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

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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 attractive. The latter operates as fluorescent light collectors such as the fluorescent planar solar collector6,7 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 decay20,21 of 150 ps; however, the solubility and fluorescence quantum yields are
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-aldehyde and the bis-carboxylic esters. The time constants of fluorescent decay remain short; however, such reactive terminal groups limit the stability. As a consequence, carbonyl derivatives without enolizable hydrogen atoms (compare ref24) in the α-position are attractive. We targeted 1,1′-[(2,2′:5′,2″-terthiophene)-5,5″-diyl]bisketones 2a; filling all conditions where the terminal tert-butyl groups are expected to be favorable concerning the solubility and minimizing the tendency of aggregation (compare ref25).

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

We started the synthesis with the readily available monobromo 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 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 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. No zinc oxide mediated reaction could be observed, and the application of the standard procedure afforded the mono-acylated products for both bisthiophene (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

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 $F_i$ until $F_4$. Right: Collector made of PMMA doped with the perylene fluorescent dye S-13. (RN 110590-84-6).
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 the tert-butyl groups in 2a causes a slight further bathochromic shift in this series and the conjugation with the terminal phenyl 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 bisthiophene 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 So. The electronic excitation to the S1 state (hv) proceeds vertically without change of the geometry. This unfavorable geometry of the excited state S1 relaxes within the fluorescence lifetime to the planarized S1′ 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 S1′ and S0 proceeds with fluorescence (hv′) to the unfavorable geometry of the S0 state and relaxes to the ground state So of lower energy. In energy, the difference between S1′ and S0 is lower than between S0 and S1 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 So is verified by means of X-ray crystal structure analysis of 2a reported in Figure 5. The planar geometry of S1 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 tertthiophene

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

| Dye | λ<sub>abs</sub><sup>a</sup> | λ<sub>flu</sub><sup>b</sup> | ε<sup>c</sup> | Φ<sup>d</sup> | λ<sub>flu</sub><sup>e</sup> − λ<sub>abs</sub><sup>e</sup> | E<sub>flu</sub><sup>f</sup> − E<sub>abs</sub><sup>f</sup> |
|-----|----------------|----------------|------|------|----------------|----------------|
| 2a  | 410.2          | 494.3          | 43   | 0.54 | 403            | 84.1           |
| 2b  | 406.2          | 490.4          | 45   | 0.52 | 391            | 84.2           |
| 2c  | 409.4          | 491.2          | 39   | 0.39 | 388            | 81.8           |
| 2d  | 409.4          | 494.3          | 41   | 0.50 | 402            | 85.2           |
| 2e  | 421.8          | 510.4<sup>i</sup> | 42   | 0.40 | 407            | 88.6           |
| 4a  | 384.0          | 447.7          | 23   | 0.62 | 1.453          | 63.7           |
| 4b  | 432.2          | 528.8          | 42   | 0.47 | 2.496          | 96.6           |

<sup>a</sup> Absorption maximum in nanometers.  
<sup>b</sup> Fluorescence maximum in nanometers.  
<sup>c</sup> Molar absorptivity.  
<sup>d</sup> Fluorescence quantum yield.  
<sup>e</sup> Fluorescence lifetime in nanoseconds.  
<sup>f</sup> Stokes’ shift (referred to total maxima) in electronvolts.  
<sup>i</sup> Second maximum (I<sub>rel</sub> = 0.97) for comparison.

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

![Diagram](https://placeHolder.com/diagram.png)

Figure 4. Dynamic process for the increase of Stokes’ shifts of the bisketones 2. The light absorption (hν) of the helical ground state (S₀) forms the electronically excited and geometrically disfavored state S₁ in a vertical process. Relaxation to the planar conjugated S₁ allows a bathochromically shifted fluorescence (hν’) to the electronic ground-state S₀’, finally reaching the initially state S₀.

Figure 5. Crystal structure of terthiophenediyl 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).

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 persistence 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 bioimaging.

### 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 CD2Cl2 (residual chloroform: δ = 5.32 ppm for 1H NMR and δ = 54.00 ppm for 13C [1H] NMR). Abbreviations for signal multiplet as follows: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sext, sextet; and m, multiplet. Infrared spectra were measured neat [attenuated total reflection (ATR), Striker 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·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 SiO2 (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). Elemental analyses were determined by 1H NMR (200 MHz, CD2Cl2): δ = 7.27 (dd, J = 5.0 Hz, J = 1.1 Hz, 2H), 7.22 (dd, J = 3.6 Hz, J = 1.1 Hz, 2H), 7.12 (s, 2H), 7.05 ppm (dd, J = 5.0 Hz, J = 3.6 Hz, 2H). 13C NMR (150 MHz, CDCl3): δ = 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, C$_2$H$_4$S$_2$): m/z = calc 247.9788, found 247.9765, Δ = −0.3 mmu. Elemental analysis C$_2$H$_4$S$_2$ (248.4 g mol$^{-1}$): calc 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)

1,1'-[(2,2':5',2''-Terthiophene)-5,5''-diyl]bis(2,2-dimethylpropan-1-one) (2a) (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 × 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 (CHCl3/iso-hexane 2:1): 0.80. IR (ATR, KBr): 2977, 2938, 2877, 1655 (s), 1507, 1412, 1378, 1354, 1254, 1221, 1086, 1060, 912, 882, 854, 787 (vs), 744, 724, 666 cm$^{-1}$. 1H NMR (200 MHz, CDCl3): δ = 7.27 (dd, J = 5.0 Hz, J = 1.1 Hz, 2H), 7.22 (dd, J = 3.6 Hz, J = 1.1 Hz, 2H), 7.12 (s, 2H), 7.05 ppm (dd, J = 5.0 Hz, J = 3.6 Hz, 2H). 13C NMR (150 MHz, CDCl3): δ = 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, C$_2$H$_4$S$_2$): m/z = calc 247.9788, found 247.9765, Δ = −0.3 mmu. Elemental analysis C$_2$H$_4$S$_2$ (248.4 g mol$^{-1}$): calc C: 58.03, H: 3.25, S: 38.72; found C: 57.81, H: 3.49, S: 38.98.
NMR (400 MHz, CD3Cl2): δ = 7.63 (d, J = 4.0 Hz, 2H), 7.29 (s, 2H), 7.24 (d, J = 4.0 Hz, 2H), 2.92 (q, J = 7.3 Hz, 4H), 1.21 ppm (t, J = 7.3 Hz, 6H). 13C NMR (100 MHz, CD3Cl2): δ = 133.0, 127.0, 125.2, 32.7, 8.8 ppm. UV/vis (CHCl3): λmax (ε) = 406.2 nm (45,300). Fluorescence (CHCl3): λmax (Irel) = 463.3 (0.91), 490.4 nm (1.00). Fluorescence quantum yield (CHCl3): λrel = 0.042, reference: tetramethyl perylene-3,4,9,10-tetracarboclylate with Φ = 1.00): 0.52. MS (70 eV, EI): m/z (%) = 360 (85) [M+], 331 (100) [M+ - C2H3], 303 (16) [M+ - C2H5O], 259 (42). HRMS (EI, C26H16O2S3): m/z = calcld 463.0314, found 463.0312, Δ = +0.2 mmu. Elemental analysis C26H16O2S3 (456.6 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/isoo-hexane 2:1), filtered through neutral alumina, and evaporated. Yield 89.6 mg (86%), m.p. 208 °C. R-value (CHCl3/isoo-hexane 1:1): 0.50. IR (ATR): δ = 2960, 2929, 2872, 1655, 1507, 1464, 1445, 1409, 1380, 1347, 1306, 1289, 1253, 1211 (s), 1113, 1077, 1067, 1038, 957, 801, 788, 566, 717, 792 (s), 757, 749, 674 cm−1. 1H NMR (400 MHz, CD3Cl2): δ = 7.62 (d, J = 4.0 Hz, 2H), 9.29 (s, 2H), 7.24 (d, J = 4.0 Hz, 2H), 2.86 (t, J = 7.3 Hz, 4H), 1.76 (b, J = 7.4 Hz, 4H), 1.00 ppm (t, J = 7.4 Hz, 6H). 13C NMR (100 MHz, CD3Cl2): 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): λmax (ε) = 409.4 nm (34,700). Fluorescence (CHCl3): λmax (Irel) = 464.2 (0.98), 491.2 nm (1.00). Fluorescence quantum yield (CHCl3): λrel = 0.042, reference: tetramethyl perylene-3,4,9,10-tetracarboclylate with Φ = 1.00): 0.71. MS (70 eV, EI): m/z = 416.02 [M+], 374.00 [M+ - C2H3], 319.98 [M+ - C2H5], 316.97 [M+ - C2H4S], HRMS (EI, C26H16O2S3): m/z = calcld 416.0933, found 416.0934, Δ = +0.1 mmu.

1,1′-[(2,2′:5′,2′′-Terthiophene)-5,5′-diyl]bis(phenylmethane) (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/isoo-hexane 2:1), filtered through neutral alumina, and evaporated. Yield 89 mg (78%), m.p. 218 °C. R-value (CHCl3/isoo-hexane 2:1): 0.75. IR (ATR): δ = 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 (400 MHz, CD3Cl2): δ = 7.86 (dd, J = 8.3 Hz, J = 1.3 Hz, 4H, p-H), 7.56 – 7.61 (m, 2H, m-H), 7.58 (d, J = 4.0 Hz, 2H), 7.54 (t, J = 7.6 Hz, 4H, m-H), 7.37 (s, 2H), 7.30 ppm (d, J = 4.0 Hz, 2H). 13C NMR (150 MHz, CD3Cl2): δ = 180.0, 145.4, 143.0, 138.5, 137.7, 136.3, 132.9, 129.5, 121.7, 128.1 ppm. UV/vis (CHCl3): λmax (ε) = 421.8 nm (42,400). Fluorescence (CHCl3): λmax (Irel) = 484.3 (1.00), 510.6 nm (0.97). Fluorescence quantum yield (CHCl3): λrel = 0.007, reference: tetramethyl perylene-3,4,9,10-tetracarboclylate with Φ = 1.00): 0.40. MS (70 eV, EI): m/z (%) = 456 (100) [M+], 379 (14) [M+ - C6H5], 351 (7) [M+ - C5H5O]. HRMS (EI, C20H16O2S3): m/z = calcld 456.0312, found 456.0308, Δ = −0.4 mmu. Elemental analysis C20H16O2S3 (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-heptafluorobutan-1-one (4a). 2,2′-Bithiophene (41.6 mg, 0.250 mmol) was dissolved in anhydrous carbon disulfide (1.0 mL) in a dry
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**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/isoo-hexane 3:1), filtered through neutral alumina, and evaporated. Yield 27.2 mg (30%), m.p. 58 °C.

**1H NMR (400 MHz, CD2Cl2):** δ = 7.91–7.88 (m, 1H), 7.48–7.47 (m, 2H), 7.31 (d, J = 4.2 Hz, 1H), 7.14–7.12 ppm (m, 1H). 13C NMR (100 MHz, CD2Cl2): δ = 151.6, 138.9, 136.3, 129.3, 129.5, 128.2, 126.2 ppm. 19F NMR (376 MHz, CD2Cl2): δ = −108.67 (t, J = 9.1 Hz, 1H), −115.66 until −115.83 (m, 83.16 ppm). UV/vis (CHCl3): λmax (λf) = 443.2 nm (420,200). Fluorescence (CH2Cl2): λmax = 432.2 nm. Fluorescence quantum yield (CHCl3): Φf = 0.47. MS (70 eV, EI): [M+], 329.95, 193.04 [M+].

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