

Terminal Terthiophenediones: Fast-Decay Fluorescent Dyes and Their Efficient Syntheses

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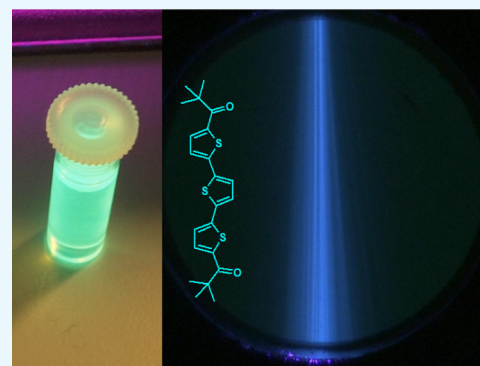


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ABSTRACT: Terminally acylated terthiophenes, in particular, the bis-pivaloyl derivative, were synthesized by Friedel–Crafts acylation with sub-stoichiometric amounts of standard zinc oxide and exhibit strong fluorescence and an ultrafast fluorescence decay of 400 ps. Their high photostability and large Stokes' shifts are good prerequisites for applications in optical GBit fast data systems such as fiber optics in slip rings.



INTRODUCTION

Modern data processing requires increasing volumes of data transfer and rely more and more on polymer optical fiber technologies.^{1,2} The interconnecting of movable machine devices for data acquisition and processing make optical fiber slip rings^{3–5} attractive. The latter operates as fluorescent light collectors such as the fluorescent planar solar collector^{6,7} where incoming light is absorbed by fluorescent dye in a polymeric glass, isotropically re-emitted as fluorescent light, mostly trapped by total reflection and guided to further processing, see Figure 1.

Fiber optics according to the fluorescent light collector is attractive for data acquisition and transmission because of light amplification where dyes with special properties are required such as high photostability and large Stokes' shifts for diminishing re-absorption of guided fluorescent light. Moreover, the rate of data transfer is limited by the time constant of fluorescent decay. The apparent time constant is close to the natural lifetime for very high fluorescence quantum yields and thus inversely proportional to the oscillator strength according to Perrin,⁸ Förster,^{9–11} and Strickler–Berg¹² where the Strickler–Berg equation is mostly applied for a quantitative description; the oscillator strengths are roughly proportional to the molar absorptivity in the absorption maximum for most chromophores with an average bandwidth. As a consequence, the fluorescence lifetime is about 4 ns (optical densities of about 1 for 1 cm) for most strongly absorbing and highly fluorescent dyes in homogeneous media such as for fluorescein (RN 518-47-8; 4.16 ns in water),¹³ rhodamine 6G (RN 989-38-8; 4.08 ns in water),¹³ perylene¹⁴ dyes (RN 83054-80-2; 3.8 ns in methanol),¹⁵ and terrylene dyes (RN 1029894-60-7; 3.01

ns in chloroform).¹⁶ This Strickler–Berg limit restricts the application of optical slip rings for very high speed data transfer.

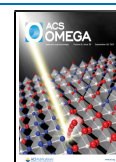
Some strongly fluorescent materials seem to operate outside this Strickler–Berg limit such as 1,4-diphenylbuta-1,3-diene (1, RN 886-65-7) with a fluorescence lifetime¹⁷ of only 354 ps (in toluene; fluorescence quantum yield¹⁸ of 0.42) where single conjugated chains instead of ribbon-like aromatics seem to be favorable for fast fluorescence decay; however, the photostability of diphenylbutadiene and higher homologues is insufficient by far. As a consequence, we followed the concept of single-chain chromophores for the development of fluorescent dyes with fast fluorescence decay, high photostability, and large Stokes' shifts and stabilized such systems by means of incorporation into heterocycles.

RESULTS AND DISCUSSION

We started according to the concept with the structure of dodecahexaene and stabilization by means of incorporation of double bonds into thiophene rings leaving some characteristics of polyenes¹⁹ because of the restricted π -overlap to the sulfur due to its large atomic size. Indeed, terthiophene (RN 1081-34-1) exhibits a short fluorescence decay^{20,21} of 150 ps; however, the solubility and fluorescence quantum yields are

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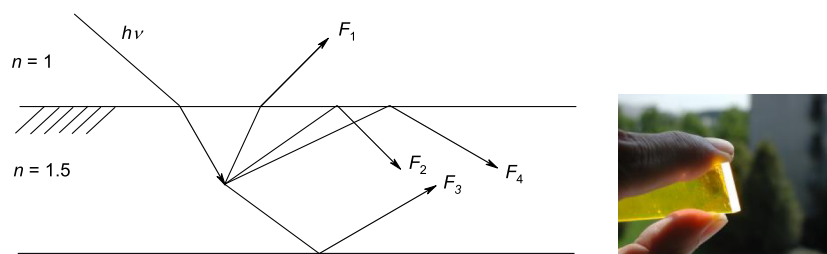
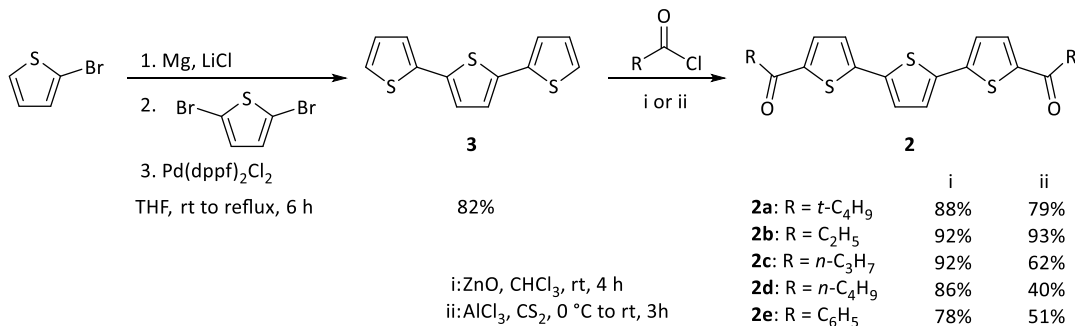


Figure 1. Light collection by the fluorescent planar collector consistent of polymeric glass doped with a fluorescent dye. Setup left: Incoming light $h\nu$ and fluorescent light F_1 until F_4 . Right: Collector made of PMMA doped with the perylene fluorescent dye S-13. (RN 110590-84-6).

Scheme 1. Synthesis of [(2,2':5',2''-Terthiophene)-5,5''-diyl]bisketones 2; Application of Two Different Lewis Acids



low, and the materials absorb in the UV (maximum at 355 nm in chloroform); a prolongation with additional thiophene rings causes a bathochromic shift of the absorption but lowers the solubility further. An extension of the chromophore of terthiophene by terminal carbonyl groups shifts the absorption into the visible as is indicated by the bis-aldehyde²² and the bis-carboxylic esters.²³ The time constants of fluorescence decay remain short; however, such reactive terminal groups limit the stability. As a consequence, carbonyl derivatives without enolizable hydrogen atoms (compare ref 24) in the α -position are attractive. We targeted 1,1'-[(2,2':5',2''-terthiophene)-5,5''-diyl]bis(2,2-dimethylpropan-1-one) (**2a**) fulfilling all conditions where the terminal *tert*-butyl groups⁶ are expected to be favorable concerning the solubility and minimizing the tendency of aggregation (compare ref 25).

Positions 3 and 4 in the thiophene units of **2a** were left unsubstituted in order to provide molecular dynamics²⁵ (see below).

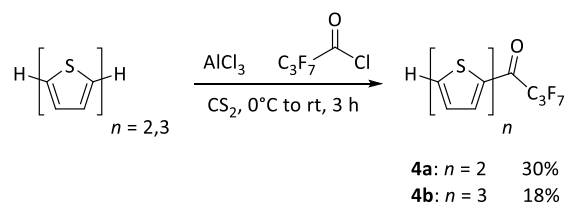
We started the synthesis with the readily available mono- and dibromo thiophenes to carry out a double-Kumada coupling reaction, as shown in Scheme 1. Using 0.2 mol % of Pd(dppf)Cl₂ as a catalyst led to **3** in a satisfying yield of 82%. **3** was allowed to react with acyl chlorides in Friedel–Crafts reactions under two different conditions (i and ii) to obtain the terminal bisketones **2**. Following the standard procedures (ii in Scheme 1) using excess of water-free aluminum chloride as the Lewis acid in anhydrous carbon disulfide^{26,27} afforded **2a** in an acceptable yield. However, some decarbonylation of pivaloyl chloride may occur with this strong Lewis acid, motivating the search to milder reaction conditions and avoiding the highly inflammable carbon disulfide. The application of simple standard solid zinc oxide in sub-stoichiometric amounts (0.25 equivalent per reactive center) in chloroform gave an appreciable improvement. The catalytic potency of zinc oxide is already described for few reactions;^{9,10} however, in most cases, activated species such as nanorods,¹¹ nanoparticles,¹² or hollow spheres¹³ had to be

prepared previously or the method was restricted to solvent-free conditions.¹⁴ The electron-rich terthiophene reacts using half an equivalent of low-cost plain powder of zinc oxide to obtain the terthiophenediyl bisketone **2a** in yields clearly exceeding those of the AlCl₃ approach. Further advantages of the ZnO pathway are the application of more convenient and more user-friendly solvents such as chloroform and the prevention of the formation of byproducts; removing the latter is laborious. The reduced activity of ZnO results exclusively in the formation of the target ketones where the residual starting material can be easily recovered.

The simple method of zinc oxide mediated acylation can be extended to other aliphatic and aromatic acid chlorides (Scheme 1, **2b–2e**) where throughout higher yield and purer raw products were obtained compared with the standard procedure. However, the enolizable hydrogen atoms in **2b** until **2d** are unfavorable concerning the stability.

We investigated the influence of stronger electron-withdrawing terminal carbonyl substituents on the spectroscopic properties of oligothiophenes and extended the acylation to perfluorobutyric chloride.²⁸ No zinc oxide mediated reaction could be observed, and the application of the standard procedure afforded the mono-acylated products for both bithiophene (**4a**) and terthiophene (**4b**) with moderate yields, see Scheme 2. Obviously, activation of perfluoro acid chloride is more difficult, and the electron depletion in the

Scheme 2. Synthesis of Perfluorobutyryl Derivatives 4 of Oligothiophenes



reaction products inhibits a second acylation. On the other hand, this reaction allows an easy access to the mono-acylated products **4a** and **4b**.

The two terminal carbonyl groups shift the absorption of unstrained **2** bathochromically into the visible (**2a–2d**) to about 410 nm and a conjugation with phenyl groups in **2e** further 10 nm, see Table 1 and Figure 2. The steric effect of

Table 1. UV/vis Spectroscopic Properties of Ketothiophenes **2** and **4** in Chloroform

Dye	λ_{abs}^a	λ_{fluo}^b	ϵ^c	Φ^d	τ^e	$\frac{\lambda_{\text{fluo}}}{\lambda_{\text{abs}}}$ ^f	$\frac{E_{\text{fluo}}}{E_{\text{abs}}}$ ^g
2a	410.2	494.3	43 800	0.54	0.403	84.1	0.505
2b	406.2	490.4	45 300	0.52	0.391	84.2	0.527
2c	409.4	491.2	39 800	0.39	0.388	81.8	0.505
2d	409.4	494.3	41 200	0.50	0.402	85.2	0.526
2e	421.8	510.4 ^h	42 400	0.40	0.407	88.6	0.507
4a	384.0	447.7	23 300	0.62	1.453	63.7	0.459
4b	432.2	528.8	42 200	0.47	2.496	96.6	0.524

^aAbsorption maximum in nanometers. ^bFluorescence maximum in nanometers. ^cMolar absorptivity. ^dFluorescence quantum yield. ^eFluorescence lifetime in nanoseconds. ^fStokes' shift (referred to total maxima) in nanometers. ^gStokes' shift (referred to total maxima) in electronvolts. ^hSecond maximum ($I_{\text{rel}} = 0.97$) for comparison.

the *tert*-butyl groups in **2a** causes a slight further bathochromic shift in this series and the conjugation with the terminal phenyl groups to 422 nm. The electron-withdrawing perfluoropropyl group in **4b** induces an appreciable bathochromic shift so that 432 nm are reached with a single carbonyl group. The effect is so pronounced that 384 nm are already reached with the bithiophene **4a**. The terthiophenes **2a–2e** and **4a** exhibit strong fluorescence in solution at about 500 nm and in polymeric glasses such as PMMA; the fluorescence quantum yields of about 50% (in chloroform) are sufficiently high for most applications (Table 1) (see Figure 3).

The appreciably large Stokes' shifts of about 80 nm (0.5 eV) are attributed to a light-induced dynamic process (compare refs 6 and 25) according to Figure 4. The aromatic rings in the

chain of thiophenes are slightly helically twisted versus each other because of the matched moderate steric interactions of the protons with the sulfur atoms in the starting electronic ground state S_0 . The electronic excitation to the S_1 state ($h\nu$) proceeds vertically without change of the geometry. This unfavorable geometry of the excited state S_1 relaxes within the fluorescence lifetime to the planarized S_1' state of lower energy; the driving force may be an increase of the double-bond characteristic between the thiophene rings. The subsequent vertical electronic transition between S_1' and S_0' proceeds with fluorescence ($h\nu'$) to the unfavorable geometry of the S_0' state and relaxes to the ground state S_0 of lower energy. In energy, the difference between S_1' and S_0' is lower than between S_0 and S_1 and causes a bathochromic shift in fluorescence and thus an increased Stokes' shift (compare the mechanism in ref 29). The helically twisted geometry of the ground state S_0 is verified by means of X-ray crystal structure analysis of **2a** reported in Figure 5. The planar geometry of S_1' supported by quantum chemical calculations is shown in Figure 6; for details, see ref 25. This process seems to be conservative even in polymeric matrix such as PMMA because identical fluorescence spectra were obtained.

The fluorescence lifetimes of the derivatives of **2a–2e** are uniformly short with time constants of about 0.4 ns; see Table 1. These short time constants persist in polymeric glasses such as PMMA as is shown for **2a** in Figure 7 and make the dyes suitable for fast data transfer where **2a** is a good compromise concerning fluorescence lifetime, matching in PMMA the open spectral window of minimal damped waveguiding, high solubility, and stability (no enolizable protons). Interestingly, the time constants of the mono keto derivatives **4a** and **4b** of more than 1 ns are still comparably short but perceptibly longer than for the derivatives of **2**. As a consequence, the symmetrical terminal substitution in **2** seems to be favorable for short time constants for fluorescence decay.

CONCLUSIONS

Terminal bisketotertthiophenes **2** can be efficiently prepared under mild conditions by Friedel–Crafts-reaction of alkyl- and arylcarboxylic chlorides with well-accessible terthiophene

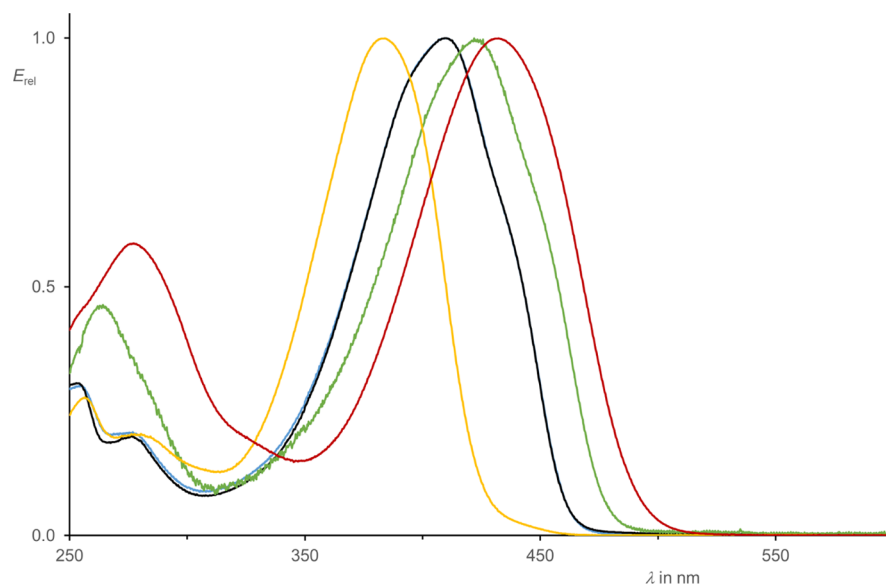


Figure 2. UV/vis absorption spectra in chloroform: **2a** (black), **2d** (blue, covered by **2a**), **2e** (green), **4a** (yellow), and **4b** (red).

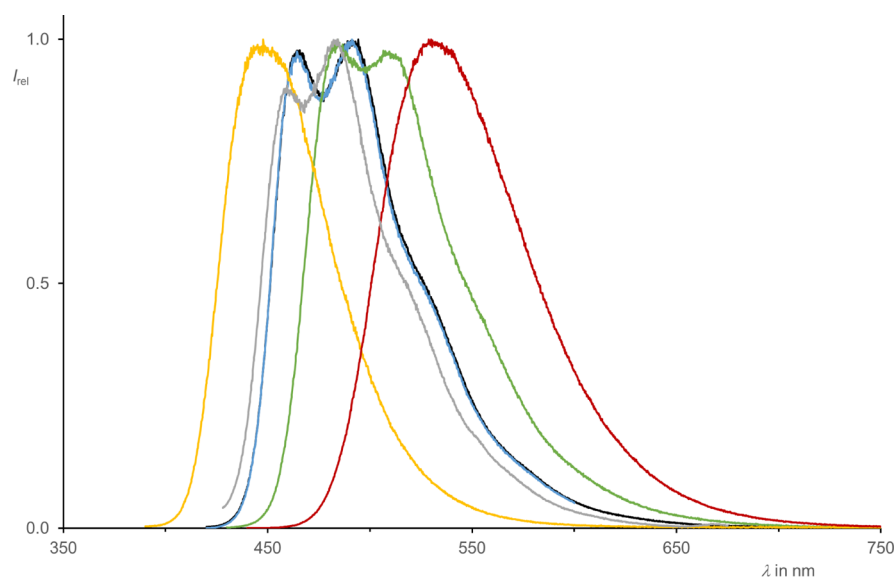


Figure 3. Fluorescence spectra in chloroform: **2a** (black), **2d** (blue), **2e** (green), **4a** (yellow), and **4b** (red). **2a** solved in solid PMMA (gray).

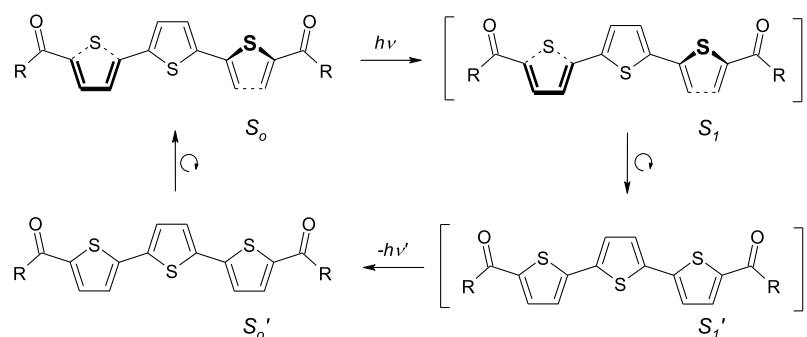


Figure 4. Dynamic process for the increase of Stokes' shifts of the bisketones **2**. The light absorption ($h\nu$) of the helical ground state (S_0) forms the electronically excited and geometrically disfavored state S_1 in a vertical process. Relaxation to the planar conjugated S_1' allows a bathochromically shifted fluorescence ($h\nu'$) to the electronic ground-state S_0' , finally reaching the initially state S_0 .

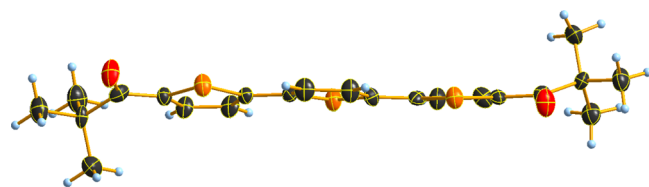


Figure 5. Crystal structure of tertthiophenediyl bisketone **2a**. The thiophene units are helically twisted to each other with dihedral angles of about 10° ; for further details, see CCDC-2062986 in the Cambridge database.

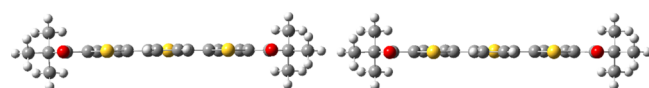


Figure 6. Quantum chemically calculated planar geometry of the excited state of **2a**. Left: CIS-311**G, right: TDSCF B3LYP 6-311**G (applied program: Gaussian 16W).

catalyzed by standard zinc oxide. More harsh condition requires the electron-depleted perfluorobutyrylcarboxylic chloride and reacts to the mono ketones **4**. Three units of thiophene are sufficient in the bisketones **2** to shift the light absorption into the visible at more than 400 nm in contrast to alkyl oligothiophenes where four and more units are required.

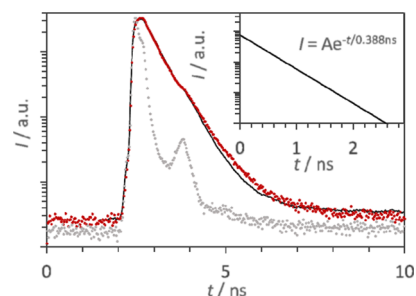


Figure 7. Fluorescence lifetime of **2a** in PMMA. IRF (gray), fluorescence decay (red), and deconvolutional fit (black line). Inset: exponential fit of **2a** in PMMA resulting in a fluorescence lifetime of 0.388 ns.

Leaving positions 3 and 4 unsubstituted in the stringed thiophenes allows molecular dynamics cause an increase of Stokes' shift of these highly fluorescent compounds (fluorescence quantum yields of about 50%). The terminal *tert*-butyl groups in **2a** favor the solubility both in solvents and in polymeric glasses and the stability of colorations because of the absence of enolizable protons. The very short fluorescent decay of **2** with a time constant of only 0.4 ns is unexpected according to the Strickler–Berg equation (2) and makes this lightfast dye a good candidate for operating in GBit optical

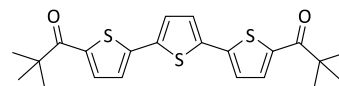
data processing such as in fiber optics where the persistency of both the short time constant of fluorescence and the large Stokes' shift even in the solid glassy matrix such as in PMMA is of special technological advantage. Moreover, the very short fluorescence decay combined with a large Stokes' shift and comparably intense fluorescence allows application as a contrast agent in lifetime imaging such as fluorescent bio-imaging.

EXPERIMENTAL SECTION

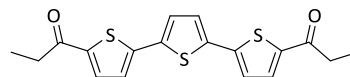
General Information. The available standard chemicals were applied in the synthesis grade without further purification. Chloroform was used in spectrophotometric grade. Yields refer to the isolated compounds estimated to be >95% pure as determined by ^1H NMR (25 °C); all dyes were uniform according to T.L.C. Chemical shifts are reported as δ values in ppm calibrated with the solvent peak. Nuclear magnetic resonance (NMR) spectra were recorded in the solution of CD_2Cl_2 (residual chloroform: $\delta = 5.32$ ppm for ^1H NMR and $\delta = 54.00$ ppm for $^{13}\text{C}\{^1\text{H}\}$ NMR). Abbreviations for signal coupling are as follows: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sxt, sextet; and m, multiplet. Infrared spectra were recorded from 4000–400 cm^{-1} on a PerkinElmer 281 IR spectrometer. Samples were measured neat [attenuated total reflection (ATR), Smiths Detection Dura Sample IR II Diamond ATR]. The absorption bands were reported in wavenumbers (cm^{-1}). Mass spectra were recorded on a Finnigan MAT 95Q or Finnigan MAT 90 instrument for electron impact ionization (EI) with direct vaporization of the sample (DEP/EI) from a platinum fiber 20 until 1600 °C at 60 °C $\cdot\text{min}^{-1}$. High-resolution mass spectra (HRMS) were recorded on the same instrument. UV/vis spectra were obtained with a Varian Cary5000 spectrometer. Fluorescence spectra were obtained with a Varian Cary Eclipse spectrometer, slit width 2.5 nm. Column chromatography was performed using SiO_2 (0.040–0.063 mm, 230–400 mesh ASTM) from Merck if not indicated. Fluorescence quantum yields were determined analogously by means of the standard 3,4,9,10-perylenetetracarboxylic acid-3,4,9,10-tetramethyl ester (CAS RN 53159-49-2).³⁰ Elemental analyses were determined using the Elementar vario EL and Elementar vario microcube. All reagents were obtained from commercial sources and used without further purification if not otherwise stated.

2,2':5',2''-Terthiophene (3). Lithium chloride (2.67 g, 63.0 mmol, 3.15 eq.) and magnesium turnings (1.53 g, 63.0 mmol, 3.15 eq.) were placed in a two-neck flask and flame-dried. Dry tetrahydrofuran (THF) (30 mL) were added under argon, and the suspension was treated with a solution of 2-bromothiophene (9.78 g, 60.0 mmol, 3 eq.) in 20 mL of THF at room temperature. The reaction mixture was heated to 65 °C and stirred at this temperature for 2 h. In a second dry two-neck flask, 2,5-dibromothiophene (4.84 g, 20.0 mmol) was dissolved in 20 mL of THF and slowly treated with the freshly prepared Grignard reagent at 0 °C under an argon atmosphere. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) was added and the reaction mixture was stirred at room temperature for 1 h and at 65 °C for subsequent 3 h. The resulting intensively green mixture was cooled to room temperature and quenched with 50 mL of saturated aqueous ammonium chloride. Extraction with chloroform (3 \times 75 mL) was followed by evaporation, and the crude product was purified via two-fold column chromatography (silica, 1st: iso-hexane/chloroform 12:1, 2nd: iso-hexane) to obtain a slightly

yellow oil, which crystallizes within several hours to form brown needles. Yield: 4.07 g (16.4 mmol, 82%). R_f -value (iso-hexane): 0.50. ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 7.27$ (dd, $^3J = 5.0$ Hz, $^4J = 1.1$ Hz, 2H), 7.22 (dd, $^3J = 3.6$ Hz, $^4J = 1.1$ Hz, 2H), 7.12 (s, 2H), 7.05 ppm (dd, $^3J = 5.0$ Hz, $^3J = 3.6$ Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3): $\delta = 136.92, 136.10, 127.88, 124.54, 124.27, 123.69$ ppm. MS (70 eV, EI): m/z (%) = 248 (100) [M^+], 171 (7), 127 (7). HRMS (EI, $\text{C}_{12}\text{H}_8\text{S}_3$): $m/z = \text{calcd } 247.9788, \text{found } 247.9765, \Delta = -2.3$ mmu. Elemental analysis $\text{C}_{12}\text{H}_8\text{S}_3$ (248.4 g mol^{-1}): calcd C: 58.03, H: 3.25, S: 38.72; found C: 57.81, H: 3.49, S: 38.98.

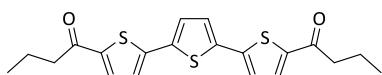


1,1'-[(2,2':5',2''-Terthiophene)-5,5''-diyl]bis(2,2-dimethylpropan-1-one) (2a). 2,2':5',2''-Terthiophene (3) (62.1 mg, 0.250 mmol) was dissolved in chloroform (1.0 mL), treated with zinc oxide (31.1 mg, 50% w/w), stirred with pivaloyl chloride (241 mg, 2.00 mmol) at room temperature (color change to purple) for 4 h, evaporated in vacuo, treated with saturated aqueous sodium carbonate solution (5 mL), extracted with chloroform (2 \times 10 mL), washed with saturated aqueous sodium carbonate solution (10 mL) and distilled water (10 mL), evaporated, purified by column separation (silica gel, chloroform/iso-hexane 2:1), filtered through neutral alumina, and evaporated. Yield 91.7 mg (88%), m.p. 206 °C. R_f -value (CHCl_3 /iso-hexane 2:1): 0.80. IR (ATR): $\tilde{\nu} = 2968, 1633$ (s), 1506, 1466, 1436 (s), 1363, 1327, 1278, 1196, 1175, 1065, 1024, 914, 854, 820, 792 (s), 748 cm^{-1} . ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.69$ (d, $^3J = 4.1$ Hz, 2H), 7.24 (s, 2H), 7.18 (d, $^3J = 4.0$ Hz, 2H), 1.41 ppm (s, 18H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 199.0, 143.7, 141.7, 137.3, 133.3, 126.8, 124.7, 44.4, 28.69$ ppm. UV/vis (CHCl_3): λ_{max} (ϵ) = 410.2 nm (43,800). Fluorescence (CHCl_3): λ_{max} (I_{rel}) = 465.6 (0.98), 494.3 nm (1.00). Fluorescence quantum yield (CHCl_3 , $\lambda_{\text{Ex}} = 410.2$ nm, $E_{410.2 \text{ nm}/1 \text{ cm}} = 0.0246$, reference: tetramethyl perylene-3,4,9,10-tetracarboxylate with $\Phi = 1.00$): 0.54. MS (70 eV, EI): $m/z = 416.07$ [M^+], 359.03 [$\text{M}^+ - \text{C}_4\text{H}_9$], 331.05 [$\text{M}^+ - \text{C}_2\text{H}_5\text{O}$]. HRMS (EI, $\text{C}_{22}\text{H}_{24}\text{O}_2\text{S}_3$): $m/z = \text{calcd } 416.0933, \text{found } 416.0930, \Delta = -0.3$ mmu. Elemental analysis $\text{C}_{22}\text{H}_{24}\text{O}_2\text{S}_3$ (416.6 g mol^{-1}): calcd C: 63.42, H: 5.81, S: 23.09; found C: 62.04, H: 5.91, S: 20.60.

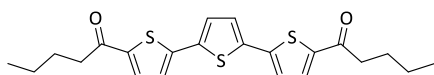


1,1'-[(2,2':5',2''-Terthiophene)-5,5''-diyl]bis(propan-1-one) (2b). 2,2':5',2''-Terthiophene (3) (62.1 mg, 0.250 mmol) was dissolved in chloroform (1.0 mL), treated with zinc oxide (31.1 mg, 50% w/w), stirred with propionyl chloride (185 mg, 2.00 mmol) at room temperature (color change to purple) for 4 h, evaporated in vacuo, treated with saturated aqueous sodium carbonate solution (5 mL), extracted with chloroform (2 \times 10 mL), washed with saturated aqueous sodium carbonate solution (10 mL) and distilled water (10 mL), evaporated, purified by column separation (silica gel, chloroform/iso-hexane 2:1), filtered through neutral alumina, and evaporated. Yield 82.6 mg (92%), m.p. 222 °C. R_f -value (CHCl_3 /iso-hexane 2:1): 0.65. IR (ATR): $\tilde{\nu} = 2977, 2938, 2877, 1655$ (s), 1507, 1441, 1412, 1378, 1354, 1254, 1221, 1086, 1060, 912, 882, 854, 787 (vs), 744, 724, 666 cm^{-1} . ^1H

NMR (400 MHz, CD₂Cl₂): δ = 7.63 (d, ³J = 4.0 Hz, 2H), 7.29 (s, 2H), 7.24 (d, ³J = 4.0 Hz, 2H), 2.92 (q, ³J = 7.3 Hz, 4H), 1.21 ppm (t, ³J = 7.3 Hz, 6H). ¹³C NMR (100 MHz, CD₂Cl₂): δ = 133.0, 127.0, 125.2, 32.7, 8.8 ppm. UV/vis (CHCl₃): λ_{max} (ϵ) = 406.2 nm (45,300). Fluorescence (CHCl₃): λ_{max} (I_{rel}) = 463.3 (0.91), 490.4 nm (1.00). Fluorescence quantum yield (CHCl₃, λ_{Ex} = 406.2 nm, $E_{406.2 \text{ nm}/1 \text{ cm}}$ = 0.0248, reference: tetramethyl perylene-3,4:9,10-tetracarboxylate with Φ = 1.00): 0.52. MS (70 eV, EI): m/z (%) = 360 (85) [M⁺], 331 (100) [M⁺ - C₂H₅], 303 (16) [M⁺ - C₃H₅O], 259 (42). HRMS (EI, C₁₈H₁₆O₂S₃): m/z = calcd 360.0312, found 360.0314, Δ = +0.2 mmu. Elemental analysis C₁₈H₁₆O₂S₃ (360.5 g mol⁻¹): calcd C: 59.97, H: 4.47, S: 26.68; found C: 60.20, H: 4.53, S: 26.82.

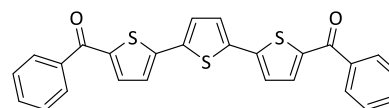


1,1'-[(2,2':5',2''-Terthiophene)-5,5''-diyl]bis(butan-1-one) (2c). 2,2':5',2''-Terthiophene (3) (62.1 mg, 0.250 mmol) was dissolved in chloroform (1.0 mL), treated with zinc oxide (31.1 mg, 50% w/w), stirred with butyric acid chloride (213 mg, 2.00 mmol) at room temperature (color change to purple) for 4 h, evaporated in vacuo, treated with saturated aqueous sodium carbonate solution (5 mL), extracted with chloroform (2 × 10 mL), washed with saturated aqueous sodium carbonate solution (10 mL) and distilled water (10 mL), evaporated, purified by column separation (silica gel, chloroform/iso-hexane 2:1), filtered through neutral alumina, and evaporated. Yield 89.4 mg (92%), m.p. 225 °C. R_f -value (CHCl₃/iso-hexane 2:1): 0.70. IR (ATR): $\tilde{\nu}$ = 3294, 3063, 2959, 2933, 2872, 2668, 1654 (s), 1506, 1483, 1464, 1439 (s), 1407, 1370, 1326, 1306, 1289, 1253, 1211 (s), 1113, 1077, 1067, 1038, 957, 901, 878, 856, 817, 792 (s), 757, 749, 674 cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.62 (d, ³J = 4.0 Hz, 2H), 9.29 (s, 2H), 7.24 (d, ³J = 4.0 Hz, 2H), 2.86 (t, ³J = 7.3 Hz, 4H), 1.76 (h, ³J = 7.4 Hz, 4H), 1.00 ppm (t, ³J = 7.4 Hz, 6H). ¹³C NMR (100 MHz, CD₂Cl₂): δ = 193.4, 144.5, 143.8, 137.6, 133.1, 127.0, 125.2, 41.3, 18.75, 14.17 ppm. UV/vis (CHCl₃): λ_{max} (ϵ) = 409.4 nm (39,800). Fluorescence (CHCl₃): λ_{max} (I_{rel}) = 465.2 (0.98), 491.2 nm (1.00). Fluorescence quantum yield (CHCl₃, λ_{Ex} = 409.4 nm, $E_{409.4 \text{ nm}/1 \text{ cm}}$ = 0.042, reference: tetramethyl perylene-3,4:9,10-tetracarboxylate with Φ = 1.00): 0.39. MS (70 eV, EI): m/z (%) = 388 (11) [M⁺], 345 (91), 273.01 (42). HRMS (EI, C₂₀H₂₀O₂S₃): m/z = calcd 388.0625, found 388.0626, Δ = +0.1 mmu. Elemental analysis C₂₀H₂₀O₂S₃ (388.1 g mol⁻¹): calcd C: 61.82, H: 5.19, S: 24.75; found C: 61.75, H: 5.06, S: 25.16.

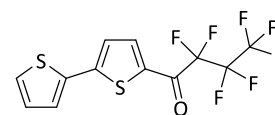


1,1'-[(2,2':5',2''-Terthiophene)-5,5''-diyl]bis(pentan-1-one) (2d). 2,2':5',2''-Terthiophene (3) (62.1 mg, 0.250 mmol) was dissolved in chloroform (1.0 mL), treated with zinc oxide (31.1 mg, 50% w/w), stirred with valeryl chloride (241 mg, 2.00 mmol) at room temperature (color change to purple) for 4 h, evaporated in vacuo, treated with saturated aqueous sodium carbonate solution (5 mL), extracted with chloroform (2 × 10 mL), washed with saturated aqueous sodium carbonate solution (10 mL) and distilled water (10 mL), evaporated, purified by column separation (silica gel, chloro-

form/iso-hexane 1:1), filtered through neutral alumina, and evaporated. Yield 89.6 mg (86%), m.p. 208 °C. R_f -value (CHCl₃/iso-hexane 1:1): 0.50. IR (ATR): $\tilde{\nu}$ = 2960, 2929, 2872, 1655, 1507, 1464, 1445, 1409, 1380, 1347, 1259, 1209, 1088, 1016 (s), 930, 858, 789 (s), 751, 735, 701, 673 cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.62 (d, ³J = 4.0 Hz, 2H), 7.29 (s, 2H), 7.24 (d, ³J = 4.0 Hz, 2H), 2.88 (t, ³J = 7.3 Hz, 4H), 1.75–1.67 (m, 4H), 1.52–1.37 (m, 4H), 0.96 ppm (t, ³J = 7.3 Hz, 6 H). ¹³C NMR (100 MHz, CD₂Cl₂): δ = 193.5, 144.5, 143.7, 137.5, 133.1, 127.0, 125.2, 39.2, 27.4, 23.0, 14.2 ppm. UV/vis (CHCl₃): λ_{max} (ϵ) = 409.4 nm (34,700). Fluorescence (CHCl₃): λ_{max} (I_{rel}) = 464.2 (0.98), 491.2 nm (1.00). Fluorescence quantum yield (CHCl₃, λ_{Ex} = 409.4 nm, $E_{409.4 \text{ nm}/1 \text{ cm}}$ = 0.0421, reference: tetramethyl perylene-3,4:9,10-tetracarboxylate with Φ = 1.00): 0.71. MS (70 eV, EI): m/z = 416.02 [M⁺], 374.00 [M⁺ - C₃H₆], 331.98 [M⁺ - C₆H₁₂], 316.97 [M⁺ - C₇H₁₅]. HRMS (EI, C₂₂H₂₄O₂S₃): m/z = calcd 416.0933, found 416.0934, Δ = +0.1 mmu.

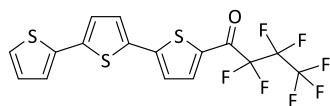


1,1'-[(2,2':5',2''-Terthiophene)-5,5''-diyl]bis(phenylmethanone) (2e). 2,2':5',2''-Terthiophene (3) (62.1 mg, 0.250 mmol) was dissolved in chloroform (1.0 mL), treated with zinc oxide (31.1 mg, 50% w/w), stirred with benzoyl chloride (281 mg, 2.00 mmol) at room temperature (color change to purple) for 4 h, evaporated in vacuo, treated with saturated aqueous sodium carbonate solution (5 mL), extracted with chloroform (2 × 10 mL), washed with saturated aqueous sodium carbonate solution (10 mL) and distilled water (10 mL), evaporated, purified by column separation (silica gel, chloroform/iso-hexane 2:1), filtered through neutral alumina, and evaporated. Yield 89 mg (78%), m.p. 218 °C. R_f -value (CHCl₃/iso-hexane 2:1): 0.75. IR (ATR): $\tilde{\nu}$ = 3057, 1612 (s), 1597, 1574, 1503, 1446, 1435 (s), 1425, 1360, 1340, 1317, 1293 (s), 1219, 1178, 1137, 1074, 1058, 1022, 999, 973, 925, 906, 886, 854, 827, 812, 791 (s), 711 (s), 699 (s), 691 (s), 669, 653 (s) cm⁻¹. ¹H NMR (600 MHz, CD₂Cl₂): δ = 7.86 (dd, ³J = 8.3 Hz, ⁴J = 1.3 Hz, 4H, *o*-H), 7.65–7.61 (m, 2H, *p*-H), 7.58 (d, ³J = 4.0 Hz, 2H), 7.54 (t, ³J = 7.6 Hz, 4H, *m*-H), 7.37 (s, 2H), 7.30 ppm (d, ³J = 4.0 Hz, 2H). ¹³C NMR (150 MHz, CD₂Cl₂): δ = 188.0, 145.4, 143.0, 138.5, 137.7, 136.3, 132.9, 129.5, 129.1, 127.4, 125.3 ppm. UV/vis (CHCl₃): λ_{max} (ϵ) = 421.8 nm (42,400). Fluorescence (CHCl₃): λ_{max} (I_{rel}) = 484.3 (1.00), 510.6 nm (0.97). Fluorescence quantum yield (CHCl₃, λ_{Ex} = 421.8 nm, $E_{421.8 \text{ nm}/1 \text{ cm}}$ = 0.067, reference: tetramethyl perylene-3,4:9,10-tetracarboxylate with Φ = 1.00): 0.40. MS (70 eV, EI): m/z (%) = 456 (100) [M⁺], 379 (14) [M⁺ - C₆H₅], 351 (7) [M⁺ - C₇H₅O]. HRMS (EI, C₂₆H₁₆O₂S₃): m/z = calcd 456.0312, found 456.0308, Δ = -0.4 mmu. Elemental analysis C₂₆H₁₆O₂S₃ (456.6 g mol⁻¹): calcd C: 68.39, H: 3.53, S: 21.06; found C: 67.02, H: 3.95, S: 21.21.



1-[(2,2'-Bithiophen)-5-yl]-2,2,3,3,4,4,4-heptafluorbutan-1-one (4a). 2,2'-Bithiophene (41.6 mg, 0.250 mmol) was dissolved in anhydrous carbon disulfide (1.0 mL) in a dry

glass apparatus flushed with argon, cooled to 0 °C under stirring, treated with stirring with heptafluorobutyl chloride (235 mg, 2.50 mmol) and anhydrous aluminum chloride (83.3 mg, 0.625 mmol) (instant color change to red), allowed to warm to room temperature, treated after 1 and 2 h with additional aluminum chloride (83.3 mg, 0.625 mmol each), stirred for 1 h, evaporated, treated with saturated aqueous ammonium chloride solution (5 mL), extracted with chloroform (2 × 10 mL), evaporated, purified by column separation (silica gel, chloroform/iso-hexane 3:1), filtered through neutral alumina, and evaporated. Yield 27.2 mg (30%), m.p. 58 °C. R_f -value (iso-hexane/ CHCl_3 3:1): 0.30. IR (ATR): $\tilde{\nu}$ = 3118, 1663 (s), 1540, 1502, 1442 (s), 1208 (s), 1117 (s), 1079, 958, 936, 843, 799 (s), 705 (s), 694 (s) cm^{-1} . ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.91–7.88 (m, 1H), 7.48–7.47 (m, 2H), 7.31 (d, 3J = 4.2 Hz, 1H), 7.14–7.12 ppm (m, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 151.6, 138.9, 136.3, 136.1, 129.3, 129.5, 128.2, 126.2 ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = -80.67 (t, J = 9.1 Hz, 1H), -115.66 until -115.83 (m), -126.17 (s) ppm. UV/vis (CHCl_3): λ_{max} (ϵ) = 384.0 nm (23,300). Fluorescence (CHCl_3): λ_{max} = 447.7 nm. Fluorescence quantum yield (CHCl_3 , λ_{Ex} = 384.0 nm, $E_{384.0 \text{ nm}/1 \text{ cm}}$ = 0.0418, reference: tetramethyl perylene-3,4:9,10-tetracarboxylate with Φ = 1.00): 0.62. MS (70 eV, EI): m/z = 361.93 [M^+], 329.95, 193.04 [$\text{M}^+ - \text{C}_3\text{F}_7$], 165.05 [$\text{M}^+ - \text{C}_4\text{F}_7\text{O}$]. HRMS (EI, $\text{C}_{12}\text{H}_6\text{F}_7\text{OS}_2$ for $\text{M} + \text{H}^+$): m/z = calcd 362.9742, found 362.9746, Δ = +0.4 mmu. Elemental analysis $\text{C}_{12}\text{H}_6\text{F}_7\text{OS}_2$ (362.3 g mol^{-1}): calcd. C: 39.78, H: 1.39, S: 17.70; found C: 40.49, H: 1.95, S: 19.04.



1-[(2,2':5',2''-Terthiophen)-5-yl]-2,2,3,3,4,4,4-heptafluorbutan-1-one (4b). 2,2':5',2''-Terthiophene (3) (62.1 mg, 0.250 mmol) was dissolved in anhydrous carbon disulfide (1.0 mL) in a dry glass apparatus flushed with argon, cooled to 0 °C under stirring, treated under stirring with heptafluorobutyl chloride (235 mg, 2.50 mmol) and anhydrous aluminum chloride (83.3 mg, 0.625 mmol) (instant color change to red), allowed to warm to room temperature, treated after 1 and 2 h with additional aluminum chloride (83.3 mg, 0.625 mmol each), stirred for 1 h, evaporated, treated with saturated aqueous ammonium chloride solution (5 mL), extracted with chloroform (2 × 10 mL), evaporated, purified by column separation (silica gel, iso-hexane 3:1), filtered through neutral alumina, and evaporated. Yield 20.0 mg (18%), m.p. 107 °C. R_f -value (iso-hexane): 0.35. IR (ATR): $\tilde{\nu}$ = 1663 (s), 1500, 1449, 1433, 1344, 1228 (s), 1208 (s), 1171, 1119, 1069, 968, 938, 823, 793 (s), 787 (s), 750, 698 (s) cm^{-1} . ^1H NMR (800 MHz, CD_2Cl_2): δ = 7.90–7.89 (m, 1H), 7.40 (d, 3J = 3.8 Hz, 1H), 7.34 (dd, 3J = 5.1 Hz, 4J = 1.1 Hz, 1H), 7.30 (d, 3J = 4.2 Hz, 1H), 7.29 (dd, 3J = 3.6 Hz, 4J = 1.1 Hz, 1H), 7.20 (d, 3J = 3.9 Hz, 1H), 7.08 ppm (dd, 3J = 5.1 Hz, 3J = 3.6 Hz, 1H). ^{13}C NMR (201 MHz, CD_2Cl_2): δ = 175.2, 150.9, 141.0, 138.7, 136.6, 135.9, 134.1, 128.7, 126.5, 125.6, 125.5 ppm. UV/vis (CHCl_3): λ_{max} (ϵ) = 432.2 nm (42,200). Fluorescence (CHCl_3): λ_{max} = 528.8 nm. Fluorescence quantum yield (CHCl_3 , λ_{Ex} = 432.2 nm, $E_{432.2 \text{ nm}/1 \text{ cm}}$ = 0.0470, reference: tetramethyl perylene-3,4:9,10-tetracarboxylate with Φ = 1.00): 0.47. MS (70 eV, EI): m/z = 443.80 [M^+], 274.97 [$\text{M}^+ - \text{C}_3\text{F}_7$]. HRMS (EI, $\text{C}_{16}\text{H}_7\text{F}_7\text{OS}_3$): m/z = calcd 443.9547, found

443.9539, Δ = -0.8 mmu. Elemental analysis $\text{C}_{16}\text{H}_7\text{F}_7\text{OS}_3$ (444.4 g mol^{-1}): calcd C: 43.24, H: 1.59, S: 21.64; found C: 43.19, H: 2.27, S: 23.27.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c04010>.

NMR and IR spectra of **2a–2e** and **4a–4b**; optical spectra of **2b**, **2c**, **4a**, and **4b**; and preparation of doped PMMA (PDF)

Crystallographic data of compound **2a** (CIF)

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Author Contributions

All authors contributed to the work in order to complete the work and played a role in writing the manuscript. X-ray crystal structure analysis was performed by K.K. Parts of this manuscript were adapted from the Ph.D. Dissertation of T.S.³¹

Notes

The authors declare no competing financial interest.

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