Supplementary Information

A photon-working on/off switch for intramolecular donor-acceptor interactions and invisible modulation of the fluorescence

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1. Experimental details

General

Chemical reactions were carried out under a dry nitrogen atmosphere. All solvents including dry tetrahydrofuran (THF) were purchased and used as received. All flash column chromatography were carried out on 230-400 mesh silica gel using ethyl acetate and hexane as eluent. Analytical thin-layer chromatography was performed on the pre-coated 0.25-mm thick silica gel TLC plates.

^{1}H NMR Spectra were recorded in deuteriochloroform ($CDCl_3$) with Bruker DRX300 (300 MHz) or DRX500 (500 MHz) NMR spectrometers. *J* values are expressed in Hz and quoted chemical shifts are in ppm. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. Infrared spectra (IR) were recorded on a JASCO FT/IR-4100 spectrometer. Low- and high-resolution mass spectra were measured by the electron impact mass spectrometry using a JEOL JMS-AX-600 mass spectrometer. MALDI-TOF-mass spectra were recorded on a Bruker Autoflex Speed mass spectrometer or a Shimadzu AXIMA-CFR mass spectrometer. Melting points were measured using a Yazawa BY-2 hot stage microscope, and those were uncorrected.

Optical measurements

Absorption spectra of **1** and **2** in hexane (**1**: 1.34 x 10^{-5} mol dm^{-3}, **2**: 1.31 x 10^{-5} mol dm^{-3}) were recorded on a JASCO V-550 spectrophotometer. Fluorescence spectra of **1** and **2** in hexane (**1**: 1.34 x 10^{-5} mol dm^{-3}, **2**: 1.31 x 10^{-5} mol dm^{-3}) were recorded on a JASCO FP-6500 spectrophotometer. Fluorescence quantum yields of **1** were determined using JASCO FP-8300 spectrophotometer equipped with an integration sphere.

Photochemical reactions were carried out in a quartz cell with 10 mm optical path length. Photoirradiation with 405 nm light was carried out using a 500 W high-pressure mercury lamp (USHIO USH-500D), separated by filters (a 5 cm water filter, a pyrex glass filter, a L-39 glass filter, a V-40 glass filter, a KL-40 and a TND-50 glass filter). Photoirradiation with 622 nm light was carried out using a 500 W xenon lamp (USHIO, UXL-500D-0), separated by filters (a 5 cm water filter, an O-57 glass filter and a KL-60 glass filter). Ultra high performance liquid chromatography (JASCO, X-LC 3000) equipped with a UV/Vis detector (JASCO X-LC 3070 UV) and a silica gel column (Agilent, ZORBAX Rx-Sil RRHT) was used to determine the concentration of isomers during photoirradiation.

Quantum yields were determined with the procedures described elsewhere.[1)]

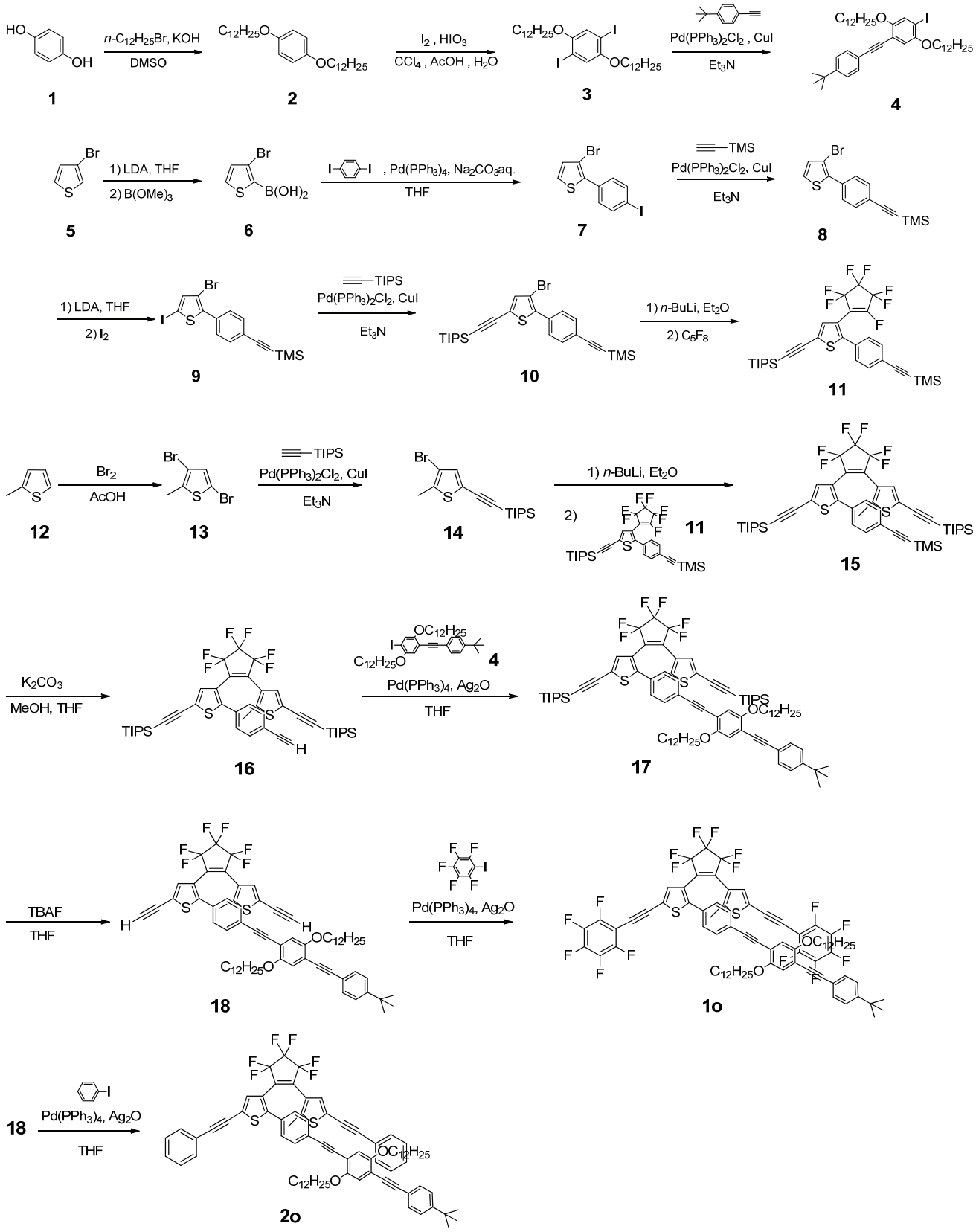
Computational details

DFT geometry optimization of **1** was carried out with the Spartan '14 package employing the three-parameter hybrid functional of Becke based on the correlation functional of Lee, Yang and Parr (B3LYP). The 6-31G(d) basis sets were used for all atoms.

1) Y. Yokoyama, T. Inoue, M. Yokoyama, T. Goto, T. Iwai, N. Kera, I. Hitomi, Y. Kurita, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 3297-3303.

2. Synthesis of 1o and 2o

Synthesis of **1o** and **2o** were carried out according to the following procedures.



Synthesis of 1,4-bis(dodecyloxy)benzene (2)

To a solution of hydroquinone (**1**) (4.02 g, 36.5 mmol) and KOH (8.17 g, 146 mmol) in DMSO (100 ml) were added dropwise a 1-bromododecane (24.0 ml, 100 mmol) under a N_2 atmosphere. The resulting solution was stirred at room temperature for overnight. The reaction was quenched by adding water, and the resultant mixture was extracted with dichloromethane. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated, to give 14.3 g of 1,4-bis(dodecyloxy)benzene (**2**) as a white solid in 90% yield.

2:

Mp: 66 – 69 ^oC.

^1H NMR (300MHz, $CDCl_3$, TMS): ð/ppm 0.89 (6H, t, *J*/Hz= 6.40), 1.27 (32H, m), 1.43 (4H, m), 1.76 (4H, quint, *J*/Hz = 6.80), 3.90 (4H, t, *J*/Hz = 6.59), 6.82 (4H, s).

EI-MS: m/z = 446.

Synthesis of 1,4-bis(dodecyloxy)-2,5-diiodobenzene (3)

A mixture of **2** (3.86 g, 8.64 mmol), I_2 (4.39 g, 17.3 mmol) and HIO_3 (3.07 g, 17.5 mmol) in acetic acid (40 mL), CCl_4 (40 mL) and H_2O (8 mL) were refluxed under a N_2 atmosphere for 8 h. The reaction mixture was quenched by 30% $Na_2S_2O_3$ aq., and extracted with chloroform. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane/ chloroform (15%) as the eluent, to give 4.10 g of 1,4-bis(dodecyloxy)-2,5-diiodobenzene (**3**) as a white solid in 68% yield.

3:

Mp: 63 – 64.5 ^oC.

^1H NMR (300MHz, $CDCl_3$, TMS): ð/ppm 0.88 (6H, t, *J*/Hz= 6.80), 1.27 (32H, m), 1.49 (4H, m), 1.80 (4H, quint, *J*/Hz = 6.80), 3.92 (4H, t, *J*/Hz = 6.59), 7.17 (2H, s).

EI-MS: m/z = 698.

Synthesis of 1-((4-(tert-butyl)phenyl)ethynyl)-2,5-bis(dodecyloxy)-4-iodobenzene (4)

To a suspension of **3** (2.70 g, 3.86 mmol), $Pd(PPh_3)Cl_2$ (54.7 mg, 0.078 mmol) and CuI (40.7 mg, 0.214 mmol) in triethylamine (55 mL) were added dropwise a 1-(tert-butyl)-4-ethynylbenzene (0.55 mL, 3.09 mmol) under a N_2 atmosphere. The resulting solution was stirred at room temperature for overnight. The reaction was quenched by adding HCl aq. (5 mol dm^{-3}), and the resultant mixture was extracted with chloroform. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane/ chloroform (20%) as the eluent, to give 1.74 g of 1-((4-(tert-butyl)phenyl)ethynyl)-2,5-bis(dodecyloxy)-4-iodobenzene (**4**) as a yellow solid in 77% yield.

4:

Mp: 38 – 41 ^oC.

^1H NMR (300MHz, $CDCl_3$, TMS): ð/ppm 0.87 (m, 6H), 1.26 (m, 32H), 1.32 (s, 9H), 1.50 (m, 4H), 1.82

(quint, 4H, *J*/Hz = 6.80), 3.97 (m, 4H), 3.99 (d, 2H , *J*/Hz = 6.59), 6.90 (s, 1H), 7.29 (s, 1H), 7.35 (d, 2H , *J*/Hz = 8.67), 7.46 (d, 2H , *J*/Hz = 8.67).
EI-MS: m/z = 728.

Synthesis of 3-bromo-2-(4-iodophenyl)thiophene (7)

To a solution of 2,2-bipyridyl (0.1 mg, 0.001 mmol) in THF (150 mL) and diisopropylamine (7.5 mL, 53.6 mmol) were added dropwise a n-BuLi in hexane (1.65 mol dm^{-3}, 26.7 mL, 43.1 mmol) at -78 ^{o}C under a N_2 atmosphere, and the reaction temperature was increased up to 0 ^{o}C. To a resulting solution was added dropwise a 3-bromothiophene (**5**) (4.28 mL, 45.1 mmol) in THF (75 mL), and the resulting mixture was stirred for 1 h at 0 ^{o}C. To this reaction mixture was then added dropwise a trimethyl borate (7.5 ml, 67.3 mmol), and a reaction mixture was stirred for 2h. The reaction was quenched by adding water, to give (3-bromothiophen-2-yl)boronic acid (**6**). To the solution of **6** was added a 1,4-diiodobenzene (14.2 g, 43.1 mmol), $Pd(PPh_3)_4$ (2.2 g, 1.9 mmol) and Na_2CO_3 aq. (2 mol dm^{-3}, 75 mL), and the reaction mixture was refluxed for 7 h. The reaction was quenched by adding HCl aq. (5 mol dm^{-3}), and the resultant mixture was extracted with diethyl ether. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent, to give 5.23 g of bromo-2-(4-iodophenyl)thiophene (**7**) as a pale yellow solid in 32% yield.

7:

Mp: 41 – 42 ^{o}C.

^{1}H NMR (300MHz, $CDCl_3$, TMS): ð/ppm 7.06 (d, 1H, *J*/Hz = 5.27), 7.30 (d, 1H, *J*/Hz = 5.27), 7.39 (d, 2H, *J*/Hz = 8.67), 7.76 (d, 2H, *J*/Hz = 8.67).

EI-LRMS: m/z = 364.

EI-HRMS: Found: m/z 363.8414 (M^+). Calcd for $C_{10}H_6BrIS$: M, 363.8418.

Synthesis of ((4-(3-bromothiophen-2-yl)phenyl)ethynyl)trimethylsilane (8)

To a suspension of **7** (9.0 g, 24.6 mmol), $Pd(PPh_3)Cl_2$ (870 mg, 1.24 mmol) and CuI (97.8 mg, 0.514 mmol) in triethylamine (220 mL) were added dropwise a trimethylsilylacetylene (3.66 mL, 25.9 mmol) under a N_2 atmosphere at 0 ^{o}C. The resulting solution was stirred at room temperature for 3 h. The reaction was quenched by adding HCl aq. (5 mol dm^{-3}), and the resultant mixture was extracted with diethyl ether. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent, to give 8.1 g of ((4-(3-bromothiophen-2-yl)phenyl)ethynyl)trimethylsilane (**8**) as a yellow liquid in 97% yield.

8:

^{1}H NMR (300MHz, $CDCl_3$, TMS): ð/ppm 0.26 (s, 9H), 7.06 (d, 1H, *J*/Hz = 5.27), 7.30 (d, 1H, *J*/Hz = 5.27), 7.51 (m, 2H), 7.61 (m, 2H).

EI-LRMS: m/z = 334.

EI-HRMS: Found: m/z 333.9844 (M^+). Calcd for $C_{15}H_{15}BrSSi$: M, 333.9847.

Synthesis of ((4-(3-bromo-5-iodothiophen-2-yl)phenyl)ethynyl)trimethylsilane (9)

To a solution of 2,2-bipyridyl (0.1 mg, 0.001 mmol) in THF (100 mL) and diisopropylamine (1.69 mL, 12.1 mmol) were added dropwise a n-BuLi in hexane (1.65 mol dm^{-3}, 6.7 mL, 11.1 mmol) at -78 °C under N_2 atmosphere, and the reaction mixture was stirred for 20 min. To the resulting reaction mixture was added dropwise a solution of **8** (3.40 g, 10.1 mmol) in THF (75 mL) at -78 °C under a N_2 atmosphere, and stirred for 30 min. To this reaction mixture was added dropwise an I_2 (2.56 g, 10.1 mmol) in THF (115 mL) at 0 °C, and stirred for overnight at room temperature. The reaction mixture was quenched by adding 30 wt% $Na_2S_2O_3$ aq., and the resultant mixture was extracted with diethyl ether. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent, to give 3.58 g of ((4-(3-bromo-5-iodothiophen-2-yl)-phenyl)ethynyl)trimethylsilane (**9**) as a yellow amorphous solid in 77% yield.

9:

^{1}H NMR (500MHz, DMSO, TMS): ð/ppm 0.24 (s, 9H), 7.46 (s, 1H), 7.55 (d, 2H, *J*/Hz = 9.14), 7.60 (d, 2H , *J*/Hz = 8.83).

EI-LRMS: m/z = 460.

EI-HRMS: Found: m/z 459.8822 (M^+). Calcd for $C_{15}H_{14}BrISSi$: M, 459.8814.

Synthesis of ((4-(3-bromo-5-((triisopropylsilyl)ethynyl)thiophen-2-yl)phenyl)ethynyl)trimethylsilane (10)

To a suspension of **9** (130 mg, 0.281 mmol), $Pd(PPh_3)Cl_2$ (11.9 mg, 0.017 mmol) and CuI (5.2 mg, 0,027 mmol) in triethylamine (10 mL) was added dropwise a triisopropylsilylacetylene (0.066 mL, 0.295 mmol) at 0 °C under a N_2 atmosphere. The resulting mixture was stirred for 4h at room temperature. The reaction was quenched by adding HCl aq. (3 mol dm^{-3}), and the resultant mixture was extracted with chloroform. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent, to give 0.122 g of ((4-(3-bromo-5-((triisopropylsilyl)ethynyl)thiophen-2-yl)phenyl)ethynyl)trimethylsilane (**10**) as a yellow liquid in 99% yield.

10:

^{1}H NMR (500MHz, $CDCl_3$, TMS): ð/ppm 0.26 (s, 9H), 1.12 (s, 21H), 7.16 (s, 1H), 7.50 (d, 2H , *J*/Hz = 7.84), 7.58 (d, 2H , *J*/Hz = 7.88).

EI-LRMS: m/z = 514.

EI-HRMS: Found: m/z 514.1152 (M^+). Calcd for $C_{26}H_{35}BrSSi_2$: M, 514.1181.

Synthesis of triisopropyl((4-(perfluorocyclopent-1-en-1-yl)-5-(4- ((trimethylsilyl)ethynyl)phenyl)-thiophen-2-yl)ethynyl)silane (11)

To a solution of **10** (2.11 g, 4.81 mmol) in diethyl ether (100 mL) was added dropwise a n-BuLi in hexane (1.65 mol dm^{-3}, 3.0 mL, 4.95 mmol) at -78 °C under a N_2 atmosphere, and the resulting mixture was stirred for 10 min. To a reaction mixture was added dropwise an octafluorocyclopentene (3.3 mL, 4.8 mmol), and the

reaction mixture was stirred for overnight at room temperature. The reaction was quenched by adding water, and the reaction mixture was extracted with diethyl ether. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent, to give 2.14 g of triisopropyl((4-(perfluorocyclopent-1-en-1-yl)-5-(4-((trimethylsilyl)ethynyl)phenyl)thiophen-2-yl)ethynyl)silane (**11**) as a yellow liquid in 71% yield.

11:

^{1}H NMR (300MHz, Acetone, TMS): ð/ppm 0.25 (s, 9H), 1.15 (m, 21H), 7.46 (d, 2H, *J*/Hz = 8.67), 7.51 (s, 1H), 7.61 (d, 2H, *J*/Hz = 8.29).

EI-LRMS: m/z = 628.

Synthesis of 3,5-dibromo-2-methylthiophene (13)[1]

To a solution of 2-methylthiophene (**12**) (2.0 g, 20.4 mmol) in acetic acid (8 mL) was added dropwise a Br_2 (2.4 mL, 47.9 mmol) in acetic acid (3.5 mL) at 4 ^{o}C. The resulting mixture was stirred for overnight at 4 ^{o}C. The reaction was quenched by adding 30 wt% $Na_2S_2O_3$ aq and 10 wt% NaOH aq., and the resultant mixture was extracted with diethyl ether. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent, to give 1.95 g of 3,5-dibromo-2-methylthiophene (**13**) as a yellow liquid in 37% yield.

13:

^{1}H NMR (300MHz, $CDCl_3$, TMS): ð/ppm 2.34 (s, 3H), 6.86 (s, 1H).

EI-LRMS: m/z = 254.

EI-HRMS: Found: m/z 253.8396 (M^+). Calcd for $C_5H_4Br_2S$: M, 253.8400.

Synthesis of ((4-bromo-5-methylthiophen-2-yl)ethynyl)triisopropylsilane (14)[2]

To a suspension of **12** (2.59 g, 10.1 mmol), $Pd(PPh_3)Cl_2$ (0.551 g, 0.78 mmol) and CuI (0.14 g, 0,73 mmol) in triethylamine (60 mL) was added dropwise a triisopropylsilylacetylene (2.4 mL, 10.7 mmol) under a N_2 atmosphere. The resulting mixture was refluxed for 13 h. The reaction was quenched by adding HCl aq. (5 moldm^{-3}), and the resultant mixture was extracted with diethyl ether. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent, to give 1.17 g of ((4-bromo-5-methylthiophen-2-yl)ethynyl)triisopropylsilane (**14**) as a yellow liquid in 33% yield.

14:

^{1}H NMR (300MHz, $CDCl_3$, TMS): ð/ppm 1.10 (m, 21H), 2.36 (s, 3H), 7.03 (s, 1H).

EI-LRMS: m/z = 356.

EI-HRMS: Found: m/z 356.0632 (M^+). Calcd for $C_{16}H_{25}BrSSi$: M, 356.0630.

Synthesis of ((4-(3-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-((triisopropylsilyl)ethynyl)thiophen-3-yl)-cyclopent-1-en-1-yl)-5-((triisopropylsilyl)ethynyl)thiophen-2-yl)phenyl)ethynyl)trimethylsilane (15)

To a solution of **14** (1.17 g, 3.23 mmol) in diethyl ether (60 mL) was added dropwise a n-BuLi in hexane (2.60 mol dm^{-3}, 1.3 mL, 3.45 mmol) at -78 ^{o}C under a N_2 atmosphere, and the resulting mixture was stirred for 10 min. To a reaction mixture was added dropwise **11** (2.08 g, 3.31 mmol) in diethyl ether (40 mL), and the reaction mixture was stirred for overnight at room temperature. The reaction was quenched by adding water, and the reaction mixture was extracted with diethyl ether. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent, to give 1.69 g of ((4-(3-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-((triisopropylsilyl)ethynyl)thiophen-3-yl)cyclopent-1-en-1-yl)-5- ((triisopropylsilyl)ethynyl)-thiophen-2-yl)phenyl)ethynyl)trimethylsilane (**15**) as a yellow solid in 58% yield.

15:

Mp: 62 – 66 ^{o}C.

^{1}H NMR (300MHz, $CDCl_3$, TMS): ð/ppm 0.25 (m, 9H), 1.12 (m, 42H), 1.80 (s, 3H), 6.07 (s, 1H), 6.84 (d, 2H , *J*/Hz = 8.67), 7.33 (d, 2H , *J*/Hz = 7.34), 7.34 (s, 1H).

EI-LRMS: m/z = 886.

Synthesis of ((5-(4-ethynylphenyl)-4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-((triisopropylsilyl)ethynyl)-thiophen-3-yl)cyclopent-1-en-1-yl)thiophen-2-yl)ethynyl)triisopropylsilane (16)

The reaction mixture of **15** (1.69 g, 1.91 mmol) and K_2CO_3 (0.265 g, 1.91 mmol) in THF (50 mL) and methanol (50 mL) were stirred for overnight at room temperature. The reaction was quenched by adding sat. NH_4Cl aq., and the reaction mixture was extracted with diethyl ether. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent, to give 0.718 g of ((5-(4-ethynylphenyl)-4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-((triisopropylsilyl)ethynyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophen-2-yl)ethynyl)triisopropylsilane (**16**) as a yellow amorphous solid in 46% yield.

16:

^{1}H NMR (300MHz, $CDCl_3$, TMS): ð/ppm 1.12 (m, 42H), 1.77 (s, 3H), 3.09 (s, 1H), 6.05 (s, 1H), 6.85 (d, 2H , *J*/Hz = 7.56), 7.36 (d, 2H , *J*/Hz = 6.78), 7.37 (s, 1H).

EI-LRMS: m/z = 814.

Synthesis of ((5-(4-((4-((4-(2,2-dimethyl-2λ^5-propan-2-yl)phenyl)ethynyl)-2,5-bis(dodecyloxy)phenyl)-ethynyl)phenyl)-4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-((triisopropylsilyl)ethynyl)thiophen-3-yl)-cyclopent-1-en-1-yl)thiophen-2-yl)ethynyl)triisopropylsilane (17)

The reaction mixture of **16** (47.0 mg, 0.058 mmol), **4** (48.8 mg, 0.067 mmol), $Pd(PPh_3)_4$ (7.7 mg, 0.007 mmol) and Ag_2O (15.5 mg, 0.067 mmol) in THF (5 mL) were refluxed for 11 h under a N_2 atmosphere. The resulting mixture was filtered by celite, and evaporated. The residue was purified by column chromatography on silica gel using hexane/ ethyl acetate (10%) as the eluent, to give 82.2 mg of ((5-(4-((4-((4-(2,2-dimethyl-2λ^5-propan-2-yl)phenyl)ethynyl)-2,5-bis(dodecyloxy)phenyl)ethynyl)phenyl)-4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-((triisopropylsilyl)ethynyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophen-2-yl)ethynyl)-

triisopropylsilane (**17**) as a black oil in 99% yield.

17:

^{1}H NMR (300MHz, $CDCl_3$, TMS): ð/ppm 0.88 (m, 6H), 1.04 (s, 21H), 1.14 (m, 21H), 1.26 (m, 32H), 1.33 (s, 9H), 1.53 (m, 4H), 1.80 (s, 3H), 1.85 (m, 4H), 4.01 (4H, m), 6.12 (s, 1H), 6.89 (d, 2H, *J*/Hz = 8.29), 6.99 (s, 1H), 7.00 (s, 1H), 7.37 (d, 2H, *J*/Hz = 6.03), 7.38 (s, 1H), 7.39 (d, 2H, *J*/Hz = 7.91), 7.48 (d, 2H, *J*/Hz = 8.67). MALDI-TOF MS: Found: 1414.96 (M^+). Calcd for $C_{86}H_{116}F_6O_2S_2Si_2$: M, 1414.7859.

Synthesis of 2-(4-((4-((4-(tert-butyl)phenyl)ethynyl)-2,5-bis(dodecyloxy)phenyl)ethynyl)phenyl)-5-ethynyl-3-(2-(5-ethynyl-2-methylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-en-1-yl)thiophene (18)

To a solution of **17** (0.88 g, 0.62 mmol) in THF (40 ml) was added dropwise a tetrabutylammonium fluoride (1 mol dm^{-3} in THF inc. 5% water, 2.4 mL, 2.5 mmol) at -78 ^oC under a N_2 atmosphere, and the resulting mixture was stirred for 90 min at room temperature. The reaction was quenched by adding sat. NH_4Cl aq., and the reaction mixture was extracted with chloroform. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using hexane as the eluent, to give 600 mg of 2-(4-((4-((4-(tert-butyl)phenyl)ethynyl)-2,5-bis-(dodecyloxy)phenyl)ethynyl)phenyl)-5-ethynyl-3-(2-(5-ethynyl-2-methylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-en-1-yl)thiophene (**18**) as a black oil in 88% yield.

18:

^{1}H NMR (300MHz, $CDCl_3$, TMS): ð/ppm 0.87 (m, 6H), 1.25 (m 32H), 1.33 (s, 9H), 1.53 (m, 4H), 1.78 (s, 3H), 1.86 (m, 4H), 3.25 (s,1H), 3.48 (s, 1H), 4.04 (4H, t, *J*/Hz = 6.00), 6.21 (s, 1H), 6.88 (d, 2H, *J*/Hz = 8.67), 7.01 (s, 1H), 7.02 (s, 1H), 7.36 (d, 2H, *J*/Hz = 8.29), 7.41 (d, 2H, *J*/Hz = 8.29), 7.46 (s, 1H), 7.47 (d, 2H, *J*/Hz = 8.30).

Neither ESI nor MALDI-TOF MS measurements showed any positive or negative ion peaks.

Synthesis of 2-(4-((4-((4-(tert-butyl)phenyl)ethynyl)-2,5-bis(dodecyloxy)phenyl)ethynyl)phenyl)-3-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-((perfluorophenyl)ethynyl)thiophen-3-yl)cyclopent-1-en-1-yl)-5-((perfluorophenyl)ethynyl)thiophene (1o)

To a solution of **18** (99.2 mg, 0.09 mmol), $Pd(PPh_3)_4$ (12.0 mg, 0.010 mmol) and Ag_2O (50.5 mg, 0.22 mmol) in THF (10 mL) was added dropwise a pentafluoroiodobenzene (0.1 mL, 0.75 mmol) at room temperature under a N_2 atmosphere, and resulting mixture was refluxed for 22 h. The resulting solution was filtered by celite, and evaporated. The residue was purified by column chromatography on silica gel using hexane/ ethyl acetate (5%) as the eluent. Further purification was performed by HPLC using hexane/ ethyl acetate (3%) as the eluent, to give 10.0 mg of 2-(4-((4-((4-(tert-butyl)phenyl)ethynyl)-2,5-bis(dodecyloxy)phenyl)ethynyl)-phenyl)-3-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-((perfluorophenyl)ethynyl)thiophen-3-yl)cyclopent-1-en-1-yl)-5-((perfluorophenyl)ethynyl)thiophene (**1o**) as a light brown oil in 8% yield.

1o:

^{1}H NMR (500MHz, $CDCl_3$, TMS): ð/ppm 0.88 (m, 6H), 1.26 (m 32H), 1.34 (s, 9H), 1.42 (m, 4H), 1.83 (m, 4H), 1.85 (s, 3H), 3.92 (t, 2H, *J*/Hz = 6.46), 3.97 (t, 2H, *J*/Hz = 6.31), 6.31 (s, 1H), 6.82 (s, 1H), 6.89 (s, 1H),

6.93 (d, 2H, *J*/Hz = 8.20), 7.38 (d, 2H, *J*/Hz = 8.51), 7.42 (d, 2H, *J*/Hz = 8.51), 7.49 (d, 2H, *J*/Hz = 8.51), 7.60 (s, 1H).

MALDI-TOF MS: Found: 1541.408 ($M + Ag^+$). Calcd for $C_{80}H_{74}F_{16}O_2S_2Ag$: M, 1541.3926.

Synthesis of 2-(4-((4-((4-(tert-butyl)phenyl)ethynyl)-2,5-bis(dodecyloxy)phenyl)ethynyl)phenyl)-3-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-(phenylethynyl)thiophen-3-yl)cyclopent-1-en-1-yl)-5-(phenylethynyl)thiophene (2o)

To a solution of **18** (113 mg, 0.102 mmol), $Pd(PPh_3)_4$ (57.5 mg, 0.050 mmol) and Ag_2O (52.2 mg, 0.23 mmol) in THF (10 mL) was added dropwise a iodobenzene(0.04 mL, 0.36 mmol) at room temperature under a N_2 atmosphere, and resulting mixture was refluxed for 8h. The resulting solution was filtered by celite, and evaporated. The residue was purified by column chromatography on silica gel using hexane/ ethyl acetate (3%) as the eluent, to give 85.5 mg of 2-(4-((4-((4-(tert-butyl)phenyl)ethynyl)-2,5-bis(dodecyloxy)phenyl)-ethynyl)-phenyl)-3-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-(phenylethynyl)thiophen-3-yl)cyclopent-1-en-1-yl)-5-(phenylethynyl)thiophene (**2o**) as a yellow oil in 67% yield.

2o:

^{1}H NMR (500MHz, $CDCl_3$, TMS): ð/ppm 0.88 (m, 6H), 1.26 (m 32H), 1.34 (s, 9H), 1.48 (m, 4H), 1.76 (m, 4H), 1.83 (s, 3H), 3.91 (4H, m), 6.18 (s, 1H), 6.90 (s, 1H), 6.93 (d, 2H, *J*/Hz = 8.20), 6.97 (s, 1H), 7.05 (t, 2H, *J*/Hz = 7.57), 7.20 (t, 1H, *J*/Hz = 7.88), 7.39 (m, 7H), 7.45 (d, 2H, *J*/Hz = 8.20), 7.47 (s, 1H), 7.49 (d, 2H, *J*/Hz = 8.20), 7.54 (m, 2H).

MALDI-TOF MS: Found: 1361.548 ($M + Ag^+$). Calcd $C_{80}H_{84}F_6O_2S_2Ag$: M, 1361.4862.

References

1. For **13**: S. Pu, C. Fan, W. Miao and G. Liu, *Dyes and Pigments*, **2010**, *84*, 25-35.

2. For **14**: Y. M. Hervault, C. M. Ndiaye, L. Norel, C. Lagrost and S. Rigaut, *Org. Lett.*, **2012**, *14*, 4454-4457.

3. ^{1}H NMR spectra of 1o and 2o

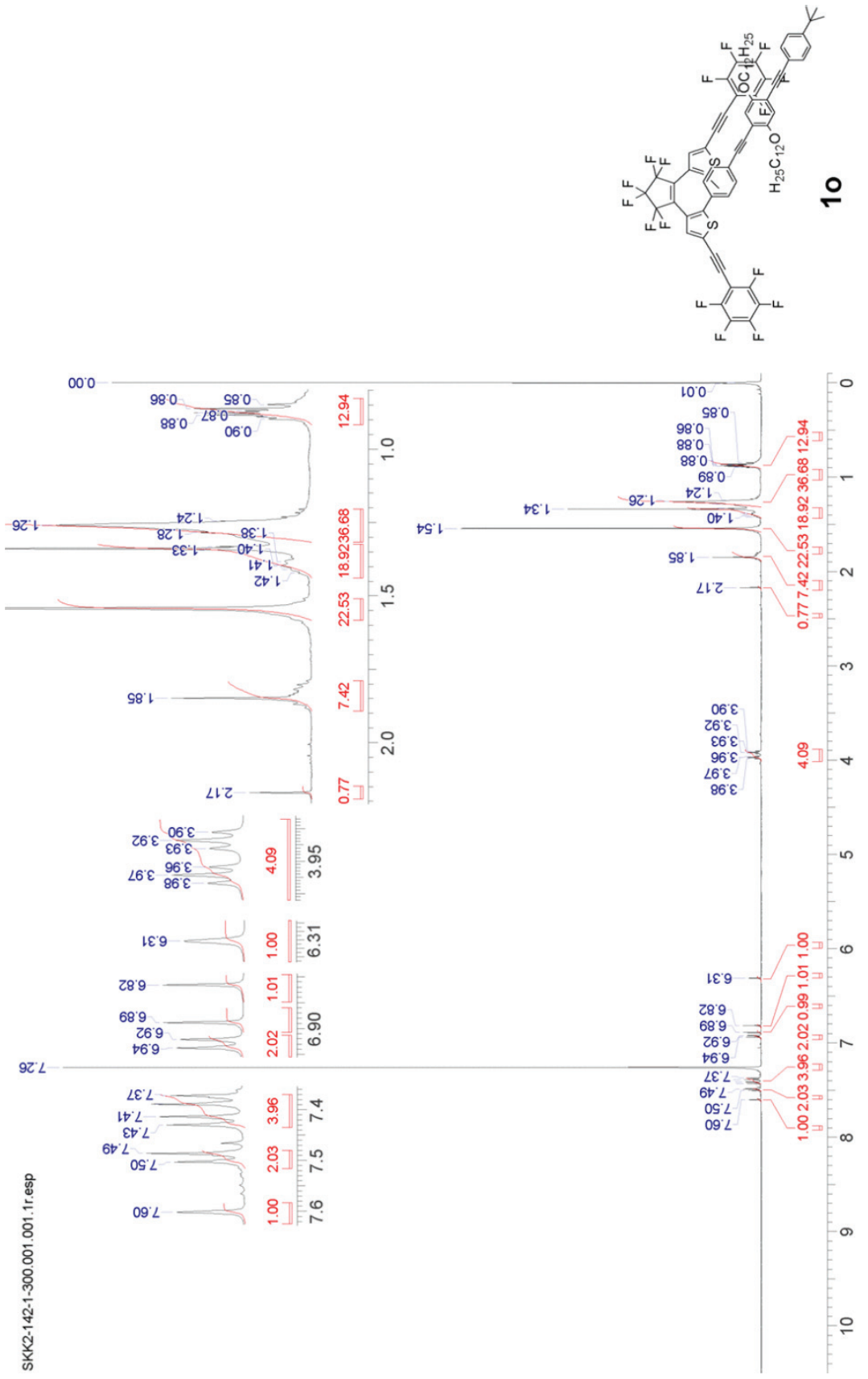


Fig. S1. ^{1}H NMR spectrum of **1o**

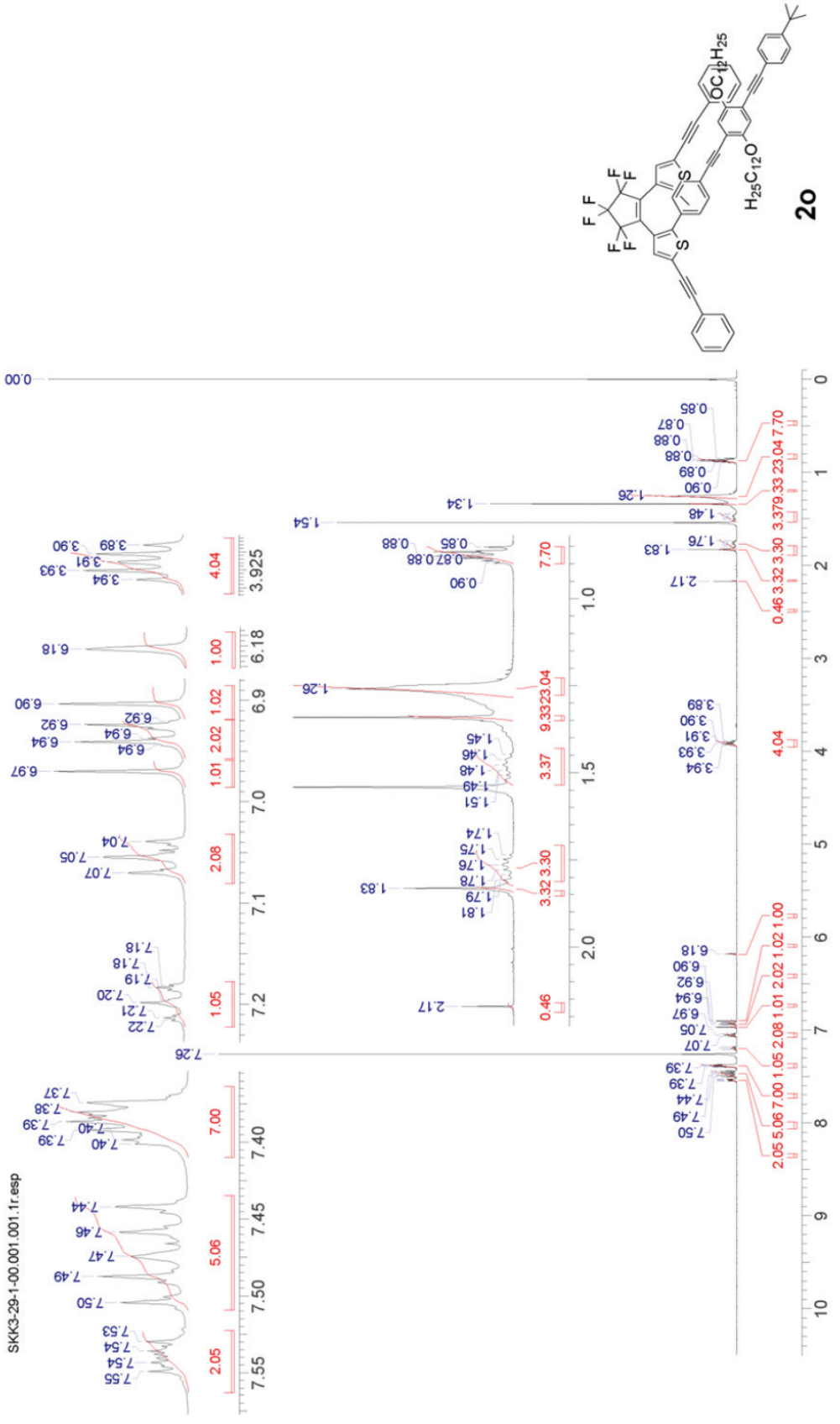


Fig. S2. ^{1}H NMR spectrum of **2o**

4. MALDI-TOF mass spectra of 1o and 2o

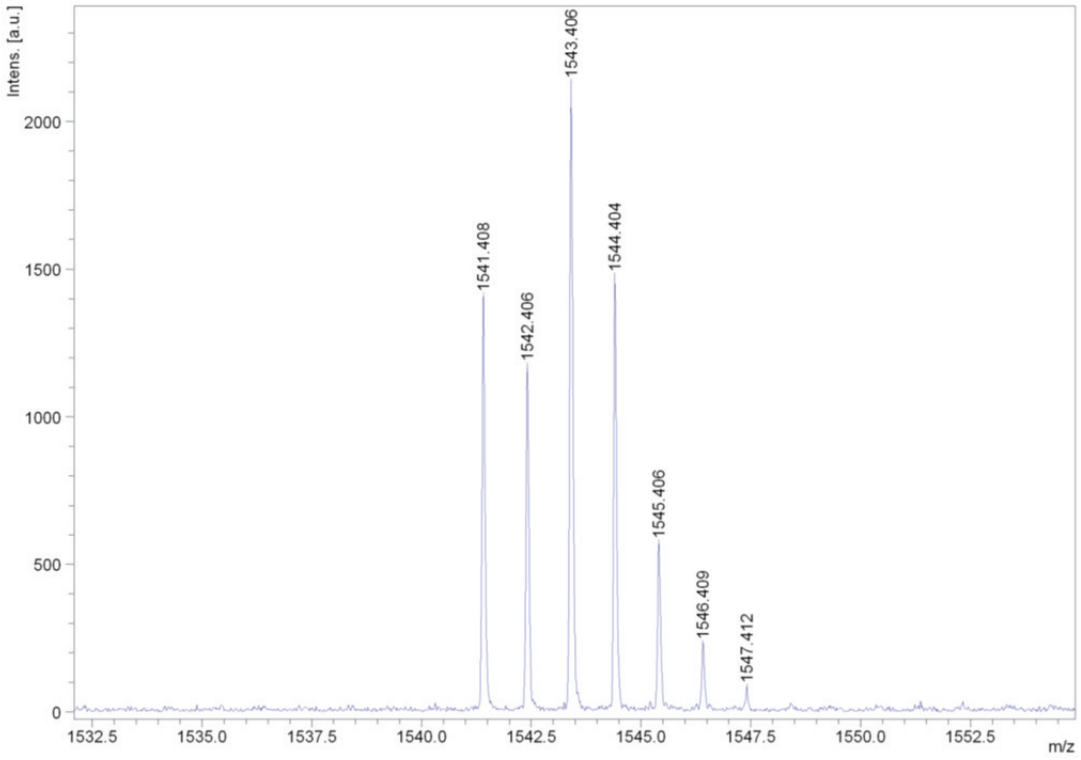


Fig. S3. MALDI-TOF Mass spectrum of **1o** (**1o** + Ag)$^+$.

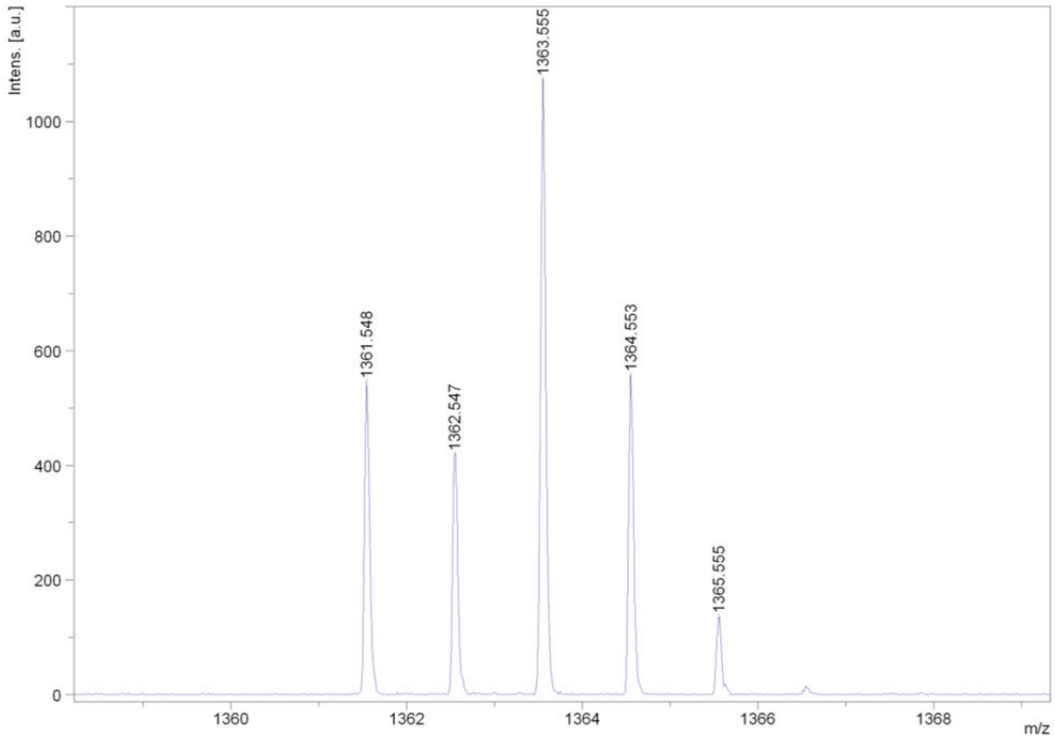


Fig. S4. MALDI-TOF Mass spectrum of **2o** (**2o** + Ag)$^+$.

5. DFT optimized molecular conformations of 1o, 2o, 1c and 2c

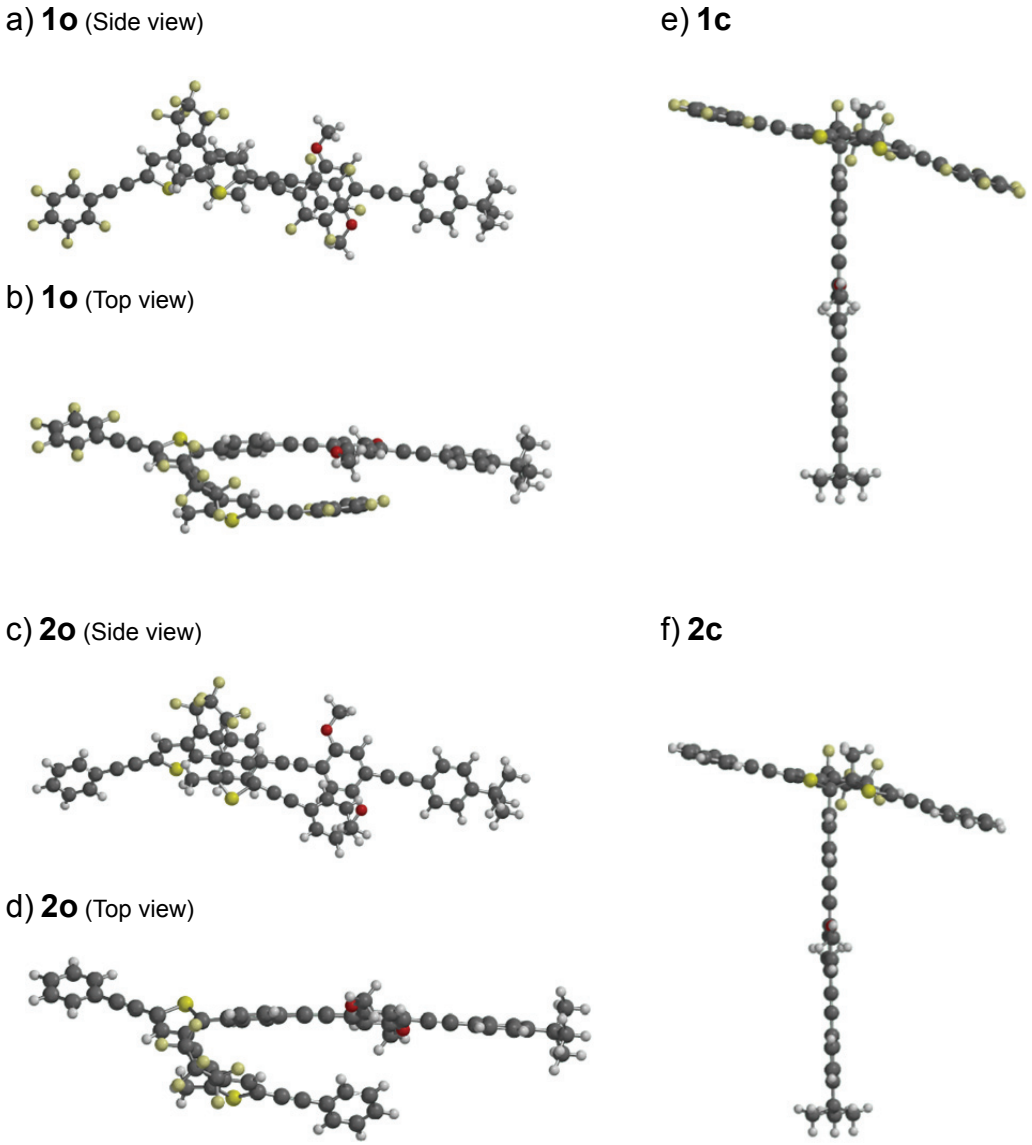


Fig. S5. DFT optimized molecular structures of **1o** (a: side view, b: top view), **2o** (c: side view, d: top view), **1c** (e) and **2c** (f) calculated at B3LYP/6-31G* level. Dodecyloxy groups are replaced by methoxy groups to reduce calculation load.

6. Emission spectra of 2o and 2-pss

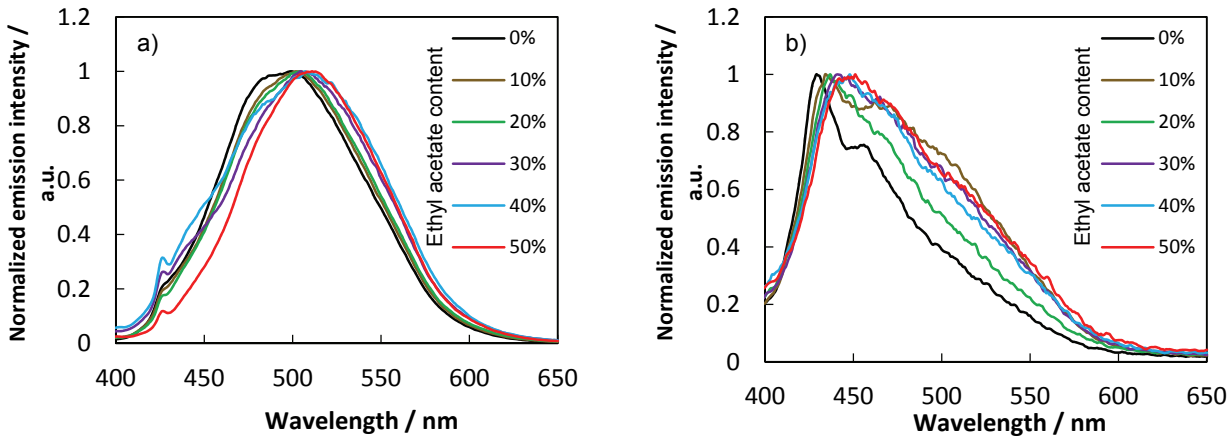


Fig. S6. Emission spectra of a) **2o** and b) **2-pss** in hexane and hexane-ethyl acetate mixed solutions.
Excitation: 382 nm. Solvent volume ratio: hexane/ethyl acetate = 100/0, 90/10, 80/20, 70/30, 60/40, 50/50.

7. Emission spectra of 3

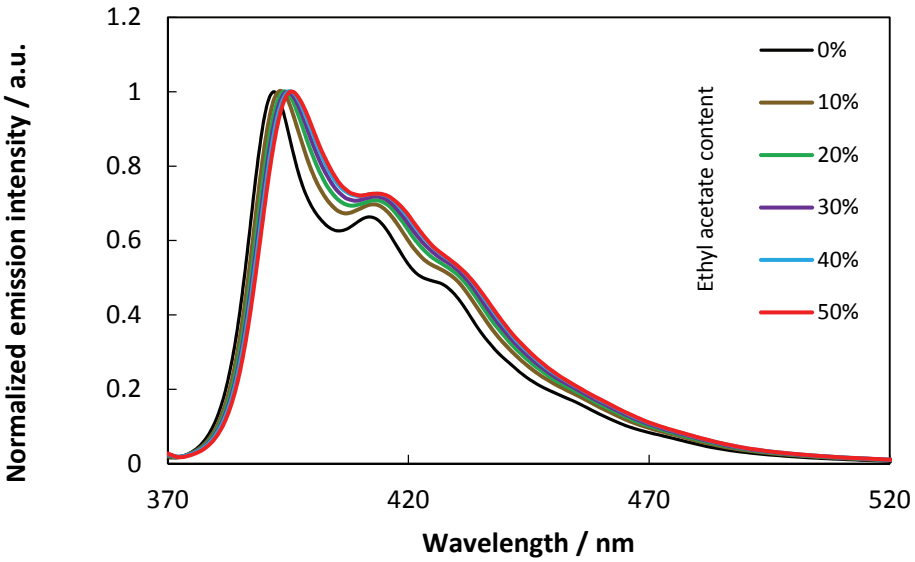


Fig. S7. Emission spectra of **3** in hexane and hexane-ethyl acetate mixed solutions.
Excitation: 368 nm. Solvent volume ratio: hexane/ethyl acetate = 100/0, 90/10, 80/20, 70/30, 60/40, 50/50.