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Alkyl-substituted bis(4-((9H-fluoren-9-ylidene) methyl)phenyl)thiophenes: weakening of intermolecular interactions and additive-assisted crystallization[†]

Alina A. Sonina,^{ab} Christina S. Becker,^a Anatoly D. Kuimov,^a Inna K. Shundrina,^a Vladislav Yu. Komarov^c and Maxim S. Kazantsev ⁽¹⁾*^a

Aggregation-induced emission (AIE) materials find their applications in organic optoelectronics, bioimaging and sensors. In this work, we introduced alkyl substituents in AIE-active bis(4-((9H-fluoren-9vlidene)methyl)phenyl)thiophene and elucidated their effect on the molecular and crystal structures, crystallization and optical properties of materials. Ethyl-containing (C2-BFMPT) and octyl-containing (C8-BFMPT) 2,5-bis(4-((2,7-dialkyl-9H-fluoren-9-ylidene)methyl)phenyl)thiophenes were synthesized in 4 steps. The introduction of alkyl groups weakened intermolecular interactions, decreased the crystal guality, melting point, and density, and increased the solubility of materials. Octyl-containing derivative was demonstrated to generate two crystal forms obtained by the native (form I) and additive-assisted (form II) crystallizations. The latter appeared to have a better crystal quality. C-H $\cdots\pi$ interactions and an extensive positional disorder were revealed for both derivatives. In C8-BFMPT crystals (form II) only a half of molecular backbones were well localized due to multiple intermolecular C-H··· π interactions, whereas another half demonstrated a high positional disorder. The AIE effect with a negligible photoluminescence (PL) quantum yield (QY) in solution and a PL QY of 5% for C2-BFMPT and 2% for C8-BFMPT (form II) crystals was demonstrated. The cooling of the C8-BFMPT form II resulted in 10-fold increase of PL QY. The introduction of alkyl-substituents and additive-assisted crystallization are highlighted as powerful tools for the control of crystal packing, morphology, polymorphism and the optical performance of AIEmaterials.

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1. Introduction

Organic highly-luminescent solids are practically demanding materials for diverse applications, such as light-emitting devices,1-6 lasers,7,8 bio-imaging,9,10 organic anticounterfeiting and optical sensors.¹¹⁻¹⁴ However, organic fluorophores typically possess bright fluorescence in solution, suffer from aggregation-caused quenching.11,15 but Aggregation-induced emission (AIE), being an opposite effect, was reported by Prof. Tang and co-workers in early 2000s.^{16,17} AIE materials demonstrate a negligible emission in the liquid

^b Novosibirsk State University, Pirogova 2, 630090, Novosibirsk, Russia ^cA. V. Nikolaev Institute of Inorganic Chemistry, Lavrentieva 3, 630090, Novosibirsk, Russia

phase and highly efficient luminescence in the solid (crystalline) state. AIE luminophores typically have a nonplanar structure with an ability of intramolecular rotations believed to be the main excited state relaxation channel in solution. The crystalline environment locks rotations and tremendously increases the emission from these molecules.¹⁸⁻²¹ Hence, the development of tools for manipulation by the crystalline structure and morphology is very important for the tuning of the optoelectronic properties of AIE-active materials, and for the design of novel high performance fluorophores. The introduction of substituents,^{22,23} polymorphism,²⁴⁻²⁶ external stimuli,²⁷⁻²⁹ various crystallization techniques^{30,31} and others are among the most efficient strategies for the crystal packing and microstructure control of conjugated materials.

Well-known representatives of AIE-active chromophores include silole-,16 tetraphenylethylene-,19 distyrylanthracene-20 and other derivatives.^{18,32-35} Compounds containing the 4-((9H-fluoren-9-ylidene)methyl)phenyl fragment³⁶⁻⁴³ have recently attracted attention as model high-torsional freedom

^a N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry. Lavrentieva 9. 630090, Novosibirsk, Russia. E-mail: maximkazantsev1988@gmail.com

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"one-rotor" AIE systems for the study of the structureproperty relationships to reveal fundamental principles for the molecular design of high-performance fluorophores. We have previously reported the AIE behavior for bis(4-((9*H*fluoren-9-ylidene)methyl)phenyl)thiophene (BFMPT) with irreversible thermo- and mechano-responsive fluorescence switching triggered by conformational change.⁴⁴ One of the drawbacks of that system is relatively strong multiple intermolecular C-H··· π interactions, resulting in low solubility and long crystallization time.⁴⁴ The introduction of substituents, particularly alkyl-groups, is an efficient way for the tuning of the crystal packing, solubility, softness and film-formation ability.⁴⁵⁻⁴⁷

In this work, we introduced alkyl substituents, viz., "short" ethyl and "long" octyl groups, in the 2 and 7 positions of the fluorene fragments of BFMPT and studied their influence on the crystallization, structure, solubility and optical properties of materials. Alkylated 2,5-bis(4-((2,7-dialkyl-9H-fluoren-9ylidene)methyl)phenyl)thiophene derivatives were synthesized in 4 steps by acylation, reduction, cross-coupling, and Knoevenagel reactions. The introduction of alkyl groups resulted in a decrease of melting points and an increase of the solubility due to the weakening of intermolecular interactions. The crystal quality of the materials was also reduced upon introduction of substituents, with the native crystallization of the octyl-containing derivative in various solvent systems leading to a polycrystalline sample. On the contrary, the additive-assisted crystallization of C8-BFMPT improved the crystal quality and gave its polymorphic phase (form II). Both derivatives demonstrated an AIE effect with a negligible photoluminescence (PL) quantum yield (QY) in solution, and a PL QY of 5% for C2-BFMPT and 2% for C8-BFMPT (form II) crystals.

2. Experimental

2.1 Synthesis and characterization

All reagents and solvents were purchased from commercial sources (Sigma-Aldrich, Acros Organics), and used without additional purification unless otherwise specified. 2,5-Bis(tributylstannyl)thiophene was distilled before coupling, b.p. 178 °C (1 Torr). 4-Bromobenzaldehyde was dried by addition of anhydrous diethyl ether and subsequent evaporation under reduced pressure, and the procedure was repeated 3 times. The ¹H NMR spectrum in CDCl₃ of the resulting white precipitate revealed no water. The reaction mixtures were monitored by TLC using Macherey-Nagel precoated TLC-sheets (Alugram Xtra SIL G/UV254). Macherey-Nagel Kieselgel 60 was used for column chromatography. Combustion analyses were performed with a CHN-analyzer (EURO EA). NMR spectra were recorded with Bruker AV 300, Bruker AV 400 and Bruker AV 500 spectrometers. Mass spectra were recorded with a Thermo Electron Corporation DFS mass spectrometer. IR spectra were recorded in the transmission mode with a Bruker Tensor 27 FT-IR spectrometer in potassium bromide pellets.

Thermogravimetry and differential scanning calorimetry analyses were performed in helium atmosphere using a NETZSCH STA 409 instrument; the heating rate was 10 °C min⁻¹. Cyclic voltammetry measurements in CH_2Cl_2 solution were performed using a computer-controlled P-8 nano potentiostat (Elins, Russia) in combination with a threeelectrode cell (Gamry); 0.1 M tetrabutylammonium hexafluorophosphate was used as supporting electrolyte. The Pt, Pt wire and Ag/AgCl were used as the working, counter and reference electrodes, respectively. The measurements were standardized by measuring the redox potential of the Fc/Fc⁺ couple after each compound analysis. The HOMO and LUMO energy levels were estimated using onset potentials according to equations:

$$E_{\rm HOMO} = -(E_{\rm ox}^{\rm onset} + 4.8)(eV)$$

$$E_{\rm LUMO} = -(E_{\rm Red}^{\rm onset} + 4.8)(eV)$$

Synthesis of the 2,7-diacyl-9*H*-fluorenes 1a, b. To a stirring mixture of 1,2-dichloroethane (48 mL) and acyl chloride (48.0 mmol) in an oven-dried round bottom flask, $AlCl_3$ (6.42 g, 48.0 mmol) was carefully added. A solution of fluorene (2.00 g, 12 mmol) in 1,2-dichloroethane (48 mL) was slowly added to a mixture within 40 minutes. The reaction mixture was stirred at room temperature for 40 minutes, and then was refluxed for 23 h. The cooled solution was poured into a mixture of ice and concentrated HCl (5 mL), and extracted with CH_2Cl_2 (3 times). The combined extracts were washed with water (3 times), dried over MgSO₄ and evaporated. The solid residue was washed on a glass filter with ethyl acetate, dried under air and additionally purified by column chromatography (silica gel/benzene).

For 1,1'-(9H-fluorene-2,7-diyl)diethanone (1a). Yield of white solid – 2.0 g (67%). $\delta_{\rm H}$ (CDCl₃, 500.1 MHz) 8.12 (2H, s), 7.99 (2H, d, J = 8.0 Hz), 7.85 (2H, d, J = 8.0), 3.95 (2H, s), 2.63 (6H, s). The ¹H NMR spectrum corresponds to that described in ref. 48.

For 1,1'-(9H-fluorene-2,7-diyl)bis(octan-1-one) (1b). Yield of white solid – 3.0 g (60%). M.p.: 138 °C (decomp.); IR (KBr): 2953, 2920, 2848, 1682, 1608, 1466, 1435, 1410, 1358, 1273, 1232, 1205, 1134, 1018, 964, 816, 771, 723, 704, 582, 430, 417 cm⁻¹; $\delta_{\rm H}$ (CDCl₃, 400.1 MHz) 8.15 (2H, s), 8.01 (2H, d, *J* = 8.1 Hz), 7.86 (2H, d, *J* = 8.1), 3.99 (2H, s), 2.99 (4H, t, *J* = 7.4 Hz), 1.70–1.78 (4H, m), 1.31–1.41 (8H, m), 1.25–1.30 (8H, m), 0.87 (6H, t, *J* = 6.5 Hz); $\delta_{\rm C}$ (CDCl₃, 100.6 MHz) 200.5 (2 CO), 145.0, 144.6, 136.6, 127.7 (2 CH), 125.0 (2 CH), 120.8 (2 CH), 39.0 (2 CH₂), 37.1 (CH₂), 31.9 (2 CH₂), 29.5 (2 CH₂), 29.3 (2 CH₂), 24.6 (2 CH₂), 22.8 (2 CH₂), 14.2 (2 CH₃); HRMS found: [M]⁺ 418.2864, C₂₉H₃₈O₂ requires [M]⁺ 418.2866; Elem. an. Found: C, 83.3; H, 9.1%; for C₂₉H₃₈O₂ requires C, 83.2; H, 9.2%.

Synthesis of 2,7-diethyl-9*H*-fluorene (2a). 1,1'-(9*H*-fluorene-2,7-diyl)diethanone (1a) (0.75 g, 3.0 mmol) was dissolved in diethylene glycol (60 mL) under heating (95 °C) and stirring. Then, hydrazine hydrate (0.96 mL, 18.0 mmol) was added;

the flask was equipped with a reflux condenser and the mixture was stirred at 130 °C for 2 h. After cooling to 80 °C, KOH powder (1.01 g, 18.0 mmol) was added. Then, the reaction mixture was heated at 200 °C for 5 h (bath temperature 230 \pm 3 °C). After cooling to room temperature, the reaction mixture was poured into 100 mL of water. The crude product was extracted with ethyl acetate $(3 \times 50 \text{ mL})$, washed with water $(3 \times 70 \text{ mL})$, dried over sodium sulfate and evaporated under reduced pressure. The product was purified by column chromatography (silica gel/hexane) to afford a white solid (0.66 g, 99%). M.p.: 123 °C; IR (KBr): 3028, 3005, 2960, 2928, 2870, 2856, 2721, 1890, 1880, 1641, 1612, 1581, 1471, 1419, 1398, 1371, 1321, 1306, 1213, 1055, 976, 862, 841, 820, 787, 721, 704, 581, 561, 505, 422 cm⁻¹; $\delta_{\rm H}$ (CDCl₃, 300.1 MHz) 7.73 (2H, d, J = 7.8 Hz), 7.43 (2H, s), 7.27 (2H, d, J = 7.8 Hz), 3.89 (2H, s), 2.80 (4H, q, J = 7.6 Hz), 1.38 (6H, t, J = 7.6 Hz); $\delta_{\rm C}$ (CDCl₃, 75.5 MHz) 143.6, 142.7, 139.6, 126.5 (2 CH), 124.6 (2 CH), 119.5 (2 CH), 36.8 (CH₂), 29.2 (2 CH₂), 16.1 (2 CH₃); HRMS found: $[M]^+$ 222.1407, C₁₇H₁₈ requires [M]⁺ 222.1403; Elem. an. Found: C, 91.4; H, 8.3%; for C₁₇H₁₈ requires C, 91.8; H, 8.2%.

Synthesis of 2,7-dioctyl-9H-fluorene (2b). Triethylene glycol (40 mL) was heated to 110 °C, and 1,1'-(9H-fluorene-2,7-diyl) bis(octan-1-one) (1b) (1.0 g, 2.4 mmol) was carefully added under stirring in order to dissolve without conglutination. Then, KOH powder (0.8 g, 14.3 mmol) followed by hydrazine hydrate (0.76 mL, 14.3 mmol) were added. The reaction flask was equipped with a reflux condenser and heated at 200 °C for 3.5 h (bath temperature: 230 ± 3 °C). After cooling to ambient temperature, the reaction mixture was poured onto 50 mL of water. The crude product was then extracted with ethyl acetate (3 \times 30 mL), washed with water (2 \times 50 mL), dried over sodium sulfate and evaporated under reduced product was purified pressure. The by column chromatography (silica gel/hexane) to afford a white solid (0.65 g, 70%). IR (KBr): 3037, 3007, 2956, 2922, 2850, 1468, 1417, 1389, 1377, 1138, 822, 785, 721, 704, 552, 424 cm $^{-1};\,\delta_{\rm H}$ (CDCl₃, 500.1 MHz) 7.63 (2H, d, J = 7.7 Hz), 7.33 (2H, s), 7.15 (2H, d, J = 7.7 Hz), 3.82 (2H, s), 2.66 (4H, t, J = 7.8 Hz), 1.63– 1.68 (4H, m), 1.33-1.39 (8H, m), 1.25-1.33 (18H, m), 0.89 (6H, t, J = 6.9 Hz); $\delta_{\rm C}$ (CDCl₃, 125.7 MHz) 143.5, 141.4, 139.6, 127.1 (2 CH), 125.2 (2 CH), 119.4 (2 CH), 36.9 (CH₂), 36.3 (2 CH₂), 32.1 (2 CH₂), 32.0 (2 CH₂), 29.7 (2 CH₂), 29.5 (2 CH₂), 29.4 (2 CH₂), 22.8 (2 CH₂), 14.2 (2 CH₃); HRMS found: [M]⁺ 390.3279, $C_{29}H_{42}$ requires $\left[M\right]^{\!+}$ 390.3281; Elem. an. Found: C, 88.8; H, 11.0%; for C₂₉H₄₂ requires C, 89.2; H, 10.8%.

Synthesis of 4,4'-(thiophene-2,5-diyl)dibenzaldehyde (3). A stirring mixture of 2,5-bis(tributylstannyl)thiophene (1.00 g, 1.5 mmol), 4-bromobenzaldehyde (1.15 g, 6.2 mmol) and toluene (10.0 mL) was purged with argon for 20 minutes, then Pd(PPh₃)₄ (0.17 g, 0.15 mmol) was added in one portion. The flask was equipped with a reflux condenser and sealed. The reaction mixture was heated at 80 °C for 2 days, and then cooled to rt. Toluene was evaporated under reduced pressure; the residue was diluted with water (10 mL) and hexane (10 mL), and left in a refrigerator for 1 night. The resulting solid

was filtered off, washed with water and a mixture of hexane and MeOH (1:1), then dried under air. The product was filtered through a short silica gel column using hot toluene as the solvent. The filtrate was then evaporated, giving dialdehyde 3 as a yellow powder (0.29 g, 66%). $\delta_{\rm H}$ ((CD₃)₂CO, 500.1 MHz) 10.04 (2H, s), 7.97 (4H, d, *J* = 8.5 Hz), 7.94 (4H, d, *J* = 8.5 Hz), 7.74 (1H, s); $\delta_{\rm C}$ ((CD₃)₂CO, 125.0 MHz) 192.2 (2 CH), 144.5, 140.0, 136.8, 131.3 (4 CH), 127.9 (2 CH), 126.7 (4 CH); the NMR spectra corresponds to that described in ref. 49.

General synthesis of 2,5-bis(4-((2,7-dialkyl-9H-fluoren-9ylidene)methyl)phenyl)thiophenes C2-BFMPT, C8-BFMPT. To an oven-dried two necked 50 ml round bottom flask containing a magnetic stir-bar, dry DMF (25 ml) and the corresponding fluorene derivative 2 (1.43 mmol) were added. The flask was purged with Ar for 20 minutes, and then t-BuONa (0.15 g, 1.56 mmol) was added and the flask was closed by rubber septum. The mixture was vigorously stirred minutes, and then 4,4'-(thiophene-2,5-diyl) for 10 dibenzaldehyde (3) (0.2 g, 0.68 mmol) in DMF (10 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1.5 h, and then poured into distilled water (50 mL).

For 2,5-bis(4-((2,7-diethyl-9H-fluoren-9-ylidene)methyl)phenyl) thiophene (C2-BFMPT). The resulting mixture was extracted with ethyl acetate, washed with water and dried over MgSO₄. The residue was evaporated under reduced pressure, and then purified by column chromatography on silica gel (hexane/toluene = 1/1) to give a yellow powder (0.3 g, 60%). M.p.: 230 °C; UV-vis λ_{max} (THF) 402 (I_{rel} , 100); IR (KBr): 3055, 3024, 2960, 2926, 2868, 2854, 1892, 1743, 1724, 1632, 1601, 1554, 1497, 1466, 1417, 1319, 1279, 1238, 1184, 1113, 1061, 970, 897, 870, 823, 800, 768, 746, 663, 571, 498, 480 cm⁻¹; $\delta_{\rm H}$ (CDCl₃, 500.1 MHz) 7.74 (4H, d, J = 8.3 Hz), 7.67 (4H, d, J = 8.3 Hz), 7.60-7.63 (6H, m), 7.58-7.60 (4H, m), 7.43 (2H, s), 7.14–7.19 (4H, m), 2.76 (4H, q, J = 7.7 Hz), 2.56 (4H, q, J = 7.7 Hz), 1.33 (6H, t, J = 7.7 Hz), 1.16 (6H, t, J = 7.7 Hz); $\delta_{\rm C}$ (CDCl₃, 125.6 MHz) 143.6, 143.0, 142.6, 140.0, 139.4, 137.2, 137.0, 136.9, 136.4, 133.9, 130.4 (4 CH), 128.6 (2 CH), 128.2 (2 CH), 126.0 (2 CH), 125.5 (4 CH), 124.6 (2 CH), 124.0 (2 CH), 119.8 (2 CH), 119.4 (2 CH), 119.3 (2 CH), 29.4 (2 CH₂), 29.1 (2 CH₂), 16.1 (2 CH₃), 15.8 (2 CH₃); HRMS found: [M]⁺ 700.3160, $C_{52}H_{44}S$ requires $[M]^+$ 700.3158; Elem. an. Found: C, 88.7; H, 6.5; S, 4.3%; for C₅₂H₄₄S requires C, 89.1; H, 6.3; S, 4.6%.

For 2,5-bis(4-((2,7-dioctyl-9H-fluoren-9-ylidene)methyl)phenyl) thiophene (C8-BFMPT). The resulting precipitate was filtered off, washed successively with water and methanol, and dried under air. The product was purified by column chromatography on silica gel (hexane/toluene = 3/1) to give a yellow powder (0.98 g, 66%). Mp 87 °C; UV-vis λ_{max} (THF) 404 (I_{rel} , 100); IR (KBr): 3024, 3003, 2953, 2922, 2850, 1632, 1601, 1497, 1466, 1419, 1348, 1279, 1113, 893, 868, 814, 800, 789, 744, 721, 669, 494, 471 cm⁻¹; δ_{H} (CDCl₃, 300.1 MHz) 7.74 (4H, d, J = 8.0 Hz), 7.67 (4H, d, J = 8.0 Hz), 7.55–7.62 (10H, m), 7.42 (2H, s), 7.18 (2H, d, J = 7.7 Hz), 7.13 (2H, d, J = 7.7 Hz), 2.71 (4H, t, J = 7.5 Hz), 2.51 (4H, t, J = 7.5 Hz), 1.64–1.76 (4H,

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m), 1.49–1.58 (4H, m), 1.24–1.38 (40H, m), 1.84–1.94 (12H, m); $\delta_{\rm C}$ (CDCl₃, 75.5 MHz) 143.6, 141.7, 141.2, 139.9, 139.4, 137.2, 137.1, 136.8, 136.5, 133.9, 130.4 (4 CH), 129.1 (2 CH), 128.7 (2 CH), 125.9 (2 CH), 125.5 (4 CH), 124.6 (2 CH), 124.5 (2 CH), 120.3 (2 CH), 119.3 (2 CH), 119.2 (2 CH), 36.5 (2 CH₂), 36.1 (2 CH₂), 32.1 (4 CH₂), 32.0 (2 CH₂), 31.5 (2 CH₂), 29.7 (4 CH₂), 29.5 (2 CH₂), 29.4 (4 CH₂), 29.3 (2 CH₂), 22.8 (4 CH₂), 14.3 (4 CH₃); HRMS found: [M]⁺ 1036.6903, C₇₆H₉₂S requires [M]⁺ 1036.6914; Elem. an. Found: C, 88.4; H, 8.9; S, 3.1%; for C₇₆H₉₂S requires C, 88.0; H, 8.9; S, 3.1%.

2.2 Crystal growth and analysis

C2-BFMPT was crystallized by slow diffusion of methanol vapors into its CH_2Cl_2 solution with a concentration of 0.6 g I^{-1} . In the case of neat C8-BFMPT, various solution methods such as solvent diffusion and slow solvent evaporation were used (CH_2Cl_2 , toluene, benzene, dichlorobenzene, ethyl acetate, THF, acetone, acetonitrile as solvents and hexane, *i*-PrOH, MeOH as antisolvents); typically, the polycrystalline sample was obtained. To improve the crystal quality of the material, it was crystallized from a toluene solution containing 15 mol% of anthracene with respect to C8-BFMPT. The crystals were examined using an optical microscope (POLAM R-312, "Lomo", Russia) in transmitted light and under blue laser irradiation (405 nm).

X-ray diffraction. The X-ray diffraction experiments at 200 K were performed using a Bruker KAPPA APEX II diffractometer with graphite monochromated Mo Ka radiation. Integration and scaling of the intensity data were accomplished with SAINT.⁵⁰ Absorption corrections were applied using SADABS.⁵¹ The structures were solved by direct methods with SHELXT.52 Refinement was carried out by the full-matrix least-squares technique with SHELXL⁵² using Olex2 software.⁵³ The structure of C2-BFMPT was refined as a merahedral twin (twin axis (001), twin component ratio 0.38). All non-hydrogen atoms in both structures were refined anisotropically. The restraints (SADI for 1,2-, 1,3- and some 1,4-distances and FLAT for the aromatic fragments, DFIX/ DANG for alkyl 1,2-, 1,3-distances), and atomic displacement restraints (RIGU) and constraints (EADP for atoms close alternative positions) were used for the refinement. Hydrogen atoms were calculated at idealized positions according to the riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$ for the alkyl H atoms and $1.2U_{eq}(C)$ otherwise. Molecules of C2-BFMPT have disordered ethyl groups over two positions with an approximate site occupancy of 1:1 and 1:2. C8-BFMPT has a disordered phenylene with a site occupancy of 1:2, and octyl groups with site occupancy of 1:1 and 1:2. Elongated atomic displacement ellipsoids with a somewhat exaggerated Uiso pointed on the static or dynamic disorder in the crystal structures. Low data-to-parameters ratio did not allow us to refine the structure using more detailed models; additional low-temperature (80 K) experiments were carried out.

The next generation Bruker D8 Venture instrument with I μ S 3.0 Cu K α radiation (Incoatech, multilayer focussing

Montel mirrors) and PHOTON III CMOS detector was used to collect diffraction intensities at 80 K. The samples were cooled from 250 K at a rate of 3-6 K min⁻¹. High-exposition tests (200-300 seconds per degree) showed an abrupt disappearance of observable diffraction intensities at d less than 1.1-1.2 Å, pointing to the high static disorder. Data reduction and structure refinement were done using the same software. Attempts to refine the non-H atoms with anisotropic atomic displacements gave irrelevant ellipsoids with U_{iso} of *ca.* 0.15 Å², which is 5 to 10 times higher than could be expected for 80 K, and even higher than that in the models obtained with 200 K data. The same restraints and constraints as for the structures at 200 K except restraints RIGU, which was replaced by SIMU for isotropic atomic displacement, were used for the refinement. No apparent local-ordered alternative positions were found, what indicates that their number exceeds half a dozen. All atoms were refined to be disordered over the two "uttermost" positions. The obtained low-temperature structure models confirmed the principal consistency of the localization of aromatic fragments with the ones at 200 K. The latter were simpler and were used for the crystal structure analysis (section 3.2). The low-temperature experiments also confirmed the principal static nature of the disorder, revealed the expansion of alternative positions of molecules upon the decrease of temperature, and allowed us to estimate the difference in the conformations (see Fig. S25[†]). Additional experimental details and parameters characterizing the data collection and refinement, as well as crystal data, are presented in ESI.†

The crystal structures were analyzed for intermolecular interactions using PLATON⁵⁴ and Mercury.⁵⁵ Crystallographic data for the structures have been deposited at the Cambridge Crystallographic Data Centre as ESI† publication CCDC no. 2047979–80 (200 K) and 2059086–7 (80 K).

Powder X-ray diffraction (PXRD) patterns were collected using Stoe Stadi-MP diffractometer (Cu Kα1 radiation, curved Ge monochromator, transmission/Debye–Scherrer mode, MYTHEN 1 K detector).

2.3 Optical spectroscopy

UV/vis spectra were recorded in a diluted (10^{-5} M) THF Varian Cary 5000 solution with а UV-vis-NIR spectrophotometer in 1 × 1 cm quartz cuvettes. The PL spectra were recorded with a Varian Cary Eclipse fluorescence spectrophotometer in 1 cm quartz cuvettes. The PL QY in THF solution was measured according to the standard procedure. A solution of fluorescein in 0.1 M NaOH (PL QY = 0.95) was used as a reference standard.⁵⁶ The PL spectra in binary THF/water mixtures were recorded in 1 cm quartz cuvettes with a constant dye concentration of about 10^{-5} M. The fraction of water/THF was varied from 0 to 90%, and the excitation wavelength was 365 nm. The PL QY of the single crystals was measured using a 3.3 inch-diameter integrating sphere (Newport 819C-SL-3.3) coupled with UV-vis spectrometer (QE Pro, Ocean Optics). The excitation was



performed with a diode laser emitting at 405 nm (Laserglow). The detailed experimental procedure is described in ref. 57. The cooling of the crystalline samples was performed by a liquid nitrogen bath with subsequent measurement of the PL signal in an integrating sphere.

3. Results and discussion

3.1 Synthesis and general properties

Scheme 1 demonstrates the synthetic approach for the ethyl (C2-BFMPT) and octyl (C8-BFMPT) substituted BFMPT. Target compounds were synthesized in 4 steps, including acylation, reduction, cross-coupling reaction and Knoevenagel condensation. 2,7-Dialkyl-9H-fluorenes 2a, b were synthesized via acylation of fluorene, followed by the reduction of the carbonyl group. The Friedel-Crafts acetylation of fluorene was previously reported to proceed preferably into positions 2 and 7, and less favorable in 4 and 5.48 The same reaction conditions were successfully applied to obtain 1,1'-(9Hfluorene-2,7-diyl)bis(octan-1-one) (1b) with 60% yield. The reduction procedure is precisely described in the Experimental section. It is noteworthy that the temperature control at this step throughout the process is very important to avoid a formation of byproducts. To reach the maximum yield, the best conditions in both cases were found (see Experimental details). Target compounds C2-BFMPT and C8-BFMPT were obtained via condensation of 4,4'-(thiophene-2,5-diyl)dibenzaldehyde (3) with two equivalents of the corresponding substituted fluorene using t-BuONa as a base (Scheme 1).

The obtained compounds were characterized by ¹H and ¹³C NMR, HRMS, and FT-IR spectroscopies (see ESI,† Fig. S1-S24) and elemental analysis. Cyclic voltammetry measurements (Fig. S23[†]) revealed reversible first oxidation and reduction waves for both compounds. The energies of the frontier molecular orbitals estimated from the onset oxidation and reduction potentials are almost identical: $E_{\text{HOMO}} = -5.5 \text{ eV}; E_{\text{LUMO}} = -2.78 \text{ eV}, \text{ indicating a negligible}$ effect of the substituents on the electronic properties of the studied compounds. Fig. 1 demonstrates the thermogravimetric and differential scanning calorimetry analyses of the as-synthesized BFMPTs in helium

atmosphere. Both compounds demonstrate a high thermal stability with a temperature of 10% weight loss of 400 °C. The melting points are significantly lower, as compared to that of the parent BFMPT compound⁴⁴ (326 °C) being 226.3 °C for C2-BFMPT and 83.9 °C for C8-BFMPT. The solubility of the material increases upon alkylation: in contrast to BFMPT having a solubility in toluene of 2.5 10^{-4} M,⁴⁴ the solubility of C2-BFMPT in toluene is 1.3 10^{-2} M and the lower estimate of the solubility of C8-BFMPT in toluene is 0.2 M.

Therefore, the introduction of the alkyl substituents significantly weakens the intermolecular interactions in crystals of the alkyl derivatives of BFMPT, which should dramatically impact the crystallinity, structure and optical properties of the materials.

3.2 Crystal growth and analysis

The crystals of C2-BFMPT grown by solvent-antisolvent method typically have a needle-like habit with a green photoluminescence under blue laser irradiation (Fig. 2a and b). C8-BFMPT was attempted to be crystallized from solution by solvent/antisolvent crystallization and solvent evaporation, but none of the used solvent systems (CH_2Cl_2 , toluene, benzene, dichlorobenzene, ethyl acetate, THF, acetone, acetonitrile as solvents; hexane, *i*-PrOH, MeOH as antisolvents) provided the crystals of sufficient quality for



Fig. 1 Thermogravimetric (dashed lines) and differential scanning calorimetry (solid lines) analyses of the C2-BFMPT (red) and C8-BFMPT neat samples (blue) in He atmosphere.

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Fig. 2 Optical images of: C2-BFMPT crystal in transmitted light (a) and under blue laser irradiation 405 nm (b); C8-BFMPT crystal grown in the presence of anthracene in transmitted light (c) and under blue laser irradiation 405 nm (d).

X-ray study. The polycrystalline powders (Fig. S24[†]) were obtained in numerous native crystallization experiments. This is assigned to the poor crystal quality due to the disordered octyl groups, inducing very weak intermolecular interactions and loose packing of the C8-BFMPT molecules in crystals.

To improve the crystal quality of C8-BFMPT, we applied a method of crystallization in the presence of an additive. "Tailor-made" auxiliaries⁵⁸ were previously demonstrated to direct the crystallization of amino-acids⁵⁹⁻⁶² and nitroaromatics.⁶³ However, to the best of our knowledge, this approach has never been used for AIE-active and fluorescent materials. As an additive, we chose a conjugated small molecule - anthracene, which was intentionally added to the crystallization solution of C8-BFMPT. The concentration of anthracene was about 15 mol% with respect to C8-BFMPT. In addition to the anthracene crystals, the thin needle-like crystals of C8-BFMPT were reproducibly obtained in these experiments (Fig. 2c and d). It should be noted that we did not noticed co-crystals, which may be formed from anthracene and C8-BFMPT as follows from the single crystal and powder X-ray diffraction study (vide infra). This is most probably due to the large structural distinction of anthracene and the C8-BFMPT molecules. Nevertheless, a smallmolecular additive significantly improves the crystal quality of the C8-BFMPT material (cf. Fig. 2 and S24[†]). Moreover, according to DSC analysis (Fig. 3) and powder X-ray diffractions (Fig. S27[†]), the crystallization with the additive



Fig. 3 Thermal gravimetric (dashed lines) and differential scanning calorimetry (solid lines) analyses of C8-BFMPT: form I (red) and form II (dark), and the same sample after melting and cooling to room temperature (blue) in He atmosphere.

allowed us to obtain a new polymorphic form of C8-BFMPT (form II) with a higher melting point of 89.4 °C. Since we did not observe any additional peaks in the DSC thermograms (Fig. 3) and PXRD patterns (Fig. S27†), both form I and form II were concluded to have sufficient phase purity. After the melting of form II, the obtained sample crystallizes upon cooling into form I (Fig. 3, blue), corresponding to the assynthesized powder. According to TGA analysis, the crystallized *Forms* did not demonstrate a weight loss up to the melting point, what excludes the formation of solvates. Since the melting point of form II is higher than that for form I, we concluded that the crystallization with anthracene resulted in stronger intermolecular interactions in form II crystals of C8-BFMPT than that in the neat sample (form I).⁶⁴

To gain further insight into the structure and properties of the alkyl-derivatives, X-ray diffraction experiments (both at 200 K and 80 K, see Experimental details) were performed. C2-BFMPT crystallizes in the chiral monoclinic space group $(P2_1)$, with two molecules in the asymmetric unit designated as molecule A and molecule B. The asymmetric unit of the structure with corresponding labeling scheme is shown in Fig. 4a. The ethyl groups exhibit extensive positional disorder because they do not form any C-H··· π interactions (Fig. 4). The conformation of the molecules is described by four torsion angles: C2–C1–C24'–C25' ($\varphi_{A/B}^1$), C26'–C21'–C5'–C4' ($\varphi_{A/B}^2$), C3'-C2'-C11'-C16' ($\varphi_{A/B}^3$), and C15'-C14'-C1-C2 ($\varphi_{A/B}^4$) (Fig. 4a). The molecular conformations of C2-BFMPT are non-planar because of the intramolecular sterical hindrance between fluorene and the phenylene fragments,44 coupled with the multiple intermolecular C-H··· π interactions of the phenylene/ thiophene backbone and fluorene groups. All noncovalent interactions are formed along axis b, corresponding to the direction of the crystal growth. Molecules A form stacks by C-H··· π interactions between the phenyl and fluorene groups (C^{13'}- $H \cdots \pi^2$, $C^{13(Cg 8)} - H \cdots \pi^4$ and $C^{15'} - H \cdots \pi^8$) (Fig. 4b and Table S2[†]). Molecules B form stacks by π -stacking between the fluorene groups $(\pi^7 - \pi^6)$, and C-H··· π interaction between the phenyl ring and fluorene group ($C^{25'}-H\cdots\pi^4$; Fig. 4c and Table S2[†]). So, the fluorene groups of molecules B form pi-stacking, whereas the fluorene groups of molecules A only participate in the C-H $\cdots\pi$ interactions. These stacks are bonded by $C-H\cdots\pi$ interactions between molecules A and B ($C^{14(Cg 5B)}$ -H··· $\pi^{1(A)}$, $C^{25'(A)}$ -H··· $\pi^{8(B)}$, $C^{26'(A)}-H\cdots\pi^{7(B)}$, $C^{4'(A)}-H\cdots\pi^{9B}$; Fig. 4d and Table S2[†]). The powder X-ray diffraction study demonstrated that the assynthesized powder of C2-BFMPT corresponds to its single crystalline structure (Fig. S26[†]).

The neat crystalized C8-BFMPT sample (form I) was not suitable for the single crystal X-ray study. The powder X-ray diffraction pattern of form I (Fig. S27†) demonstrated broadened peaks and low-resolution, which makes it unsuitable for structure solution from powder data. However, we managed to solve the structure of C8-BFMPT form II obtained by the additive-assisted crystallization. Form II crystallized in the centrosymmetric monoclinic space group ($P2_1/c$) with one molecule in the asymmetric unit; the corresponding labeling scheme is



Fig. 4 Molecular structure of C2-BFMPT with the disordered ethyl groups, dihedral angles (ϕ_L , ϕ_2 , ϕ_3 , ϕ_4), atom and cycle numbering involved in the noncovalent interactions drawn at 50% probability atomic displacement ellipsoids (a); fragments of the crystal structure C2-BFMPT, and the intermolecular interactions with molecules A (b) and molecules B (c), and between A and B (d). Dashed blue lines represent the π -stacking and C-H $\cdots\pi$ interactions. The arrows indicate the orientation of the crystallographic axes.



Fig. 5 Molecular structure of C8-BFMPT with disordered groups (translucent) drawn with fixed atomic radii for clarity, dihedral angles (ϕ_1 , ϕ_2 , ϕ_3 , ϕ_4 and translucent ϕ_3 , ϕ_4 for disordered part), atom numbering and cycle numbering involved in the noncovalent interactions (a); fragment of the crystal structure C8-BFMPT (cut for clarity) demonstrating the intermolecular interactions between the well-localized fluorene and octyl groups (b). Dashed blue lines represent the C-H… π interactions. The arrows indicate the orientation of the crystallographic axes.

shown in Fig. 5a. The conformation of C8-BFMPT is also non-planar due to the steric hindrance of the fluorene and phenyl groups, which is confirmed by the disorder of the phenylene and fluorene groups (Fig. 5a). Remarkably, the coordinate sites of one octyl group and half of the molecular backbones are well localized, and do not demonstrate positional disorder due to the formation of C-H… π interactions between the fluorene and octyl groups (C²⁸– H^{28b}… π ⁹, C^{2A}–H^{2AA}… π ⁷; Fig. 5b and Table S2†). This half of the molecules are additionally stabilized by the interaction between the phenyl ring and fluorene fragment (C^{25'}–H… π ⁷; Table S2†). Molecules form stacks along axis *a*,

corresponding to the direction of crystal growth. Another three octyl groups and one phenylene group exhibited extensive positional disorder, and do not participate in numerous C-H… π interactions as the former (Fig. 5a). Half of the octyl groups are curved due to the close crystal packing. Their extensive positional disorder in connection with the lack of short contacts are in accordance with the low crystal density (1.099 g cm⁻³), as compared with that for C2-BFMPT (1.214 g cm⁻³) and parent BFMPT compound (1.285).⁴⁴ So, the increasing of the length of the alkyl substituent leads to the loose crystal packing and decrease of the crystal density.

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3.3 Optical properties

Absorption and photoluminescence (PL) spectra for C2-BFMPT and C8-BFMPT were recorded in THF solution. The corresponding curves and photophysical data are presented in Fig. 6 and Table 1, respectively. Both C2-BFMPT and C8-BFMPT exhibit very weak emission with unstructured PL spectra in solution, which might be assigned to the high torsional freedom and fast relaxation of the excited state, as demonstrated for the parent BFMPT compound.⁴⁴ The



Fig. 6 Optical spectra for C2-BFMPT (left) and C8-BFMPT (right): a) and b) absorption (black) and PL (red) in THF solution (10^{-5} M) , c) and d) PL spectra of the binary mixtures of THF and water with different volume water contents (0–90%) at constant dye concentration (10^{-5} M) ; the insets demonstrate the dependence of the ratio of the spectral intensity (*l*) to the initial spectral intensity (*l*₀) on the water fraction; the excitation wavelength was 365 nm, e) and f) PL spectra of the crystals at room temperature (blue) and liquid nitrogen (red) conditions; the spectrum of the neat crystallized C8-BFMPT sample form I (olive).

	$\lambda_{\rm abs} ({\rm nm})$	$\lambda_{\rm em} ({\rm nm})$	Stokes shift (eV)	PL QY (%)
C2-BFMPT in THF	402	542	0.80	<0.1
C8-BFMPT in THF	404	528	0.72	< 0.1
C2-BFMPT crystal	_	562	_	5
C8-BFMPT crystal. Form II	_	562	_	2
C2-BFMPT crystal in liquid nitrogen (\sim 77 K)	_	547, 562	_	5
C8-BFMPT crystal form II in liquid nitrogen (~77 K)	—	553, 578	_	19
λ_{abs} and λ_{em} – absorption and PL maxima.				

relatively high Stokes shift for C2-BFMPT and C8-BFMPT (0.8 eV and 0.72, respectively) also indicates the substantial reorganization of the molecular geometry in the excited state.

To investigate the AIE behavior of the obtained compounds, the PL spectra of the binary mixtures of THF and water with different volume water fractions were investigated (Fig. 6c and d). Both studied molecules have a clear AIE behavior, and the PL intensity increased about 32 and 11 times upon the addition of 90% of water for C2-BFMPT and C8-BFMPT, respectively (Fig. 6c and d). The higher AIE activity of C2-BFMPT is assigned to the stronger intermolecular interactions in its crystals, which corresponds to the lower solubility and higher melting point of the former.

To further reveal the optical properties of the studied compounds, we measured the PL of the C2-BFMPT and C8-BFMPT crystals. C2-BFMPT demonstrated a red-shifted PL maximum, as compared to that in solution and a PL quantum yield (PL QY) of 5%. We were unable to measure any meaningful PL signal from the neatcrystallized C8-BFMPT form I sample, which is assigned to the high structural disorder, defects within the sample and the scattering effect (Fig. 6f, olive). On the other hand, the crystals of form II grown by additive method demonstrated a PL QY of 2% and red-shifted PL maxima, as compared to that in solution. The PL efficiency of the alkyl-substituted BFMPTs is higher than that in solution (Table 1), but significantly lower than that of the unsubstituted BFMPT.44 Therefore, the weakening of the intermolecular interactions in the alkyl-substituted BFMPTs deteriorates the PL efficiency in the studied crystalline materials. The longer the alkyl substituent is, the less ordered material and the lower PL QY obtained. However, by the additive-assisted crystallization, we improved the crystal quality and enhanced the intermolecular interactions in C8-BFMPT form II, resulting in the increase of PL QY (no emission for form I vs. measurable signal for form II). To further reveal the PL behavior of the studied compounds and the effect of the rigidification of environment on the photophysical properties, we have studied the PL of crystals under cooling by liquid nitrogen. C2-BFMPT did not show any significant influence of cooling on PL QY, although the small blue shift of PL was observed. However, the PL spectra of C8BFMPT form II upon cooling demonstrated a structured PL spectrum, and the PL QY sharply increased up to 19% (Fig. 6 and Table 1). The same procedure for form I did not result in the improvement of the PL. This is assigned to the different crystal packing, defects, intermolecular interactions and rigidity of the molecular environment in the studied polymorphs. Therefore, the structural ordering achieved by the crystallization with the additive not only the crystal quality and enhanced improved the intermolecular interactions, but also improved the PL performance of the C8-BFMPT crystals and their response to the cooling.

Conclusions

In summary, we studied the effect of the alkyl-substituents and additive-assisted crystallization on the structure and optical properties of the AIE-active bis(4-((9H-fluoren-9ylidene)methyl)phenyl)thiophenes. The alkylated 2,5-bis(4-((2,7-dialkyl-9H-fluoren-9-ylidene)methyl)phenyl)thiophenes were synthesized in 4 steps by acylation, reduction, crosscoupling, and Knoevenagel condensation reactions. The introduction of the alkyl groups resulted in the weakening of intermolecular interactions and decreasing the crystal density, melting points. The solubility of the materials also increased upon the introduction of the alkyl groups. To improve the crystal quality of the octyl-containing derivative, we applied an additive-assisted crystallization strategy that resulted in the polymorphism of C8-BFMPT evidenced from the thermal analysis and X-ray diffraction data. C-H $\cdots\pi$ intermolecular interactions with an extensive disorder were revealed for both derivatives, with the crystal density being reduced upon the elongation of the alkyl groups. Only half of the C8-BFMPT molecular backbones were demonstrated to participate in the intermolecular C-H \cdots π interactions. Both derivatives demonstrated an AIE effect with a negligible photoluminescence (PL) quantum yield (QY) in solution, and a PL QY of 5% for C2-BFMPT and 2% for C8-BFMPT form II. In contrast to the neat crystallized form I, cooling of the C8-BFMPT form II resulted in a 10-fold increase of the PL QY. The introduction of alkyl groups and the additive-assisted crystallization are highlighted as powerful tools for manipulation by the crystal structure, morphology and optical properties of the materials.

Conflicts of interest

There are no conflicts to declare.

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