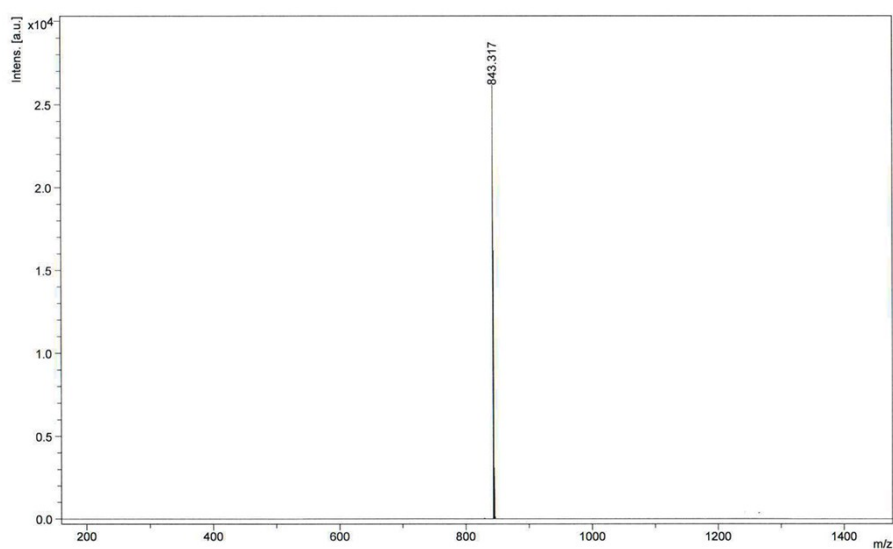
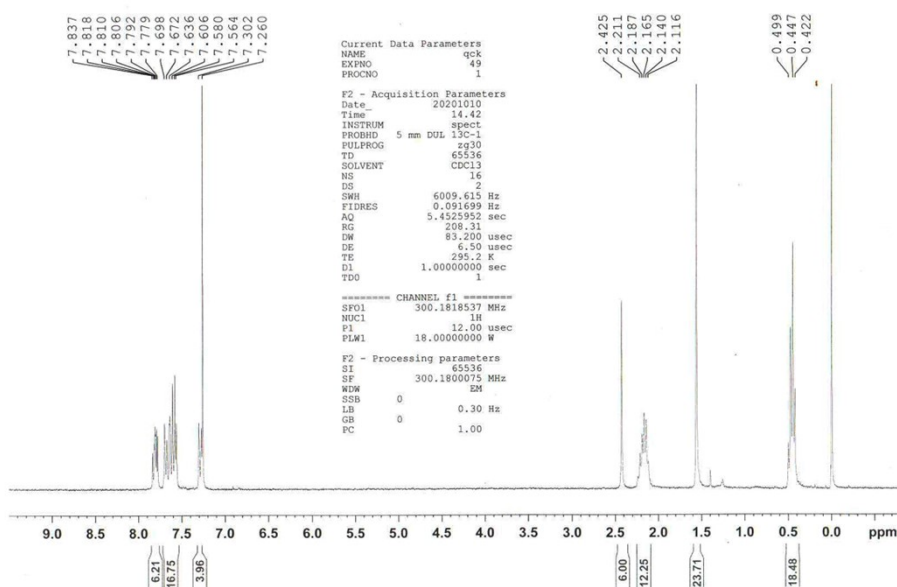
Compound 4: ¹H NMR (300 MHz, CDCl₃): δ 7.81-7.79 (m, 2 H), 7.74-7.71 (m, 4 H), 2.12-2.03 (m, 4 H), 1.10 (s, 12 H), 0.54 (t, *J* = 8.0 Hz, 6 H).

2-bromo-9,9-diethyl-7-(p-tolyl)-9H-fluorene (5). To a stirred solution of p-tolylboronic acid (0.98 g, 7.25 mmol), 2,7-dibromo-9,9-diethyl-9H-fluorene (3.30 g, 8.7 mmol), and tetrakis(triphenylphosphine)palladium (419 mg, 0.36 mmol) in deoxygenated 1,4-dioxane (40 mL), aqueous solution of potassium carbonate (7 mL, 2.0 M) was added. Then the mixture was heated to 80 °C and stirred overnight under Ar. The solvent was evaporated under vacuum. The residue was poured into water (50 mL) and extracted with ethyl acetate (3 * 40 mL). The combined organic layer was washed with brine (saturated), dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by column chromatography on the silica gel (petroleum: ethyl acetate = 30:1 as the eluent) to afford 4 (1.47 g, 3.77 mmol, 52% yield).

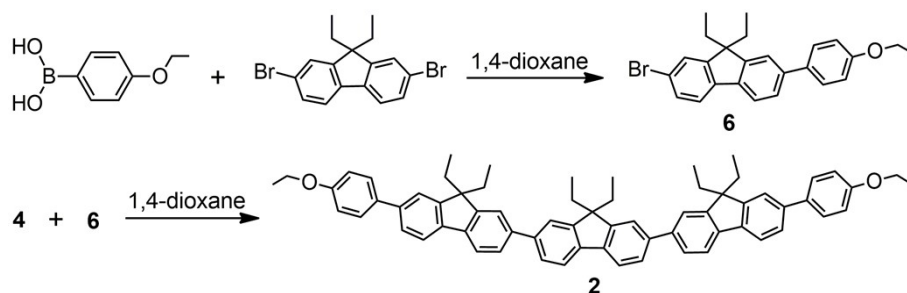
Compound 5: ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.76-7.63 (m, 4H), 7.56-7.47 (m, 3H), 7.30 (d, *J* = 8.7 Hz, 2H), 2.39 (s, 3H), 2.32-2.01 (m, 4H), 0.52 (t, *J* = 8.0 Hz, 6 H).

9,9,9',9',9'',9''-hexaethyl-7,7''-di-p-tolyl-9H,9'H,9''H-2,2':7',2''-terfluorene (1). To a stirred solution of **4** (0.71 g, 1.5 mmol), **5** (1.29 g, 3.3 mmol), and tetrakis(triphenylphosphine)palladium (87 mg, 0.075 mmol) in deoxygenated 1,4-dioxane (30 mL), aqueous solution of potassium carbonate (5 mL, 2.0 M) was added. Then the mixture was heated to 80 °C and stirred overnight under Ar. The solvent was evaporated under vacuum. The residue was poured into water (40 mL) and extracted with ethyl acetate (3 * 30 mL). The combined organic layer was washed with brine (saturated), dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum: ethyl acetate = 30:1 as the eluent) to afford **1** (0.47 g, 0.55 mmol, 37% yield). The resulting target compound was confirmed by ¹H NMR and MALDI-MS as below.

Molecule 1. ¹H NMR (300 MHz, CDCl₃): δ 7.89-7.76 (m, 6H), 7.70-7.56 (m, 16H), 7.30 (d, *J* = 8.0 Hz, 4H), 2.42 (s, 6 H), 2.21-2.11 (m, 12H), 0.44 (t, *J* = 8.0 Hz, 18 H). MALDI-MS: (*m/z*) = 1295. MALDI-MS calcd for C₆₅H₆₂ 842.3, found 843.3.



Synthesis of molecule 2.



Scheme 2. Synthesis of molecule 2.

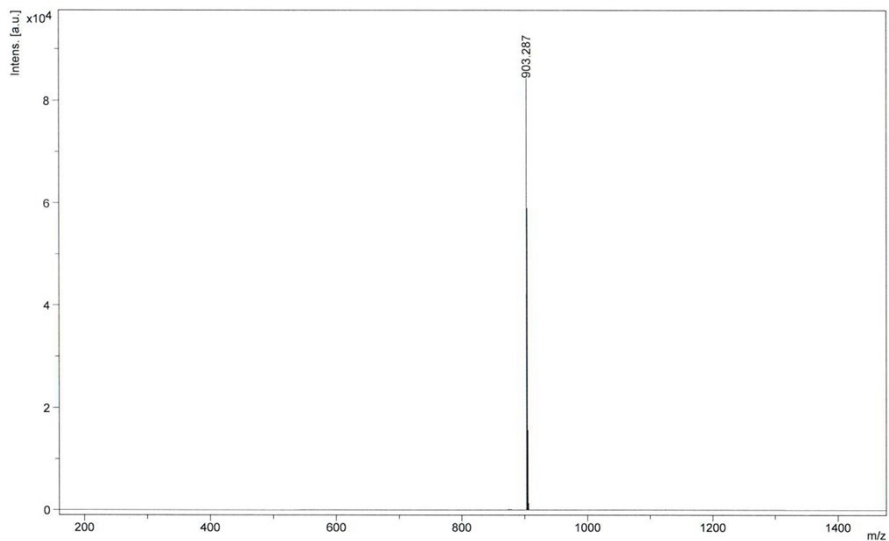
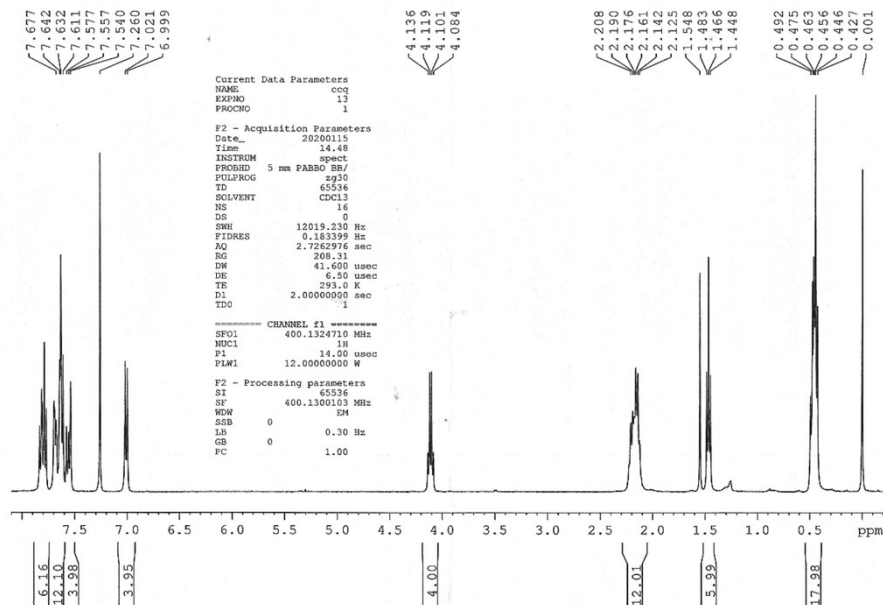
2-bromo-7-(4-ethoxyphenyl)-9,9-diethyl-9H-fluorene (6). To a stirred solution of (4-ethoxyphenyl)boronic acid (1.2 g, 7.25 mmol), 2,7-dibromo-9,9-diethyl-9H-fluorene (3.30 g, 8.7 mmol), and tetrakis(triphenylphosphine)palladium (419 mg, 0.36 mmol) in deoxygenated 1,4-dioxane (40 mL), aqueous solution of potassium carbonate (7 mL, 2.0 M) was added. Then the mixture was heated to 80 °C and stirred overnight under Ar. The solvent was evaporated under vacuum. The residue was poured into water (50 mL) and extracted with ethyl acetate (3 * 40 mL). The combined organic layer was washed with brine (saturated), dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by column chromatography on the silica gel (petroleum: ethyl acetate = 25:1 as the eluent) to afford **6** (1.49 g, 3.55 mmol, 49% yield).

Compound **6**: ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.67-7.55 (m, 4H), 7.53-7.44 (m, 3H), 7.05 (d, *J* = 8.7 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.24-2.14 (m, 4 H), 1.52 (t, *J* = 6.8 Hz, 3 H), 0.52-0.45 (m, 6 H).

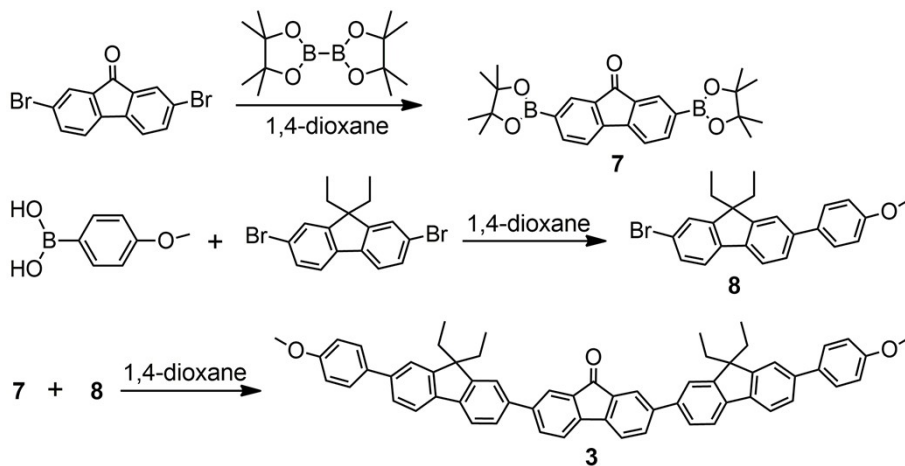
7,7''-bis(4-ethoxyphenyl)-9,9,9',9'',9''-hexaethyl-9H,9'H,9''H-2,2':7',2''-terfluorene (2). To a stirred solution of **4** (0.80 g, 1.69 mmol), **6** (1.49 g, 3.55 mmol), and tetrakis(triphenylphosphine)palladium (85 mg, 0.088 mmol) in deoxygenated 1,4-dioxane (30 mL), aqueous solution of potassium carbonate (5 mL, 2.0 M) was added. Then the mixture was heated to 80 °C and stirred overnight under Ar. The solvent was evaporated under vacuum. The residue was poured into water (40 mL) and extracted with ethyl acetate (3 * 30 mL). The combined organic layer was washed with brine (saturated), dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum: ethyl acetate = 25:1 as the eluent) to afford **2** (0.68 g, 0.76 mmol, 45% yield). The resulting target compound was confirmed by ¹H NMR and MALDI-MS as below.

Molecule 2. ¹H NMR (300 MHz, CDCl₃): δ 7.85-7.77 (m, 6H), 7.67-7.54 (m, 16H), 7.01 (d, *J* = 8.8 Hz, 4H), 4.11 (q, *J* = 7.2 Hz, 4 H), 2.21-2.12 (m, 12 H), 1.46 (t, *J* = 6.8 Hz, 6 H), 0.49-0.42 (m, 18 H).

MALDI-MS calcd for C₆₆H₆₇O₂ 902.5, found 903.3.



Synthesis of molecule 3.



Scheme 3. Synthesis of molecule 3.

2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-9-one (7). A mixture of 2,7-dibromo-9H-fluoren-9-one (2.03 g, 6 mmol), potassium acetate (1.76 g, 18 mmol), bis(pinacolato)diboron (6.10 g, 24 mmol), and Pd(dppf)Cl₂ (220 mg, 0.3 mmol) in deoxygenated 1,4-dioxane (50 mL) was heated to 80 °C and stirred overnight under Ar. The solvent was evaporated under vacuum. The residue was poured into water (100 mL) and extracted with ethyl acetate (3 * 100 mL). The combined organic layer was washed with brine (saturated), dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by column chromatography on the silica gel (petroleum: dichloromethane = 1:5 as the eluent). Recrystallization in methanol affords 1.84 g (4.3 mmol, 71% yield) white crystals.

Compound 7: ¹H NMR (300 MHz, CDCl₃): δ 8.83-8.78 (m, 2 H), 8.75-8.72 (m, 4 H), 1.30 (s, 12 H).

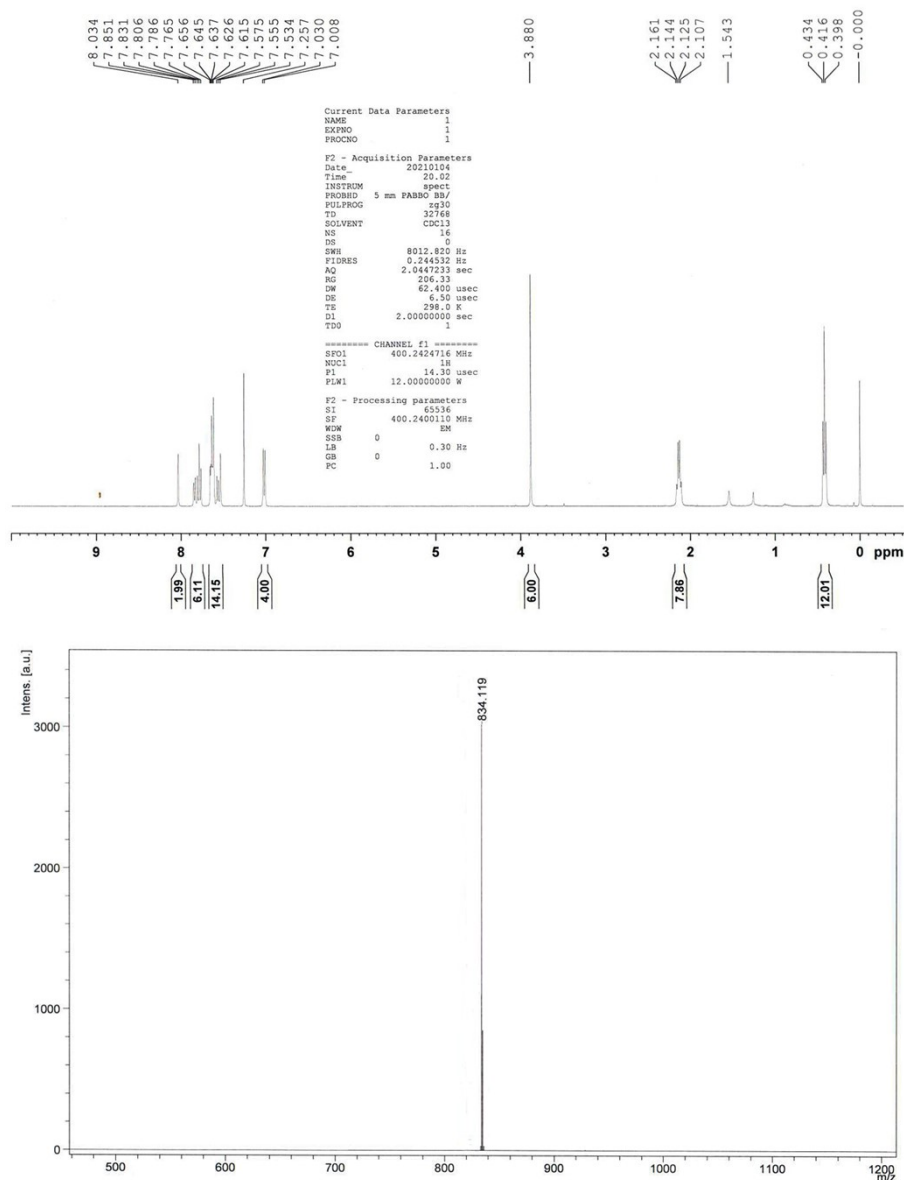
2-bromo-9,9-diethyl-7-(4-methoxyphenyl)-9H-fluorene (8). To a stirred solution of (4-methoxyphenyl)boronic acid (1.1 g, 7.25 mmol), 2,7-dibromo-9,9-diethyl-9H-fluorene (3.30 g, 8.7 mmol), and tetrakis(triphenylphosphine)palladium (419 mg, 0.36 mmol) in deoxygenated 1,4-dioxane (40 mL), aqueous solution of potassium carbonate (7 mL, 2.0 M) was added. Then the mixture was heated to 80 °C and stirred overnight under Ar. The solvent was evaporated under vacuum. The residue was poured into water (50 mL) and extracted with ethyl acetate (3 * 40 mL). The combined organic layer was washed with brine (saturated), dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by column chromatography on the silica gel (petroleum: ethyl acetate = 25:1 as the eluent) to afford **8** (1.33 g, 3.26 mmol, 45% yield).

Compound 8: ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.69-7.54 (m, 4H), 7.51-7.42 (m, 3H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H), 2.26-2.15 (m, 4 H), 0.43 (t, *J* = 7.2 Hz, 6 H).

9,9,9'',9''-tetraethyl-7,7''-bis(4-methoxyphenyl)-9H,9'H,9''H-[2,2':7',2''-terfluoren]-9'-one (3). To a stirred solution of **7** (0.63 g, 1.55 mmol), **8** (1.41 g, 3.26 mmol), and tetrakis(triphenylphosphine)palladium (89 mg, 0.077 mmol) in deoxygenated 1,4-dioxane (30 mL), aqueous solution of potassium carbonate (5 mL, 2.0 M) was added. Then the mixture was heated to 80 °C and stirred overnight under Ar. The solvent was evaporated under vacuum. The residue was poured into water (40 mL) and extracted with ethyl acetate (3 * 30 mL). The combined organic layer was washed with brine (saturated), dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (dichloromethane as the eluent) to afford **3** (0.43 g, 0.51 mmol, 33% yield). The resulting target compound was confirmed by ¹H NMR and MALDI-MS as below.

Molecule 3. ¹H NMR (300 MHz, CDCl₃): δ 8.03 (s, 2 H), 7.85-7.76 (m, 6 H), 7.65-7.53 (m, 14 H), 7.02 (d, *J* = 8.8 Hz, 4 H), 3.88 (s, 6 H), 2.16-2.11 (m, 8 H), 0.42 (t, *J* = 7.2 Hz, 12 H).

MALDI-MS calcd for C₆₁H₅₂O₃ 832.4, found 834.1.



2. Preparation of the microribbon seeds from **1** and **1-3** co-assembled hierarchical heterostructures.

Microribbon seeds from **1** were prepared by injecting a chloroform solution (1 mL) of **3** (2 mM) into ethanol (15 mL) in a vial (20 mL) followed by fully mixing and aging for 3 d. Then short microribbon seeds from **1** were prepared by ultrasonication the above resulting solution at $-50\text{ }^{\circ}\text{C}$ for 10 minutes. **1-3** co-assembled hierarchical heterostructures with various molar ratios of **1** and **3** were self-assembled by injecting a chloroform solution (1 mL) of **1** and **3** at various molar ratios into ethanol (15 mL) in a vial (20 mL) followed by fully mixing and aging for 5 d.

3. Seeded self-assembly of molecules **1**, **2**, and **3**.

The metastable nanospheres from **2** were prefabricated by injecting a chloroform solution (1 mL) of the corresponding compound (2 mM) into ethanol (15 mL) in a vial (20 mL) followed by fully mixing and aging for 10 minutes. The microribbon-seeded growth of molecule **2** was processed by adding a different amount of prefabricated metastable nanospheres from **2** in above solution into the short microribbon seeds from **1** (0.005 μmol , 1 mL) in 1:15 (v/v) chloroform/ethanol followed by fully mixing and aging. The **1-3** co-assembled microribbon-seeded growth of molecule **2** was processed by adding prefabricated metastable nanospheres (0.002 μmol , 1 mL) from **2** into **1-3** co-assembled microribbon seeds from **1** (0.002 μmol , 1 mL) in 1:15 (v/v) chloroform/ethanol followed by fully mixing and aging.

4. Structural and property characterizations.

SEM images of the seeded self-assembly of **1**, **2**, and **3** were obtained on a Hitachi SU8010 field-emission microscope. SEM samples were prepared by drop-casting the suspending aggregates in solution onto a silica substrate followed by sputtering Pt on the surface. The Pt sputtering was performed on a Leica EM SCD 500 instrument where the current and time were set as 15 mA and 120 s, respectively. The thickness of the sputtered Pt layer was about 5.4 nm. Fluorescence images were obtained using an Olympus FV1000 inverted confocal laser scanning fluorescence microscopy (CLSM), where the samples were excited by a continuous wave laser of $\lambda_{\text{exc}} = 350\text{-}390$ nm. The fluorescent spectra were collected using the lambda-mode option of the Olympus FV1000 CLSM. The raw data recorded by means of the lambda-mode were processed by Olympus Fluoview software. The CLSM samples in solid phase were prepared by drop-casting the suspending aggregates in solution onto the glass substrates. UV-vis absorption spectra were obtained on a PerkinElmer Lambda 35.

5. Other supporting figures:

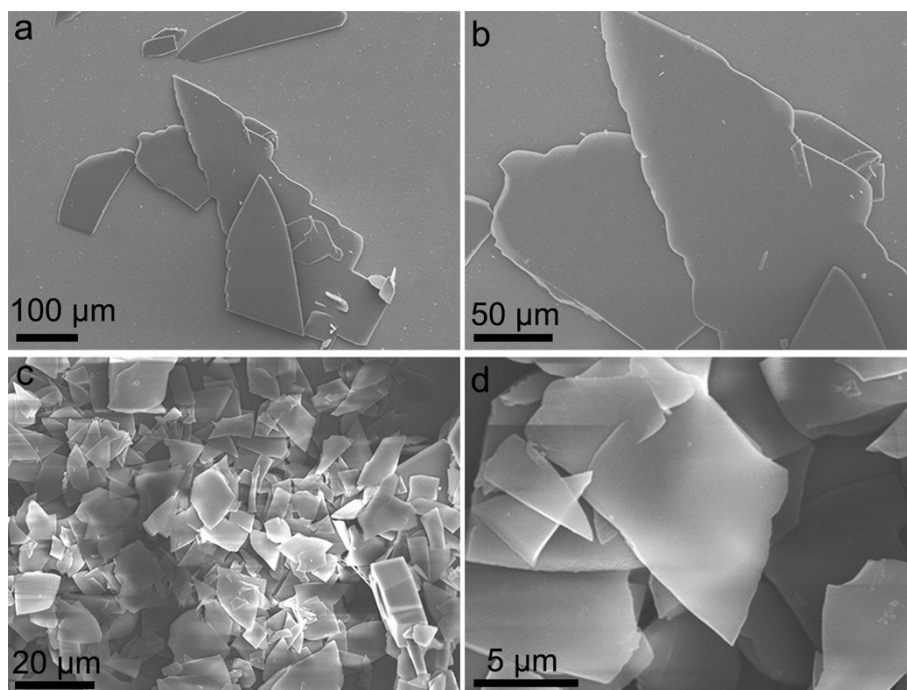


Fig. S1 (a, b) SEM images of microribbons from **1** formed by adding a chloroform solution (1 mL) of **1** (2 mM) into ethanol (15 mL) followed by fully mixing and aging for 3 d. (c, d) SEM images of short microribbon seeds from **1** obtained by ultrasonically treating the stable microribbons in ethanol at -50 °C for 10 minutes.

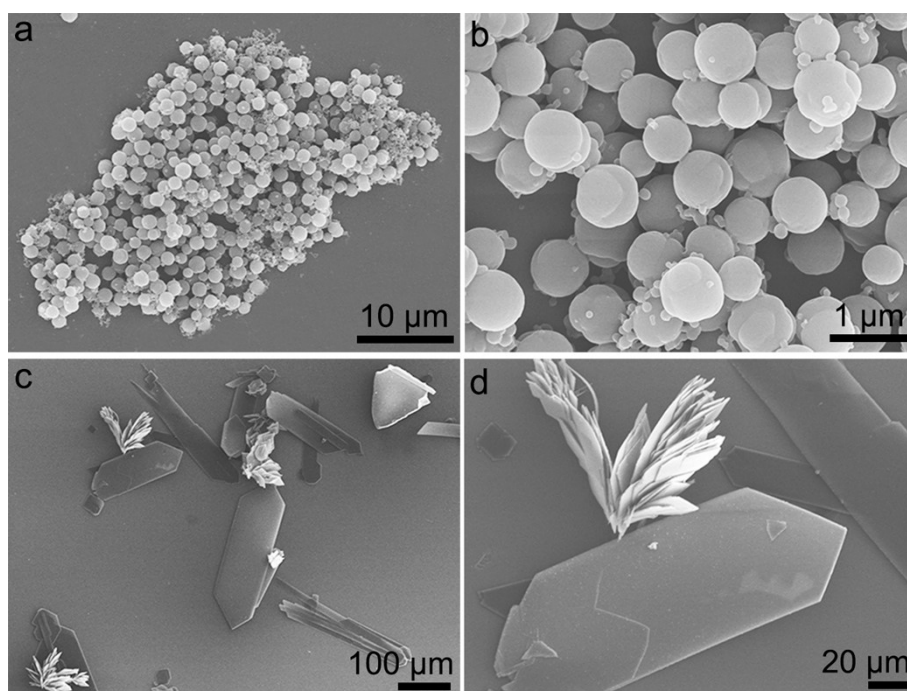


Fig. S2 (a-d) SEM images of metastable nanospheres and stable microsheets from **2** formed by adding a chloroform solution (1 mL) of **2** (0.1 mM) into ethanol (15 mL) followed by fully mixing and aging for 10 minutes (a, b) and 3 d (c, d), respectively.

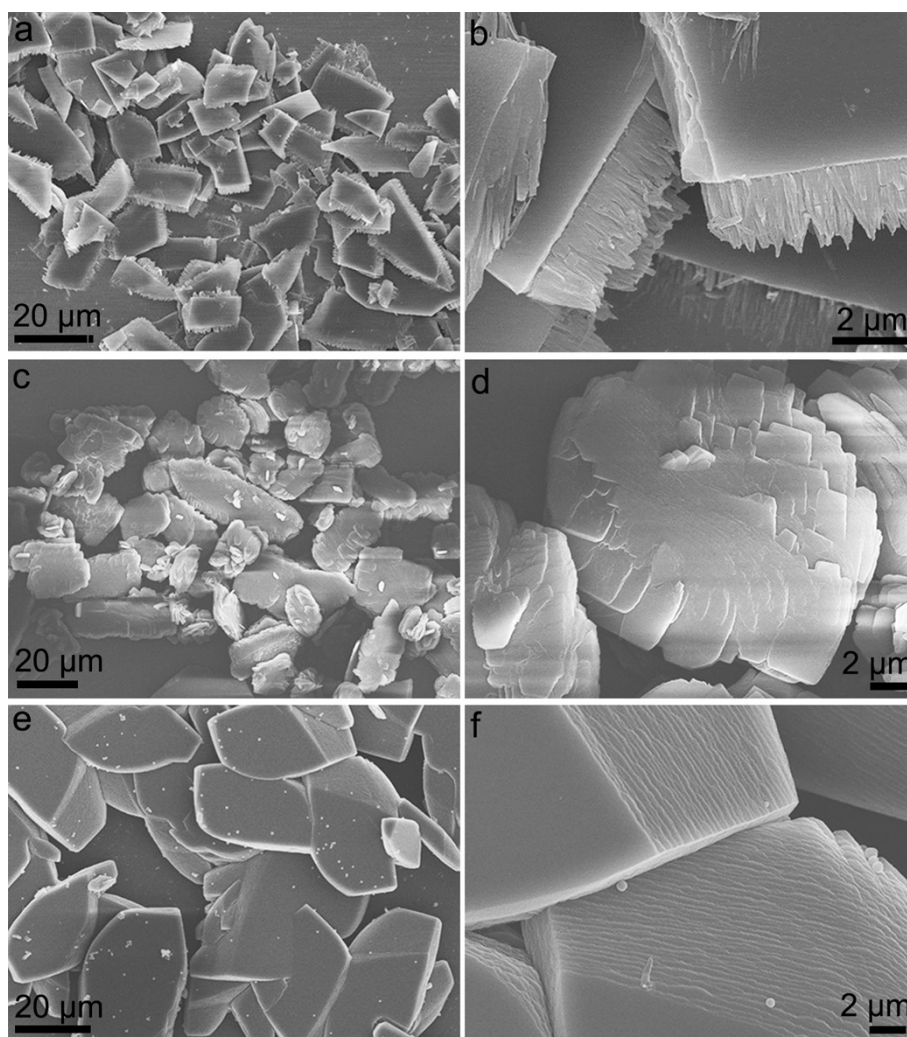


Fig. S3 (a-c) SEM images of hierarchical heterostructures in solution obtained by adding microribbon seeds from **1** in 1:15 (v/v) chloroform/ethanol into metastable nanospheres from **2** in 1:15 (v/v) chloroform/ethanol at the molar ratio of 1:1 (a, b), 1:5 (c, d), and 1:10 (e, f).

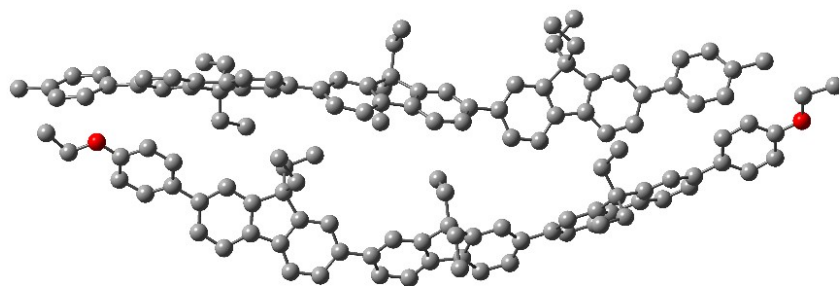


Fig. S4 Calculated intermolecular interactions between molecules **1** and **2**.

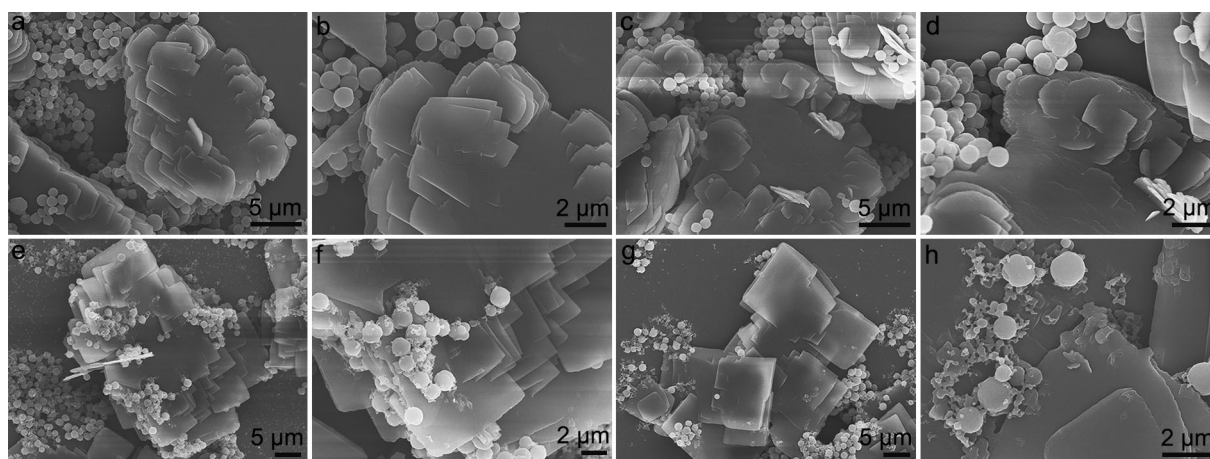


Fig. S5 (a-h) SEM images of the time-dependent morphological evolution of hierarchical heterostructures from **1** and **2** at the molar ratio of 1:5 via seeded self-assembly: 8 h (a-d), 1 d (e-h).

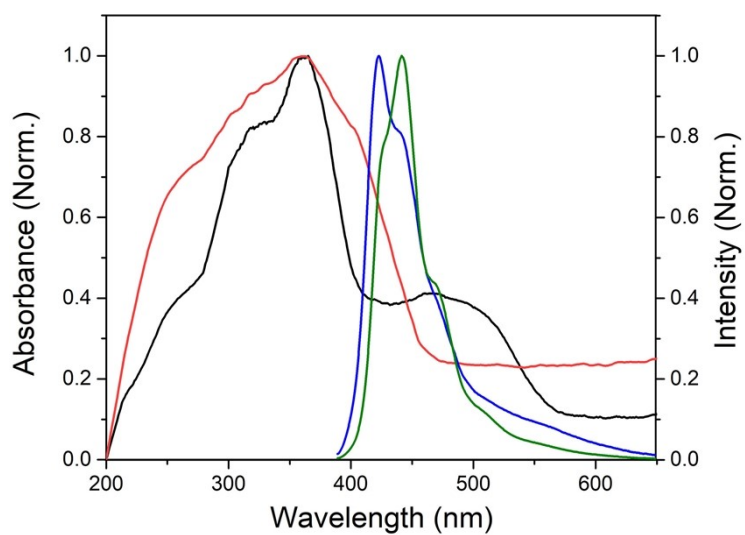


Fig. S6 Normalized UV-vis absorption spectrum of molecule **3** (black), fluorescence spectrum of molecule **1** (blue), absorption (red) and fluorescence spectrum (olive) of molecule **2** in solid.

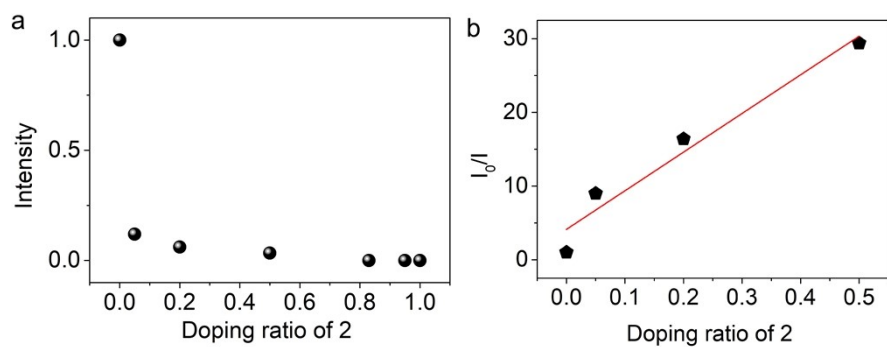


Fig. S7 FRET efficiencies of the 1-3 co-assemblies.

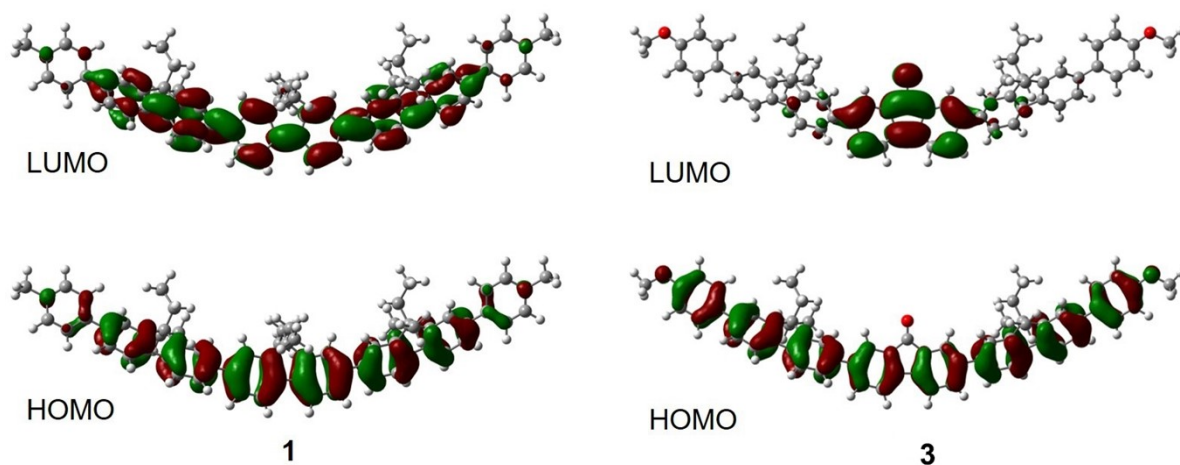


Fig. S8 DFT-calculated frontier molecular orbitals of molecule 1 and 3.

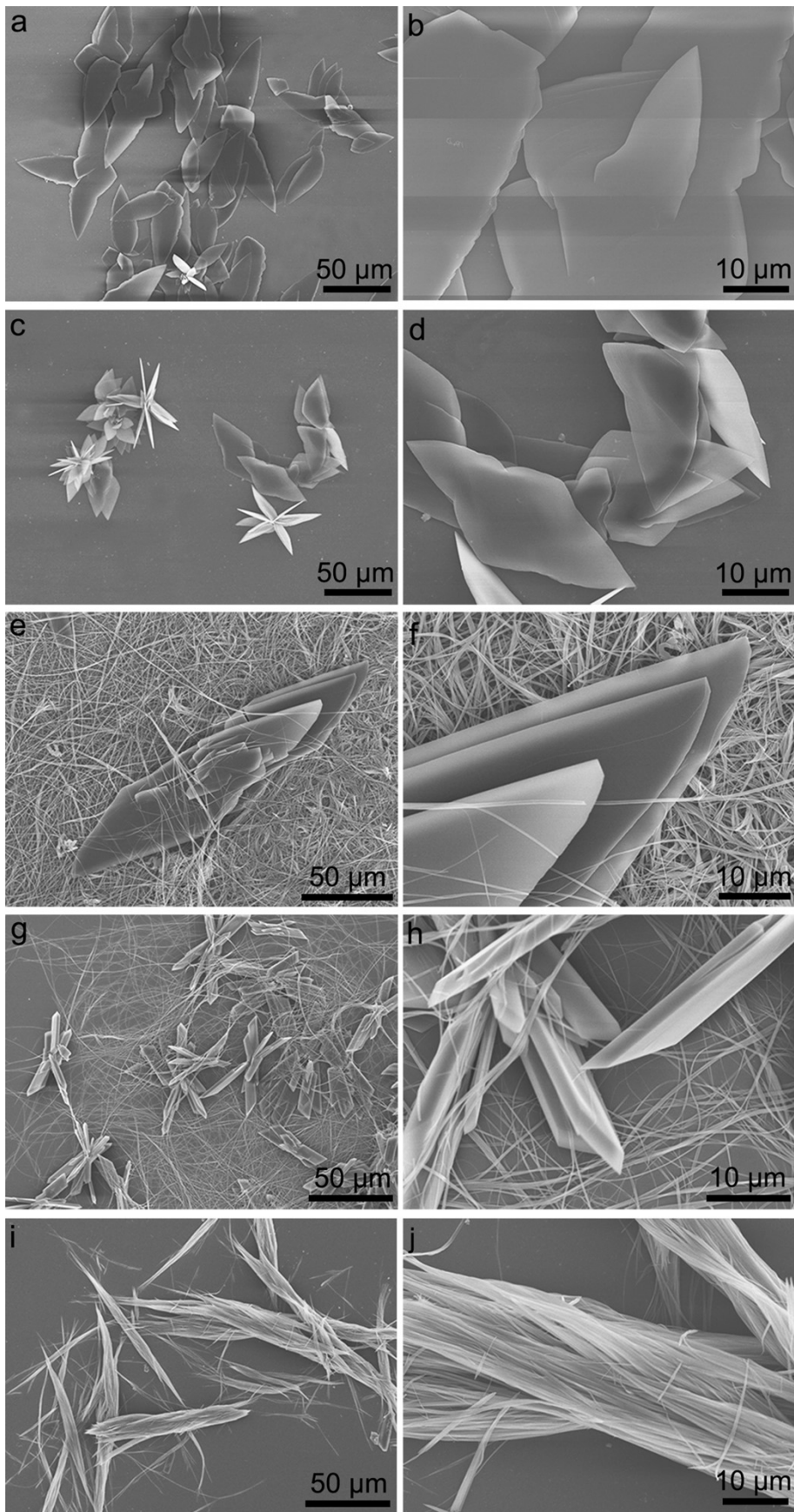


Fig. S9 (a-h) SEM images of **1-3** co-assembled aggregates with different molar ratios at 20:1 (a, b), 5:1 (c, d), 1:5 (e, f), and 1:20 (g, h). (i, j) SEM images of nanoribbons from **3** formed by adding a chloroform solution (1 mL) of **1** (2 mM) into ethanol (15 mL) followed by fully mixing and aging for 5 d.

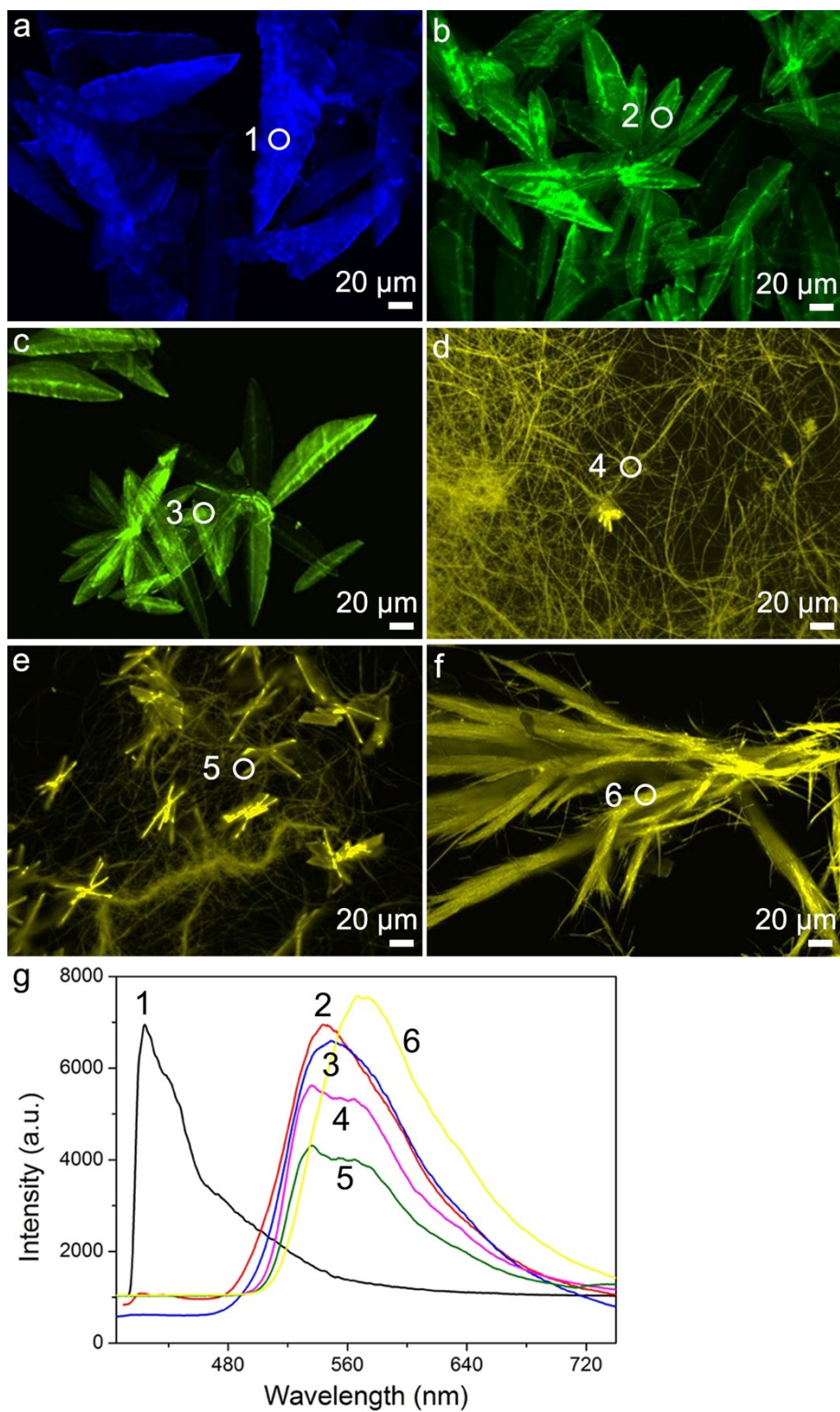


Fig. S10 (a-e) CLSM images of the microribbon seeds from **1** (a), **1-3** co-assembled aggregates with different molar ratios at 20:1 (b), 5:1 (c), 1:5 (d), 1:20 (e), and nanoribbons from **3** (f). (g) Fluorescence spectra of the circled areas 1-6 in (a-f).

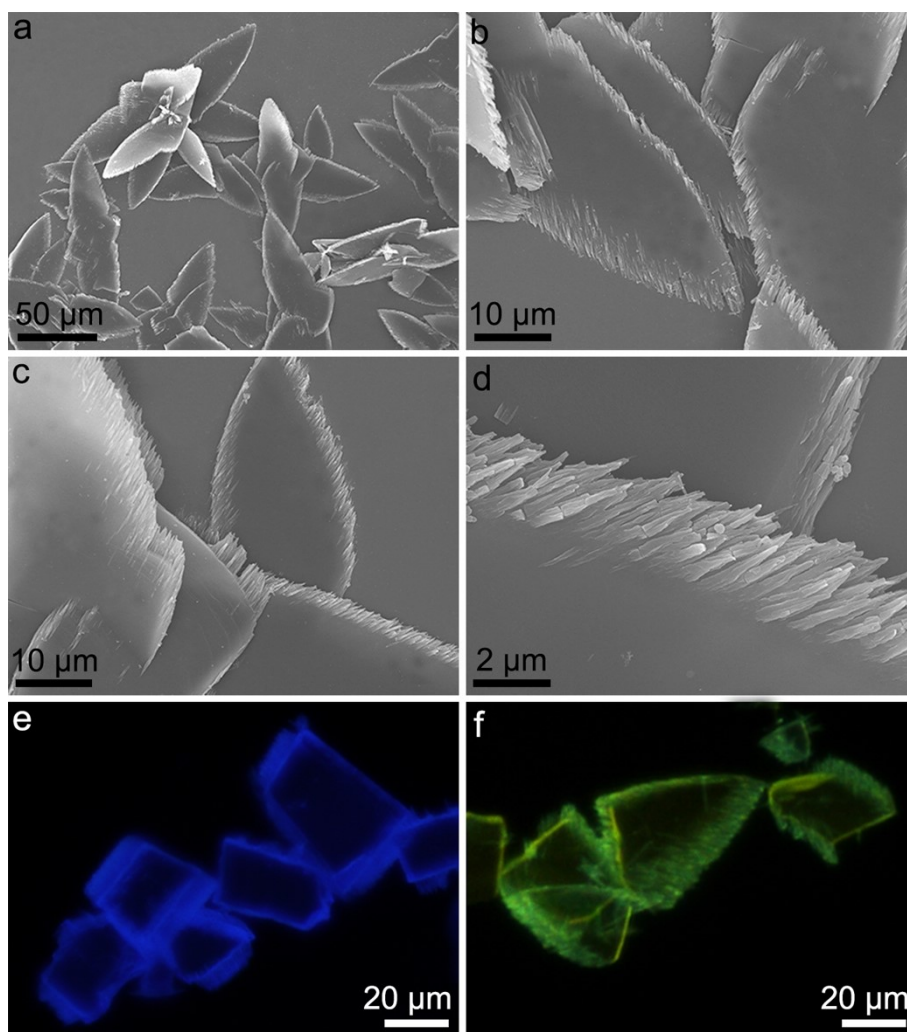


Fig. S11 (a-d) SEM images of hierarchical heterostructures obtained by adding microribbon seeds from **1** in 1:15 (v/v) chloroform/ethanol into metastable nanospheres from **2** in 1:15 (v/v) chloroform/ethanol at the molar ratio of 1:1. (e-f) CLSM images of the hierarchical heterostructures obtained by adding short microribbon seeds from **1** (e) and **1-3** co-assembled seeds (f) in 1:15 (v/v) chloroform/ethanol into metastable nanospheres from **2** in 1:15 (v/v) chloroform/ethanol at the molar ratio of 1:1.