NJC

Cite this: *New J. Chem.*, 2012, **36**, 768–773

www.rsc.org/njc

PAPER

Thiophene-substituted aza-bodipy as a strategic synthon for the design of near-infrared dyes†

Quentin Bellier,[a] Fabrice Dalier,[a] Erwann Jeanneau,[b] Olivier Maury*[a] and Chantal Andraud*[a]

Received (in Montpellier, France) 7th November 2011, Accepted 13th December 2011
DOI: 10.1039/c2nj20943h

Original aza-bodipy dyes functionalised by thiophene moieties in 3,5 or 1,7 positions were prepared and characterised by X-ray crystallography. The 3,5 substituted compound **3** exhibits promising photophysical properties red-shifted in the NIR spectral range. Furthermore, the presence of bromide atoms has allowed π-conjugated skeleton extension *via* Sonogashira cross-coupling.

Introduction

The research for chromophores absorbing and/or emitting in the near-infrared (NIR) spectral range is of growing interest for various applications ranging from materials science to biology and medicine.[1] Among the various NIR chromophore families, boron-dipyrromethene and its sub-class aza-boron-dipyrromethene experienced a tremendous development due to their exceptional photophysical properties, high photostability and very versatile structure.[2] In few years, these monomethine cyanine analogues were designed for NIR applications like photovoltaics,[3a] organic light emitting diodes, advanced optoelectronics,[3b] nonlinear optics,[3c–e] bioimaging or sensing[3f–g] and photodynamic therapy…[3h–j]

The ubiquitous utilisation of these dyes prompted chemists to find new strategies for shifting their photophysical properties farther and farther in the red conserving the luminescence quantum yield efficiency. As example, absorption and emission red-shift can be achieved by: (i) the replacement of the C-*meso* atom by an N atom;[4] (ii) the extension of the conjugated skeleton and/or substitution of the central bodipy core by electron-donating moieties resulting in the induction of a charge transfer contribution in the lowest energy transition;[5] (iii) annulation of benzo ring to the pyrrole;[6] (iv) rigidification of the chromophore π-skeleton either by annulation[7a,b] or by formation of intramolecular B–O six member rings.[7c] These various strategies have allowed the design of chromophores absorbing and emitting in the NIR as illustrated by the aza-bodipy dyes **1** and **5** (Chart 1 and Table 1).[3c,5c] Thanks to an important internal charge transfer, chromophore **5** presents red-shifted linear properties combined with remarkable non-linear optical properties, *e.g.* an optical limiter behaviour at

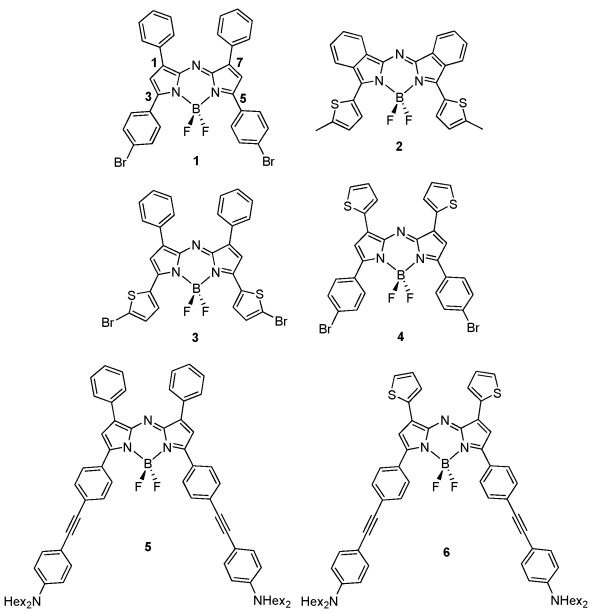


Chart 1 Benchmark aza-bodipy (**1**, **5**) and thiophene containing aza-bodipy dyes (**2**, **3**, **4**, **6**).

Table 1 Spectroscopic data in diluted solution

Dye	λ_{abs}/nm	λ_{em}/nm	ε/L mol^{-1} cm^{-1}	$\omega_{1/2}$/cm^{-1}	τ/ns	Φ^a
1[b]	658	687	90 000	1270	1.4	0.15
3[b]	735	751	111 000	770	3.1	0.19
4[b]	694	729	82 000	1690	0.8	0.04
5[c]	740	804	60 000	2850	0.7	0.04
6[c]	760	818	57 000	3110	0.7	0.02

[a] Aza-bodipy substituted by methoxyphenyl in positions 3/5 as reference[3h,14] ($CHCl_3$, Φ = 0.36). [b] In dichloromethane solution. [c] In toluene solution.

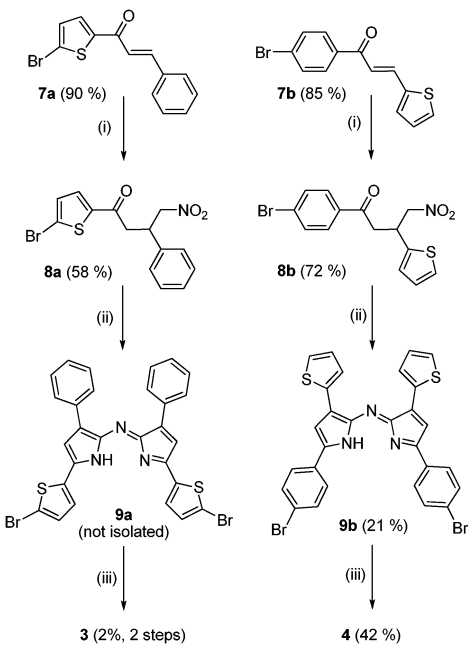
[a] *Laboratoire de Chimie CNRS—Ecole Normale Supérieure de Lyon- Université de Lyon 1, 46 allée d'Italie, Lyon 69007, France. E-mail: chantal.andraud@ens-lyon.fr, olivier.maury@ens-lyon.fr*
[b] *Centre de Diffractométrie Henri Longchambon, ICL, Université Claude Bernard Lyon1, 69622 Villeurbanne Cedex, France*

† Electronic supplementary information (ESI) available: Crystallographic data. CCDC reference number 836074 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2nj20943h

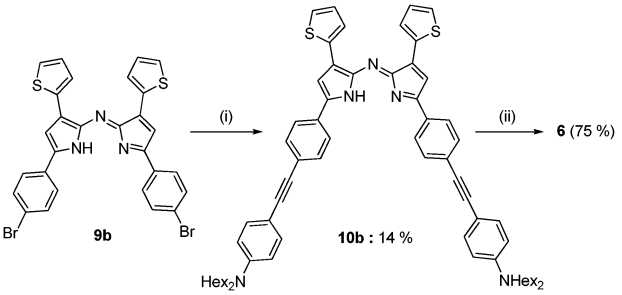
telecommunication wavelengths.[3c] In addition, it has been demonstrated that an additional red-shift can be achieved by substitution of the (aza)-bodipy core by thiophenyl moieties as illustrated by the recent reports of Goeb and Ziessel[8] and Gresser *et al.*[9] for fused-bodipy or fused-azabodipy (**2**) reaching 780 nm (ϕ = 0.20) and 840 nm (ϕ not reported) in emission, respectively. Using a similar approach, we report here the synthesis, characterisation, X-ray structure and photophysical properties of original aza-bodipy dyes substituted by thiophene units either in the 3,5 (**3**) or 1,7 (**4**) positions (Chart 1). It is worth noting that during the redaction of this article, Hartmann and co-workers published the synthesis, the electrochemical and photophysical properties of similar thiophene-substituted aza-bodipy dyes.[10] Furthermore, the presence of additional bromide atoms allows the extension of the π-skeleton using Pd-catalyzed cross-coupling reaction and induction of additional charge-transfer character into the dye. As a preliminary example, we describe the synthesis of chromophore **6** (Chart 1) that merges the two aforementioned strategies to red-shift the photophysical properties: substitutions by thiophene in 1,7 positions and by dialkylaminophenylethynyl moieties in 3,5 positions.

Results and discussion

The synthesis of the target compounds **3**, **4** (Scheme 1) used the classical O'Shea's procedure[3h] involving the formation of chalcone **7a**,**b** followed by the addition of nitromethane leading to the formation of **8a**,**b** in good yield (52 and 72%, respectively). The formation of aza-dipyrromethene **9a**,**b** remains very problematic and is accompanied by many unidentified side-products. Only **9b** could be isolated after precipitation in acceptable 21% yield, leading to the formation of **4** (42% yield) upon reaction with $BF_3{\cdot}Et_2O$ in the presence of Hünig's base.



Scheme 1 Synthesis of the target compounds **3** and **4**. (i) CH_3NO_2, $HNEt_2$ MeOH, reflux; (ii) NH_4OAc, dry BuOH, reflux; (iii) $BF_3{\cdot}Et_2O$, $^iPr_2EtN$, dry CH_2Cl_2, RT.



Scheme 2 Synthesis of the target compound **6**. (i) 4-Ethynyl-*N*,*N*-dihexylaniline, $Pd(PPh_3)_4$, Et_3N, THF, reflux; (ii) $BF_3{\cdot}Et_2O$, $^iPr_2EtN$, dry CH_2Cl_2, RT.

On the other hand, **9a** could not be isolated and was directly engaged in the borylation step allowing the isolation of the desired product **3** in only 2% yield over the two steps after column chromatography.

The synthesis of chromophore **6**, featuring an extended π-conjugated skeleton, involves a copper-free Sonogashira cross-coupling using $Pd(PPh_3)_4$ as catalyst between **9b** and a 4-ethynyl-*N*,*N*-dihexylaniline donor, followed by classical complexation with $BF_3{\cdot}Et_2O$ (Scheme 2). It is worth noting that, contrarily to *C*-bodipy analogues,[11] Pd-catalyzed cross-coupling reaction results in the loss of a BF_2 fragment[5c,12] and therefore aza-dipyrromethene intermediates are used as starting materials.

All compounds and intermediates were fully characterized by NMR spectroscopy and high resolution mass spectrometry (see ESI† for experimental details). Crystals suitable for X-ray diffraction analysis were obtained for **3** by diffusion of diethyl-ether into a dichloromethane solution (Fig. 1 and ESI†). The asymmetric unit is composed of two independent molecules (Z' = 2) which form a three-dimensional framework through π–π, C–H···π, C–Br···π and C–H···F interactions. These two independent molecules display similar structural parameters and for clarity only one will be described.

At the molecular level, the structure is similar to other already described aza-boron-dipyrromethene dyes: the two central pyrrolic rings fused by a BF_2 fragment are completely planar and the aryl peripheral substituents are slightly twisted. For **3**, the average twist angle of the thienyl substituent in the 3,5 positions $\varphi_{3,5}$(Th) is about 10°. It is worth noting that this latter value is significantly lower compared to the twist angle

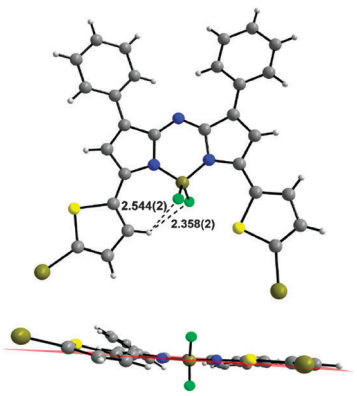


Fig. 1 X-Ray structure of **3** showing H–F distances.

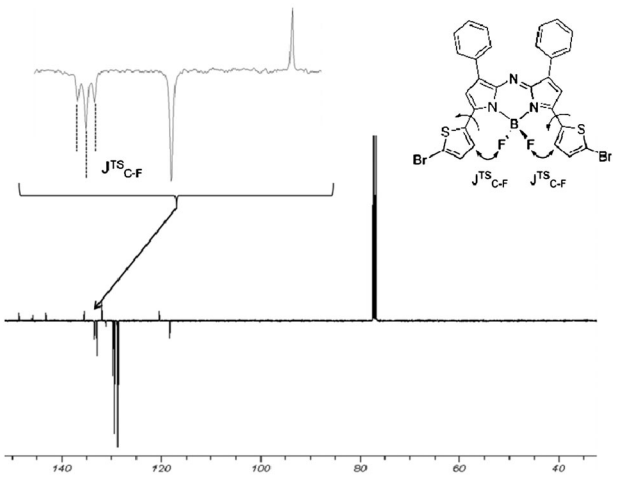


Fig. 2 JMOD ^{13}C NMR (125.75 MHz, $CDCl_3$) of **3**.

of tetraphenyl substituted aza-bodipy dyes reported in the literature where $\varphi_{3,5}$(Ph) is generally between 30–40°.[3h,5c] This flattening of the structure is attributable to the less sterically demanding five members thienyl ring compared to the six members phenyl one. The bond lengths are very classical for this type of structures and the already observed intramolecular interaction between the two fluorine atoms of the BF_2 moiety and the *ortho*-protons of the thienyl ring is also present in **3** with distances about 2.4 Å slightly shorter but in the same range than that observed with phenyl (2.5–2.7 Å).[5c]

Interestingly, this C–H···F interaction is also observed for **3** by $^{13}C\{^1H\}$JMOD NMR where the signal assigned to the *ortho*-carbon atom of the thiophene (δ: 133.5 ppm) appears as a well resolved triplet (Fig. 2) due to the through space coupling with the two fluorine atoms with a coupling constant J^{TS}_{C-F} = 7.3 Hz.[13] This coupling constant is intermediate between that observed for 3,5 phenyl substituted aza-bodipy described in this article like **4** (J^{TS}_{C-F} = 4.0 Hz) or **6** (J^{TS}_{C-F} = 4.5 Hz) or in the literature (average J^{TS}_{C-F} about 4 Hz)[5c] featuring a $\varphi_{3,5}$(Ph) value of about 30–40° and that of the rigidified dimethylene annulated bodipy reported by Burgess J^{TS}_{C-F} = 12 Hz.[13a] Therefore, in this class of chromophores, the J^{TS}_{C-F} coupling constant seems to be strongly correlated to the twist angle between the 3,5 substituted aryl group and the central bodipy core, both allowing the estimation of the planarity of the conjugated skeleton.

The spectroscopic properties, measured in diluted solution, are reported in Fig. 3 and Table 1 and are discussed *versus* the benchmark dyes **1** and **5**.[3c,5c] Substitution by thiophene in the 3,5 or in 1,7 positions (**3** and **4**) involves a significant bathochromic shift compared to **1**, both in absorption (735 and 694 nm, respectively) and in emission (751 and 729 nm, respectively). The thiophene is an electron rich heterocycle and consequently acts as a donor group inducing a charge transfer contribution in the lower energy transition. As a result, the absorption band of **4** is relatively broad for an aza-bodipy dye ($\omega_{1/2}$(**4**) = 1690 cm^{-1} compared to $\omega_{1/2}$(**1**) = 1270 cm^{-1}) and the Stokes shift is larger (about 690 cm^{-1}). However, **4** presents very low quantum yield (0.04) and lifetime (0.8 ns) compared to **1** and is not competitive for any fluorescence based applications. On the other hand, compound **3** presents

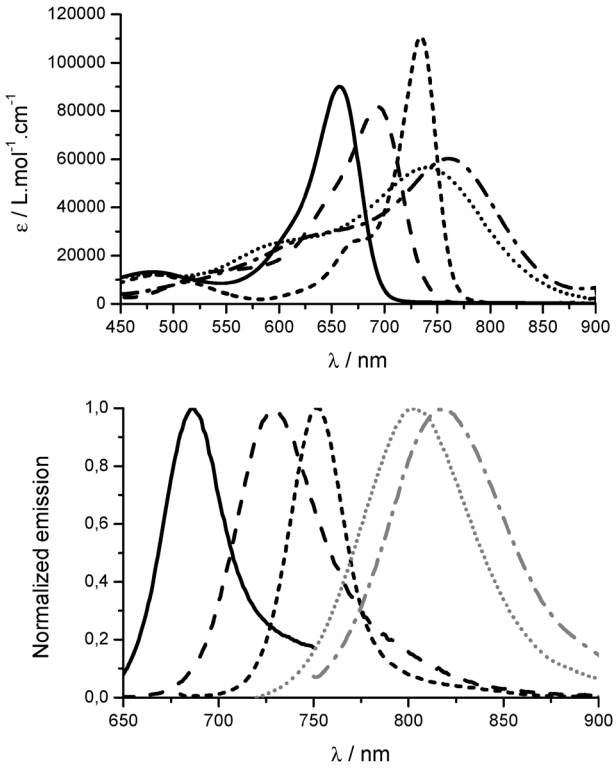


Fig. 3 Absorption (up) and emission (bottom) spectra of **1** (—), **3** (- -), **4** (––), **5** (···) and **6** (-·-) in dichloromethane (black) and toluene (gray) solution.

a very different behaviour: it conserves a significant fluorescence quantum yield of 0.2 and a long lifetime of 3.1 ns possibly because of the reduced non-radiative losses due to rigidification of the π-skeleton induced by the C–H···F interactions.[5c] More surprisingly, this compound exhibits an almost pure "extended cyanine" character[15] with a very sharp absorption transition ($\omega_{1/2}$(**3**) = 770 cm^{-1}) and a rather small Stokes shift (289 cm^{-1}). These photophysical results are in agreement with the recent ones reported for a related compound featuring no bromine substitution.[10] In our case, the presence of bromine results in an almost twice lower quantum yield efficiency, a phenomenon that could be ascribed to the heavy atom effect favouring nonradiative deexcitation pathways. Finally, the functionalisation by an extended π-conjugated donor group in positions 3,5 provokes a pronounced red-shift in absorption of 80 and 65 nm for molecules **5** and **6**, respectively, compared to the unsubstituted compounds **1** and **4**. This shift is accompanied by an important broadening of the lower energy absorption band ($\omega_{1/2}$(**5**) = 2850 cm^{-1} and $\omega_{1/2}$(**6**) = 3110 cm^{-1}) due to the induction of an additional strong charge transfer character from the dialkylamino-donor to the accepting aza-bodipy core.[16] It is worth noting that the contribution of a thiophene group in positions 3,5 to the optical properties is conserved for chromophore **6**, which presents a more pronounced red-shift of 20 nm compared to **5**. Whereas no emission is detected in dichloromethane solution, compounds **5** and **6** show in a less polar solvent, such as toluene, a weak emission strongly shifted into the NIR spectral range, with wavelength maxima at 804 and 818 nm, respectively (Fig. 3).

Conclusion

The synthesis, X-ray structure and photophysical characterization of original thiophene-functionalised aza-bodipy dyes are reported. Compound **4**, substituted in the 1,7 position, exhibits very poor spectroscopic properties. On the other hand, derivative **3**, substituted in the 3,5 position, presents red-shifted absorption and emission properties with an acceptable quantum yield efficiency. This thiophene substitution combines an increased electron-donating effect, a less steric hindrance with stronger C–H···F interactions, compared to the phenyl one which explains its interesting spectroscopic properties. Finally the incorporation of electron-donating moieties as aniline in 3,5 positions thanks to the bromine functionalisation was accomplished successfully. The resulting compound **6** presents absorption and emission largely shifted into the near infra-red spectral range. Furthermore, the presence of thiophene in positions 1,7 as a secondary donor opens interesting perspective for the optimization of non-linear optical properties like two-photon absorption at telecommunication wavelengths.[3c]

Experimental

Methods

NMR spectra (^{1}H, ^{13}C) were recorded at room temperature on a BRUKER AC 200 operating at 200.13 MHz and 50.33 MHz for ^{1}H and ^{13}C, respectively, and on a VARIAN Unity Plus operating at 500.10 MHZ and 125.75 MHz for ^{1}H and ^{13}C, respectively. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (^{1}H, ^{13}C), residual solvent peaks being used as internal standard ($CHCl_3$ ^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm). UV-visible spectra were recorded on a Jasco V-550 spectrophotometer in diluted dichloromethane solution (*ca.* 10^{-6} mol L^{-1}). The luminescence spectra were measured using a Horiba-JobinYvon Fluorolog-3® spectrofluorimeter, equipped with a three slit double grating excitation and emission monochromator with dispersions of 2.1 nm mm^{-1} (1200 grooves mm^{-1}). The steady-state luminescence was excited by unpolarized light from a 450 W xenon CW lamp and detected at an angle of 90° for diluted solution measurements by a Peltier-cooled red-sensitive Hamamatsu R2658P photomultiplier tube (300–1010 nm). High resolution mass spectrometry measurements and elemental analysis were performed at the Service Central d'Analayse du CNRS (Vernaison, France). Column chromatography was performed on a Merck Gerduran 60 (40–63 μm) silica.

Syntheses

7a. 2-Acetyl-5-bromothiophene (2.50 g, 12.2 mmol, 1 eq.) and benzaldehyde (1.54 g, 14.6 mmol, 1.5 mL, 1.2 eq.) were dissolved in methanol (150 mL). An aqueous potassium hydroxide solution (100 mL, 2.5 M) was added dropwise at 0 °C. Then the solution was stirred at room temperature overnight. During the course of the reaction, the product precipitated from the reaction mixture. After cooling down to 0 °C, the reaction mixture was filtered off and the resulting solid was washed with pentane to yield product **7a** as a light yellow solid (3.18 g, 90%). ^{1}H-NMR (200.13 MHz, $CDCl_3$): δ 7.85 (d, $^3J_{trans}$ = 16 Hz, 1H), 7.66-7.59 (m, 3H), 7.44-7.41 (m, 3H), 7.31 (d, $^3J_{trans}$ = 16 Hz, 1H), 7.16 (d, 1H, ^3J = 4.0 Hz). ^{13}C-NMR (50.33 MHz, $CDCl_3$): δ 181.0, 147.2, 144.8, 134.6, 131.9, 131.5, 130.9, 129.1, 128.7, 123.0, 120.6.

HRMS (ES+) calcd. for $[M + Na]^+$: 314.9455. Found: 314.9456.

Anal. calcd. for $C_{13}H_9BrOS\cdot(H_2O)_{0.5}$: C, 51.67; H, 3.34%. Found: C, 51.48; H, 3.01%.

7b. Thiophene-2-carboxaldehyde (3.36 g, 2.8 mL, 30 mmol, 1.2 eq.) and 4-bromoacetophenone (5.0 g, 25.1 mmol, 1 eq.) were dissolved in methanol (150 mL). An aqueous potassium hydroxide solution (100 mL, 2.5 M) was added dropwise at 0 °C. Then the solution was stirred at room temperature overnight. During the course of the reaction, the product precipitated from the reaction mixture. After cooling down to 0 °C, the reaction mixture was filtrated off and the resulting solid was washed with pentane. The crude product was recrystallized in ethanol to yield product **7b** as a yellow solid (6.20 g, 85%). ^{1}H-NMR (200.13 MHz, $CDCl_3$): δ 7.95 (d, $^3J_{trans}$ = 15 Hz, 1H), 7.87 (d, ^3J = 8.5 Hz, 2H), 7.64 (d, ^3J = 8.5 Hz, 2H), 7.44 (d, ^3J = 5 Hz, 1H), 7.37 (d, ^3J = 3.5 Hz, 1H), 7.27 (d, $^3J_{trans}$ = 15 Hz, 1H), 7.10 (dd, ^3J = 5 Hz and ^3J = 3.5 Hz, 1H). ^{13}C-NMR (50.33 MHz, $CDCl_3$): δ 188.8, 140.3, 137.9, 137.0, 132.5, 132.1, 130.1, 129.3, 128.6, 128.0, 120.3. HRMS (ES+) calcd. for $[M + H]^+$: 292.9636. Found: 292.9625. Anal. calcd. for $C_{13}H_9BrOS$: C, 53.26; H, 3.09%. Found: C, 52.81; H, 3.08%.

8a. **7a** (2.96 g, 10.1 mmol, 1 eq.), nitromethane (3.08 g, 2.8 mL, 50 mmol, 5 eq.) and diethylamine (3.69 g, 5.2 mL, 50 mmol, 5 eq.) were dissolved in methanol (60 mL) and heated under reflux overnight. After cooling down to 0 °C, the solution was quenched with an aqueous solution of hydrochloric acid (75 mL, 2.5 M) until pH = 2/3. During the course of the quenching, the product precipitated. The reaction mixture was filtrated off and the resulting solid was washed with pentane. The crude product was recrystallized in methanol to yield product **8a** as a white solid (2.04 g, 58%). ^{1}H-NMR (200.13 MHz, $CDCl_3$): δ 7.42 (d, ^3J = 4 Hz, 1H), 7.35-7.29 (m, 5H), 7.09 (d, ^3J = 4 Hz, 1H), 4.80 (dd, J_{gem} = 12.5 Hz and ^3J = 7 Hz, 1H), 4.70 (dd, J_{gem} = 12.5 Hz and ^3J = 7 Hz, 1H), 4.16 (q, ^3J = 7 Hz, 1H), 3.30 (d, ^3J = 7 Hz, 2H).

^{13}C-NMR (50.33 MHz, $CDCl_3$): δ 188.8, 145.1, 138.7, 132.5, 131.5, 129.3, 128.2, 127.5, 123.7, 79.5, 41.6, 39.6. HRMS (ES+) calcd. for $[M + Na]^+$: 375.9619. Found: 375.9632. Anal. calcd. for $C_{14}H_{12}BrNO_3S$: C, 47.47; H, 3.41; N, 3.95%. Found: C, 46.99; H, 3.39; N, 3.83%.

8b. **7b** (6 g, 20.5 mmol, 1 eq.), nitromethane (6.25 g, 5.6 mL, 0.102 mol, 5 eq.) and diethylamine (7.48 g, 10.5 mL, 0.102 mol, 5 eq.) were dissolved in methanol (120 mL) and heated under reflux overnight. After cooling down to 0 °C, the solution was quenched with an aqueous solution of hydrochloric acid (200 mL, 2.5 M) until pH = 2/3. Methanol was evaporated and then by dissolving the crude product with dichloromethane, the solution was washed with water and brine. The organic layer was dried over sodium sulfate and the solvents were evaporated. The crude residue was purified by flash chromatography on silica gel (1 : 5 ether : petroleum ether) to afford a yellow oil **8b** (5.23 g, 72%). ^{1}H-NMR

(200.13 MHz, $CDCl_3$): δ 7.80 (d, ^3J = 8.5 Hz, 2H), 7.61 (d, ^3J = 8.5 Hz, 2H), 7.21 (dd, ^3J = 4 Hz, ^4J = 1.5 Hz, 1H), 6.96-6.92 (m, 2H), 4.82 (dd, J_{gem} = 12.5 Hz and ^3J = 7 Hz, 1H), 4.72 (dd, J_{gem} = 12.5 Hz and ^3J = 7 Hz, 1H), 4.53 (q, ^3J = 7 Hz, 1H), 3.47 (d, ^3J = 7 Hz, 2H). ^{13}C-NMR (50.33 MHz, $CDCl_3$): δ 195.4, 141.7, 134.8, 131.9, 129.4, 128.7, 127.1, 125.6, 124.7, 79.7, 42.1, 34.5. HRMS (ES+) calcd. for $[M + Na]^+$: 375.9619. Found: 375.9612. Anal. calcd. for $C_{14}H_{12}BrNO_3S$: C, 47.47; H, 3.41; N, 3.95%. Found: C, 47.57; H, 3.34; N, 4.01%.

9b. In a Schlenk vessel, ammonium acetate was sublimated under vacuum (7.6 g, 98 mmol, 35 eq.), **8b** (1 g, 2.82 mmol, 1 eq.) and anhydrous butanol (20 mL) were added under argon. The solution was heated under reflux for 24 h. The reaction mixture was cooled down to room temperature. The solvent was concentrated to half and filtered. The isolated solid was washed with pentane to yield product **9b** as a blue solid (0.196 g, 21%). ^{1}H-NMR (200.13 MHz, CD_2Cl_2): δ 7.85 (d, ^3J = 3 Hz, 2H), 7.78 (d, ^3J = 8.5 Hz, 4H), 7.66 (d, ^3J = 8.5 Hz, 4H), 7.48 (d, ^3J = 5 Hz, 2H), 7.18 (dd, ^3J = 5 Hz and ^3J = 3 Hz, 2H), 7.09 (s, 2H). ^{13}C NMR (125.75 MHz, CD_2Cl_2): δ 155.3, 150.1, 138.0, 136.4, 133.2, 131.6, 128.9, 128.74, 128.66, 128.6, 125.4, 114.0. HRMS (ES+) calcd. for $[M + H]^+$: 619.9465. Found: 619.9458.

3. In a Schlenk vessel, ammonium acetate was sublimated under vacuum (7.6 g, 98 mmol, 35 eq.), **8a** (1 g, 2.82 mmol, 1 eq.) and anhydrous butanol (20 mL) were added under argon. The solution was heated under reflux for 24 h. The reaction mixture was cooled down to room temperature. The solvent was concentrated to half and filtered. The isolated solid was washed with pentane to yield the not purified intermediate as a blue solid. The crude (124 mg, 0.20 mmol, 1 eq.) was dissolved in distilled dichloromethane (15 mL) and distilled diisopropylethylamine (259 mg, 0.33 mL, 2.0 mmol, 10 eq.) was added dropwise. The solution was stirred at room temperature for 1 h and then $BF_3{\cdot}Et_2O$ (426 mg, 0.38 mL, 3.0 mmol, 15 eq.) was added. The solution was stirred at room temperature for 48 h under argon and the solution was washed with brine and water. The organic layer was dried over sodium sulfate and the solvent was evaporated. The crude product was purified by chromatography on silica gel (1 : 4 dichloromethane : petroleum ether) to afford a brown solid **3** (20 mg, 2% over the two steps). ^{1}H-NMR (500.10 MHz, $CDCl_3$): δ 8.04-8.01 (m, 6H), 7.47-7.42 (m, 6H), 7.22 (d, ^3J = 4 Hz, 2H), 7.08 (s, 2H). ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 148.6, 145.9, 143.2, 135.6, 133.5 (t, J^{TS}_{C-F} = 7.5 Hz), 132.9, 132.1, 129.8, 129.4, 128.8, 120.5, 118.4. HRMS (APCI) calcd. for $[M]^+$: 664.9209. Found: 664.9218.

4. **9b** (50 mg, 0.075 mmol, 1 eq.) was dissolved in distilled dichloromethane (5 mL) and distilled diisopropylethylamine (97 mg, 0.12 mL, 0.75 mmol, 10 eq.) was added dropwise. The solution was stirred at room temperature for 1 h and then $BF_3{\cdot}Et_2O$ (160 mg, 0.14 mL, 1.13 mmol, 15 eq.) was added. The solution was stirred at room temperature for 48 h under argon and the solution was washed with brine and water. The organic layer was dried over sodium sulfate and the solvent was evaporated. The crude product was purified by chromatography on silica gel (1 : 4 dichloromethane : petroleum ether) to afford a blue solid **4** (28 mg, 42%). ^{1}H-NMR (500.10 MHz, $CDCl_3$): δ 7.92 (d, ^3J = 4 Hz, 2H), 7.86 (d, ^3J = 8 Hz, 4H), 7.61-7.58 (m, 6H), 7.20 (t, ^3J = 4 Hz, 2H), 6.87 (s, 2H). ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 158.4, 145.3, 138.8, 134.7, 132.1, 131.0 (t, J^{TS}_{C-F} = 4 Hz), 130.9, 130.4, 128.6, 126.0, 116.6. HRMS (APCI) calcd. for $[M]^+$: 664.9209. Found: 664.9220.

10b. Aza-dipyrromethene **9b** (100 mg, 0.16 mmol, 1 eq.) and 4-ethynyl-*N*,*N*-dihexylaniline (138 mg, 0.48 mmol, 3 eq.) were dissolved in a THF/triethylamine mixture (V/V = 2.5/2.5 mL). The solution was degassed three times by a freeze–pump method. Then $Pd(PPh_3)_4$ (20 mg, 0.016 mmol, 0.1 eq.) was added. The dark blue solution was stirred overnight at reflux under argon. After cooling down to room temperature, the reaction mixture was diluted in dichloromethane, washed with saturated aqueous ammonium chloride solution, brine and water, then dried over sodium sulfate and concentrated under vacuum. The crude residue was purified twice by flash chromatography on silica gel (1 : 4 dichloromethane : pentane and 1 : 8 diethyl ether : petroleum ether) to afford **10b** as a blue solid (23 mg, 14%). ^{1}H-NMR (200.13 MHz, $CDCl_3$): δ 7.84-7.80 (m, 6H), 7.59 (d, ^3J = 8 Hz, 4H), 7.43-7.39 (m, 6H), 7.13 (t, ^3J = 4.5 Hz, 2H), 7.05 (s, 2H), 6.60 (d, ^3J = 8.5 Hz, 4H), 3.29 (t, ^3J = 7 Hz, 8H), 1.67-1.51 (m, 8H), 1.40-1.30 (m, 24H), 0.93-0.86 (m, 12H). ^{13}C-NMR (50.33 MHz, $CDCl_3$): δ 154.6, 149.7, 148.3, 137.0, 136.2, 133.3, 131.9, 130.5, 128.0, 127.9, 127.3, 126.5, 126.4, 113.4, 111.4, 108.6, 94.5, 87.8, 51.1, 31.9, 27.4, 27.0, 22.8, 14.2. HRMS (ES+) calcd. for $[M + H]^+$: 1028.5699. Found: 1028.5720.

6. **10b** (23 mg, 0.022 mmol, 1 eq.) was dissolved in distilled dichloromethane (5 mL) and distilled diisopropylethylamine (28 mg, 36 µL, 0.22 mmol, 10 eq.) was added dropwise. The solution was stirred at room temperature for 1 h and then $BF_3{\cdot}Et_2O$ (48 mg, 42 µL, 0.34 mmol, 15 eq.) was added. The solution was stirred at room temperature for one night under argon and the solution was washed with brine and water. The organic layer was dried over sodium sulfate and the solvent was evaporated. The crude product was purified by chromatography on silica gel (1 : 3 dichloromethane : petroleum ether) to afford a blue solid **6** (18 mg, 75%). ^{1}H-NMR (200.13 MHz, $CDCl_3$): δ 8.04 (d, ^3J = 8.5 Hz, 4H), 7.93 (d, ^3J = 3.5 Hz, 2H), 7.59-7.55 (m, 6H), 7.39 (d, ^3J = 8.5 Hz, 4H), 7.20 (t, ^3J = 4.5 Hz, 2H), 6.97 (s, 2H), 6.59 (d, ^3J = 8.5 Hz, 4H), 3.29 (t, ^3J = 7.5 Hz, 8H), 1.70-1.49 (m, 8H), 1.40-1.24 (m, 24H), 0.96-0.85 (m, 12H). ^{13}C-NMR (125.75 MHz, $CDCl_3$): δ 158.3, 148.4, 145.4, 137.9, 134.9, 133.3, 131.4, 130.2, 130.0, 129.71, 129.67 (t, J^{TS}_{C-F} = 4.5 Hz), 128.4, 127.4, 117.0, 111.3, 108.5, 95.1, 88.0, 51.1, 31.9, 27.3, 27.0, 22.8, 14.2. HRMS (ES+) calcd. for $[M]^+$: 664.9209. Found: 664.9220.

Crystallography

X-Ray crystallographic data were collected on a Gemini kappa-geometry diffractometer (Agilent Technologies UK Ltd.) equipped with an Atlas CCD detector and using Cu radiation (λ = 1.5418 Å). Intensities were collected at 100 K by means of CrysalisPro software.[17] Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrysalisPro software. An analytical absorption

correction was applied using the modeled faces of the crystal.[18] The structure was solved by direct methods with SIR97[19] and the least-square refinement on F^2 was achieved with the CRYSTALS software.[20] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all located in a difference map and initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93–0.98 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. Crystal data of **3**: $C_{28}H_{16}BBr_2F_2N_3S_2$, M = 667.19 g mol^{-1}, crystal size: 0.08 × 0.17 × 0.36 mm, monoclinic $P2_1/c$ (No. 14), a = 14.606(1) Å, b = 14.212(1) Å, c = 25.060(2) Å, β = 106.091(7)°, V = 4998.2(7) Å^3, Z = 8, D_c = 1.773 g cm^{-3}, F_{000} = 2640, λ(CuKα) = 1.5418 Å, μ = 6.02 mm^{-1}, T = 110(1) K, 54 285 refl. collected, 8863 unique (R_{int} = 0.073), 8407 gt. with $I > 2\sigma(I)$, R_1 = 0.040, wR_2 = 0.113, GoF = 1.01, ρ_{max} = 0.66 e Å^{-1}, ρ_{min} = −0071 e Å^{-1}. CCDC 836074.

Acknowledgements

We thank F. Albrieux, C. Duchamp, and N. Henriques from the Université de Lyon for assistance and access to the mass spectrometry facility. The authors thank the Direction Générale de l'Armement for a grant to Q.B.

Notes and references

1 (*a*) G. Qian and Z. Y. Wang, *Chem.–Asian J.*, 2010, **5**, 1006; (*b*) A. V. Kulinich and A. A. Ishchenko, *Russ. Chem. Rev. (Engl. Transl.)*, 2009, **78**, 141; (*c*) K. Kiyose, H. Kojima and T. Nagano, *Chem.–Asian J.*, 2008, **3**, 506; (*d*) J. Fabian, H. Nakazumi and M. Matsuoka, *Chem. Rev.*, 1992, **92**, 1197.

2 (*a*) G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem., Int. Ed.*, 2008, **47**, 1184; (*b*) A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891.

3 For selected recent examples, see: (*a*) T. Rousseau, A. Cravino, T. Bura, G. Ulrich, R. Ziessel and J. Roncali, *Chem. Commun.*, 2009, 1673; (*b*) M. T. Whited, P. I. Djurovich, S. T. Roberts, A. C. Durrell, C. W. Schlenker, S. E. Bradforth and M. E. Thompson, *J. Am. Chem. Soc.*, 2011, **133**, 88; (*c*) P.-A. Bouit, K. Kamada, P. Feneyrou, G. Berginc, L. Toupet, O. Maury and C. Andraud, *Adv. Mater.*, 2009, **21**, 1151; (*d*) P. Didier, G. Ulrich, Y. Mely and R. Ziessel, *Org. Biomol. Chem.*, 2009, **7**, 3639; (*e*) Q. Zheng, G. Xu and P. N. Prasad, *Chem.–Eur. J.*, 2008, **14**, 5812; (*f*) J. Murtagh, D. O. Frimannsson and D. F. O'Shea, *Org. Lett.*, 2009, **11**, 5386; (*g*) O. A. Bozdemir, R. Guliyev, O. Buyukcakir, S. Selcuk, S. Kolemene, G. Gulseren, T. Nalbantoglu, H. Boyaci and E. U. Akkaya, *J. Am. Chem. Soc.*, 2010, **132**, 8029; (*h*) A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher and D. F. O'Shea, *J. Am. Chem. Soc.*, 2004, **126**, 10619; (*i*) S. Atilgan, Z. Ekmekci, A. L. Dogan, D. Guc and E. U. Akkaya, *Chem. Commun.*, 2006, 4398; (*j*) S. G. Awuah, J. Polreis, V. Biradar and Y. You, *Org. Lett.*, 2011, **13**, 3884–3887.

4 J. Killoran, L. Allen, J. F. Gallagher, W. M. Gallagher and D. F. O'Shea, *Chem. Commun.*, 2002, 1862.

5 (*a*) Y.-H. Yu, A. B. Descalzo, Z. Shen, H. Röhr, Q. Liu, Y. W. Wang, M. Spieles, Y.-Z. Li, K. Rurack and X.-Z. You, *Chem.–Asian J.*, 2006, **1–2**, 176; (*b*) O. Buyukcakir, O. A. Bozdemir, S. Kolemen, S. Erbas and E. U. Akkaya, *Org. Lett.*, 2009, **11**, 4644; (*c*) Q. Bellier, S. Pegaz, C. Aronica, B. Le Guennic, C. Andraud and O. Maury, *Org. Lett.*, 2011, **13**, 22; (*d*) D. Zhang, V. Martin, I. Garcia-Moreno, A. Costela, M. E. Perez-Ojeda and Y. Xiao, *Phys. Chem. Chem. Phys.*, 2011, **13**, 13026–13033.

6 Z. Shen, H. Röhr, K. Rurack, H. Uno, M. Spieles, B. Schulz, G. Reck and N. Ono, *Chem.–Eur. J.*, 2004, **10**, 4853.

7 (*a*) W. Zhao and E. M. Carreira, *Chem.–Eur. J.*, 2006, **12**, 7254; (*b*) K. Umezawa, Y. Nakamura, H. Makino, D. Citterio and K. Suzuki, *J. Am. Chem. Soc.*, 2008, **130**, 1550; (*c*) A. Loudet, R. Bandichhor, K. Burgess, A. Palma, S. O. McDonell, M. J. Hall and D. F. O'Shea, *Org. Lett.*, 2008, **10**, 4771.

8 S. Goeb and R. Ziessel, *Org. Lett.*, 2007, **9**, 737.

9 R. Gresser, M. Hummert, H. Hartmann, K. Leo and M. Riede, *Chem.–Eur. J.*, 2011, **17**, 2939.

10 R. Gresser, H. Hartmann, M. Wrackmeyer, K. Leo and M. Riede, *Tetrahedron*, 2011, **67**, 7148.

11 for a recent example, see: S. Niu, G. Ullrich, P. Retailleau and R. Ziessel, *Tetrahedron Lett.*, 2011, **52**, 4848.

12 L. Gao, W. Senevirathna and G. Sauve, *Org. Lett.*, 2011, **13**, 5354.

13 (*a*) J. Chen, J. Reibenspies, A. Derecskei-Kovacs and K. Burgess, *Chem. Commun.*, 1999, 2501; (*b*) X. Xie, Y. Yuan, R. Krüger and M. Bröring, *Magn. Reson. Chem.*, 2009, **47**, 1024.

14 P. Batat, M. Cantuel, G. Jonusauskas, L. Scarpantonio, A. Palma, D. F. O'Shea and N. D. McClenaghan, *J. Phys. Chem. A*, 2011, **115**, 14034.

15 P.-A. Bouit, C. Aronica, L. Toupet, B. Le Guennic, C. Andraud and O. Maury, *J. Am. Chem. Soc.*, 2010, **132**, 4328.

16 B. Le Guennic, O. Maury and D. Jacquemin, *Phys. Chem. Chem. Phys.*, 2012, **14**, 157–164.

17 CrysAlisPro, Agilent Technologies, Version 1.171.34.49 (release 20-01-2011 CrysAlis171 .NET) (compiled Jan 20 2011,15:58:25).

18 R. C. Clark and J. S. Reid, *Acta Crystallogr.*, 1995, **A51**, 887.

19 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. Grazia, G. Moliterni, G. Polidori and R. J. Spagna, *Appl. Crystallogr.*, 1999, **32**, 115.

20 P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.