Acetylenic dithiafulvene derived donor $-\pi$ -acceptor dyads: synthesis, electrochemistry and non-linear optical properties[†]

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A selection of donor-acceptor chromophores containing the redox-active dithiafulvene unit about acetylenic and aryl scaffolds has been synthesised. The molecules were studied for their optical, redox and structural properties. Moreover, third-order non-linear optical properties were investigated as a function of molecular structure.

1. Introduction

The design and synthesis of new organic materials with good non-linear optical (NLO) properties has attracted considerable attention in organic chemistry,¹ since such materials are important for the development of high performance electro-optical switching elements for telecommunication and optical information processing. One advantage of organic materials over inorganic crystals is the possibility for fine-tuning the NLO properties for the desired applications. The general structural element for NLO chromophores is a conjugated molecule with donor–acceptor (D–A) substitution.² The successful design of new NLO materials is promoted by systematic investigations where structure–property relationships are established by varying the D and A entities as well as the conjugated spacer unit.

Tetrathiafulvalene (TTF) is a reversible two-electron donor that has found applications in both materials and supramolecular chemistry on account of its unique redox properties.³ Yet the first NLO investigations on TTF D– π –A dyads first appeared in 1997,⁴ focusing on second-order optical non-linearities. We and others have investigated the third-order NLO properties of different extended TTFs, such as bis(1,3-dithiole) polymethine dyes,⁵ alkene- and alkyne-extended TTFs⁶ and pyrrolo-annelated TTFs.⁷ As a continuation of this work, we describe the syntheses and characterisations of new extended TTFs and D– π –A dyads based on acetylenic derivatives of the dithiafulvene donor unit.⁸ These chromophores were investigated for their linear and non-linear optical properties and redox behaviour.



† Electronic supplementary information (ESI) available: Full experimental details and crystallographic data. See http://www.rsc.org/ suppdata/jm/b5/b504124d/ *mbn@kiku.dk

2. Results and discussion

Synthesis

First, acetylene-spaced donor-acceptor dyads were prepared from suitable starting materials, phosphonium salts 1^9 and 2^{10} and the aldehyde 3^{11} (Scheme 1). Thus, deprotonation of 1 and 2, respectively, followed by treatment of each phosphorous ylide with 3 afforded in a Wittig reaction the novel chromophores 4 and 5.

Next, we decided to incorporate the D- π -A dyad 4 into larger scaffolds. As precursors for such target molecules, we chose benzene-extended TTFs with lateral acetylene appendages. The acceptor functionalities are then to be attached in a final step via a suitable cross-coupling reaction at the terminal acetylene positions. The synthesis is depicted in Scheme 2.^{8*a*} In the first step, terephthalaldehyde **6** was treated with lithium triisopropylsilylacetylide generated in situ. The resulting diol 7 was oxidised by PCC to the diketone 8 that was subsequently reacted with two equivalents of the ylide of 1. The outcome of this two-fold Wittig reaction was the benzene-extended TTF derivative 9. Trans-esterification (to enhance solubility) under basic conditions was accomplished by reacting 9 with 1-decanol and potassium carbonate, which afforded the decyl ester 10. Both TTFs 9 and 10 are very stable compounds that were subjected to normal chromatographic work-up and stored at room temperature. Removal of the silyl



Scheme 1 Reagents and conditions: i, $(1 + 3 \rightarrow 4)$ BuⁿLi, THF, -78 °C, 65%; ii, $(2 + 3 \rightarrow 5)$ NEt₃, THF, MeCN, rt, 53%.



Scheme 2 Reagents and conditions: i, triisopropylsilylacetylene, BuⁿLi, THF, -78 °C, 55%; ii, PCC, CH₂Cl₂, rt, 77%; iii, 1, BuⁿLi, THF, -78 °C, 66%; iv, 1-decanol, THF, K₂CO₃, rt, 55%; v, Buⁿ₄F, THF; rt, 76%; vi, (11 \rightarrow 12) phenylacetylene, CuCl, TMEDA, CH₂Cl₂, air, rt, 60%; vii, (11 \rightarrow 13) *p*-iodonitrobenzene, [PdCl₂(PPh₃)₂], CuI, THF, Prⁱ₂NH, rt, 29%. PCC = pyridinium chlorochromate; TMEDA = *N*,*N*,*N*',*N*'-tetramethylethylenediamine.

protecting groups was accomplished with two equivalents of tetrabutylammonium fluoride. This deprotection step was very fast, and the mixture was worked up after only 15 min of stirring at room temperature. After chromatographic purification, TTF **11** containing two terminal acetylene units was obtained. This desilylated compound was rather unstable and decomposed after prolonged standing at room temperature. ¹H NMR spectroscopy confirmed the presence of terminal acetylene protons resonating as a singlet at $\delta_{\rm H}$ 3.76 ppm. Moreover, IR spectroscopy revealed the C–H stretching band at 3307 cm⁻¹.

The compound **11** is a useful building block for further scaffolding. Thus, **11** was treated with an excess of phenylacetylene under oxidative Hay conditions¹² (Scheme 2), *i.e.* employing the CuCl, N,N,N',N'-tetramethylethylenediamine (TMEDA) catalyst system in the presence of oxygen (from the air). This reaction afforded in good yield the extended TTF **12** in which each dithiole ring is in linear conjugation to a phenyl ring *via* a buta-1,3-diynediyl spacer. The *p*-nitrophenyl electron acceptor was incorporated by subjecting **11** to a Pd-catalysed cross-coupling reaction with 4-iodonitrobenzene under Sonogashira conditions¹³ (Scheme 2). This reaction gave TTF **13** that corresponds structurally to two units of D– π -A dyad **4** separated by a *p*-phenylene spacer, except for the different peripheral ester groups.

The acetylenic dithiafulvene **14** (Scheme 3) was earlier successfully employed for the construction of oligoyneextended TTFs *via* sequential Hay coupling reactions.^{6b-d} Subjecting instead **14** to a Sonogashira cross-coupling with 1,4-diiodobenzene (**15**) gave the *p*-diethynylbenzene-extended TTF **16** in good yield.^{8b}

An extended TTF based on three dithiafulvene units was prepared according to Scheme 4. The diacetylenic dithiafulvene $17^{6b,c}$ was subjected to a trans-esterification reaction upon treatment with 1-decanol and potassium carbonate,



Scheme 3 Reagents and conditions: i, [PdCl₂(PPh₃)₂], CuI, THF, Et₃N, rt, 79%.

which afforded the decyl ester 18. Desilylation followed by two-fold cross-coupling with two equivalents of 15 (present in excess) gave 19. This diiodide was subsequently cross-coupled with the acetylenic dithiafulvene 14, which provided the extended tris-dithiafulvene 20. The reaction seemed to proceed almost quantitatively as judged by ¹H NMR spectroscopy after a first crude column chromatographic work-up. However, repeated chromatography to provide pure compound resulted in almost complete decomposition. We managed nevertheless to characterize the unstable compound 20 by ¹H , ¹³C NMR and high-resolution mass spectrometry.

X-Ray crystallography

Single crystals of **4** were grown by slow diffusion of hexane into a CH_2Cl_2 solution and used for X-ray crystal structure analysis (Fig. 1). This analysis revealed that the two halves are both planar and almost co-planar (dihedral angle 8.5° , *cf.* supplementary material). The bond length alternation in the



Scheme 4 Reagents and conditions: i, 1-decanol, THF, K_2CO_3 , rt, 85%; ii, Bu^n_4NF , THF, 0 °C-rt; iii, 15 (excess), $[PdCl_2(PPh_3)_2]$, CuI, THF, Et₃N, rt, 24% (two steps); iv, 14, $[PdCl_2(PPh_3)_2]$, CuI, THF, Et₃N, rt, 97% (not isolated yield).

p-nitrophenyl ring can be expressed by the quinoid character (δr) of the ring defined by¹⁴

$$\delta r = [(a - b) + (c - b)]/2 \approx [(a' - b') + (c' - b')]/2,$$

where *a*, *b* and *c* are defined according to Fig. 2. A relatively small value of $\delta r = 0.027$ Å is obtained, which indicates that little charge transfer (CT) is present in the ground state of **4**. Yet, the quinoid character is more than twice than that of the *p*-NO₂Ph ring of *p*-NO₂C₆H₄-C=C-C₆H₄NH₂ ($\delta r = 0.011$ Å).¹⁴

Electronic absorption spectroscopy

The UV–vis spectral data of the compounds measured in CHCl₃ are listed in Table 1, and spectra of selected compounds are displayed in Fig. 3. Compound 4 shows a strong CT absorption band at λ_{max} 414 nm. For 13, the absorption maximum of this band is red-shifted to λ_{max} 426 nm, and the end-absorption (absorption onset) reaches *ca.* 550 nm (2.3 eV).



Fig. 1 X-Ray crystal structure of **4**. Selected bond lengths (Å) and angles (°): C1–C2 1.382(4), C2–C3 1.368(4), C3–C4 1.407(3), C4–C7 1.427(4), C7–C8 1.198(4), C8–C9 1.402(4), C9–C10 1.352(3), C11–C12 1.346(3), N1–C1 1.462(3), N1–O5 1.226(3), N1–O6 1.234(3), S1–C10 1.747(3), S1–C12 1.748(2); C3–C4–C7 119.8(2), C4–C7–C8 177.6(3), C7–C8–C9 176.1(3), C8–C9–C10 123.7(2).



Fig. 2 Definition of bond lengths for calculation of quinoid character (δr).



Fig. 3 UV-vis absorption spectra in CHCl₃.

This red-shift indicates the existence of some electronic communication across the phenylene spacer. The longest-wavelength absorption maximum of **4** is close to that of the known compound 21^{15} (λ_{max} 412 nm), devoid of the acetylene spacer. In contrast, the longest-wavelength absorption

Table 1 Absorption band maxima and molar extinction coefficients in the UV-vis spectra of compounds in CHCl₃^a

Compound	$\lambda_{\rm max}/{\rm nm} ~(\epsilon/{\rm M}^{-1}{\rm cm}^{-1})$)			
4	292 (14000)	312 (sh, 11400)	414 (22600)		
9	287 (15700)	352 (sh, 21700)	393 (30900)		
10	287 (17100)	350 (sh, 22100)	394 (32900)		
12	260 (sh, 56300)	295 (35000)	326 (33500)	380 (43900)	397 (43600)
13	289 (35500)	386 (42900)	426 (38500)		
16	272 (16100)	396 (49400)	415 (sh, 42900)		
20	250–270 (br)	300 (br)	360 (br sh)	394	415 (sh)
21	256 (12600)	412 (22100)			
^{<i>a</i>} sh = shoulder;	br = broad.				

maximum of TTF 16 (λ_{max} 415 nm, shoulder) is significantly red-shifted relative to that of 9 (λ_{max} 393 nm) and 10 (λ_{max} 394 nm). The π -systems in these three TTFs contain the same number of atoms, but differ in their connectivity. The acetylene moieties are linearly conjugated with the phenylene group in 16 but cross-conjugated with respect hereto in 9 and 10. Bryce and co-workers¹⁶ have shown that cross-ethylenic extended TTFs (dendralenes) are not planar, and UV-vis absorption data revealed poor cross-conjugation in these molecules. In order to elucidate the preferred conformations of 9 and 16, semi-empirical PM3 geometry optimisations were carried out using the Gaussian program package.¹⁷ The conjugated moiety of 16 took a planar conformation whatever the starting geometry for optimisation. In contrast, two energy minima exist for the conjugated moiety of 9. One of these minima corresponds to a planar conformation, whereas the other corresponds to a conformation in which the phenylene spacer is vertical to the two acetylenic dithiafulvene groups. DFT single point energy calculations at the B3LYP/6-31G(d) level reveal that the non-planar conformation is $23.8 \text{ kcal mol}^{-1}$ more stable than the planar conformation. This preferred nonplanar conformation of 9 does not allow for π -electron delocalisation through the entire π -system, which explains the lower wavelength of absorption for this compound as compared to that of 16. The tris-dithiafulvene 20 (expanded dendralene) exhibits almost the same longest-wavelength absorption maxima (λ_{max} 394 nm, followed by shoulder at ca. 415 nm) as the related TTF 16. This result reflects again the less efficient π -electron delocalisation *via* cross-conjugation, here across the central dithiafulvene.

Electrochemistry

The redox properties of the extended TTFs 9, 10, 13 and 16 were examined by cyclic voltammetry (CV) and rotating disk voltammetry (RDV). The redox potentials versus Fc^{+/}/Fc (ferricinium/ferrocene couple) are listed in Table 2. The TTFs 9, 10 and 13 undergo two reversible one-electron oxidation steps separated by 100 mV for 9, 130 mV for 10 and 100 mV for 13, whereas 16 experiences an irreversible two electron oxidation. The single two electron oxidation observed for 16, compared to two well separated one electron transfers for 9, 10 and 13, results from an increasing distance between the two redox centres and a decrease of the electrostatic repulsion between the two generated cations as observed previously with other extended TTFs.⁶ The lack of lateral appendages in 16 may decrease the stability of the generated radical cation and dication. Therefore a fast follow-up chemical reaction occurs, which explains the irreversible behaviour observed during oxidation. Indeed, it has been observed for other benzeneextended TTFs that the lack of substituents on the fulvene double bonds generates rather active species which undergo

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Table 2 Electrochemical data measured in $CH_2Cl_2 + 0.1 M$ Bu''_4NPF_6 . All potentials versus Fc^{++}/Fc . Working electrode: glassycarbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl

	Cyclic voltam	Rotating disk voltammetry			
Compound	E°/V^{a}	$\frac{\Delta E_{\rm p}}{{ m mV}}$	$E_{\rm p}/{\rm V}^b$	$E_{1/2}/V$	Slope / mV
TTF	$-0.08(1 e^{-})$		$+0.40^{\circ}$		
9	$+0.56(1 e^{-})$	80		+0.56	60
	$+0.66(1 e^{-1})$	70		+0.68	60
			-1.83	-1.87	150
			-1.95		
			-2.28		
10	$+0.54 (1 e^{-})$	70		+0.55	75
	$+0.67(1 e^{-1})$	75		+0.71	70
			-2.03	-1.98	100
13	$+0.61 (1 e^{-})$	60		+0.61	60
	+0.71 (1 e ⁻)	60		+0.71	60
	$-1.42(2 e^{-1})$	85		-1.48	85
			-1.92	-1.94	120
16			+0.65 (2 e ⁻) -1.88 (2 e ⁻)	d e	

 ${}^{a} E^{\circ} = (E_{\rm pc} + E_{\rm pa})/2$, where $E_{\rm pc}$ and $E_{\rm pa}$ = cathodic and anodic peak potentials. ${}^{b} E_{\rm p}$ = irreversible peak potential. c Precipitation on electrode. d Electrode inhibition during oxidation. e Spread-out unresolved wave.

further chemical reactions (oligomerization).^{3/,18} The oxidations are shifted to more positive potentials for **13** relative to **9** and **10** owing to the electron-withdrawing properties of the nitrophenyl moieties. The compounds were also reduced electrochemically. Only irreversible electron transfers are observed at any sweep rate, except for **13** which exhibits a reversible two electron reduction centered on the two $p-C_6H_4NO_2$ moieties at a potential of -1.42 V versus Fc^{++/} Fc. The position of this reduction is in agreement with previously studied tetraethynylethene derivatives bearing $p-C_6H_4NO_2$ groups.¹⁹ Since both $p-C_6H_4NO_2$ groups are reduced in a single step, they behave as independent redox centres. From the first oxidation and reduction potentials, an electrochemical HOMO–LUMO gap of 2.0 eV is obtained, while the optical gap is estimated to be 2.3 eV (vide supra).

Third-order NLO properties

The NLO properties of **4**, **13** and **21** were investigated by third harmonic generation (THG) measurements on thin films containing the compounds in a matrix of poly(methyl methacrylate) (PMMA). The Maker fringe patterns were measured at 1064 and 1907 nm. The second hyperpolarisabilities (γ) are listed in Table 3 together with the results published previously

Table 3 Second hyperpolarisabilities ($\langle \gamma \rangle$) of compounds in PMMA films^{*a*}

Compound	$<\gamma>_{1064 \text{ nm}}/10^{-36} \text{ esu}$	$<\gamma>_{1907 \text{ nm}} /10^{-36} \text{ esu}$
4	265	195
13	550	135
21	500	160
22	1400^{b}	1700^{b}
23	1500^{c}	

 a THG measurements at two fundamental wavelengths (1064 and 1907 nm). b Ref. 5. c Ref. 7.

for other dithiafulvene-containing compounds, methine salt 22^5 and pyrrolo-annelated TTF D–A dyad 23,⁷ investigated under the same conditions. The more extended compound 13 exhibits roughly twice as high a γ value as 4 at a fundamental of 1064 nm. In contrast, however, γ decreases at 1907 nm. The optical third-order non-linearities for compounds 4, 13 and 21 are one order of magnitude smaller than those of 22 and 23.



3. Conclusions

With the objective to establish structure–property relationships for acetylenic dithiafulvenes, we have prepared a selection of D– π –A dyads and extended TTFs and elucidated their optical and electrochemical properties. The dyads are interesting building blocks for future construction of larger opto-electronic materials.

4. Experimental

For full experimental details, including synthetic procedures for all new compounds, see the Electronic Supplementary Information(ESI)[†].

Third harmonic generation

The experimental set-up for thin-film THG Maker fringe measurements has previously been described.²⁰

Electrochemistry

The electrochemical experiments were carried out at 20 ± 2 °C in CH₂Cl₂ containing 0.1 M Bu^{*n*}₄NPF₆ in a classical three electrode cell. The working electrode was a glassy carbon disk electrode (3 mm in diameter) used either motionless for CV (0.1 to 10 V s⁻¹) or as rotating-disk electrode for RDV. The counter electrode was a platinum wire and the reference electrode either an aqueous Ag/AgCl electrode or a platinum wire used as pseudo-reference. All potentials are referenced to the ferricinium/ferrocene (Fc⁺⁺/Fc) couple used as an internal standard.

Selected syntheses

1,4-Bis[1-{4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene}-3-triisopropylsilyl-2-propynyl]benzene 9. To a solution of **1** (1.79 g, 3.52 mmol) in dry THF (55 mL) at -78 °C was slowly added Bu^{*n*}Li (1.6 M in hexane, 2.2 mL, 3.5 mmol) under an atmosphere of argon, which resulted in a red solution. Then **8** (789 mg, 1.59 mmol) in dry THF (25 mL) was slowly added. The solution was stirred at -78 °C for 2.5 h, whereupon sat. aq. NH₄Cl (200 mL) was added. Then Et₂O (300 mL) was added, and the organic phase was separated, dried (MgSO₄) and concentrated *in vacuo*. Column chromatography (SiO₂, CH₂Cl₂) afforded **9** (0.92 g, 64%) as an orange solid. m.p. 155–156 °C; IR (KBr): $\nu/\text{cm}^{-1} = 2944$ (s), 2890 (m), 2864 (s), 2126 (m), 1734 (s), 1584 (s), 1518 (m), 1462 (m), 1434 (s), 1403 (w), 1365 (w), 1259 (s), 1096 (m), 1028 (m), 997 (m), 918 (w), 883 (m), 837 (w), 802 (w), 772 (w), 679 (m), 560 (w), 468 (w); ¹H NMR (300 MHz, CDCl₃): $\delta/\text{ppm} = 1.14$ (s, 42 H), 3.84 (s, 6 H), 3.89 (s, 6 H), 7.55 (s, 4 H); ¹³C NMR (75 MHz, CDCl₃): $\delta/\text{ppm} = 11.3$, 18.7, 53.3, 53.5, 101.6, 104.8, 107.7, 126.5, 129.6, 133.0, 135.4, 141.2, 159.4, 160.2; MALDI-TOF-MS (matrix: 2,5-dihydroxybenzoic acid, DHB): m/z = 898 (M⁺). Anal. calc. for C₄₄H₅₈O₈S₄Si₂ (899.35): C 58.76, H 6.50, S 14.26; found: C 58.94, H 6.38, S 14.38.

1,4-Bis[1-{4,5-bis(decyloxycarbonyl)-1,3-dithiol-2-ylidene}-3triisopropylsilyl-2-propynyllbenzene 10. A mixture of 9 (260 mg. 0.29 mmol) and K₂CO₃ (1.379 g) in 1-decanol (10 mL) and THF (5 mL) was stirred at rt for 17 h. Then Et₂O (250 mL) was added, and the mixture was washed with H₂O (200 mL), dried (MgSO₄) and concentrated in vacuo. The residue was passed through a short column (SiO₂, cyclohexane) in order to remove most of the 1-decanol. A second column chromatographic purification (SiO₂, cyclohexane– CH_2Cl_2 2 : 1 to 1 : 1) gave 10 (224 mg, 55%) as an orange oil. IR (KBr): $v/cm^{-1} =$ 2924 (s), 2853 (s), 2128 (w), 1736 (s), 1703 (s), 1575 (s), 1514 (s), 1491 (s), 1466 (s), 1442 (w), 1402 (m), 1277 (s), 1233 (s), 1098 (m), 1000 (m), 966 (m), 914 (w), 838 (w), 792 (m), 755 (s), 722 (m), 689 (s), 618 (w), 525 (w), 481 (m); ¹H NMR (300 MHz, CDCl₃): δ /ppm = 0.85–0.88 (m, 12 H), 1.14 (s, 42 H), 1.28 (br m, 56 H), 1.68 (m, 8 H), 4.22 (t, 6.8 Hz, 4 H), 4.25 (t, 6.8 Hz, 4 H), 7.55 (s, 4 H); 13 C NMR (75 MHz, CDCl₃): δ /ppm = 11.3, 14.1, 18.7, 22.7, 25.7, 25.8, 28.3 (× 2), 29.1, 29.2, 29.3, 29.5(× 2), 29.6, 31.9, 66.9, 101.4, 105.0, 107.4, 126.5, 130.5, 132.4, 135.3, 141.6, 159.2, 159.6; MALDI-TOF-MS (DHB): m/z =1402 (M⁺). Anal. calc. for C₈₀H₁₃₀O₈S₄Si₂ (1404.31): C 68.42, H 9.33, S 9.13; found: C 68.61, H 9.48, S 9.15.

1,4-Bis[1-{4,5-bis(decyloxycarbonyl)-1,3-dithiol-2-ylidene}-2propynyllbenzene 11. A mixture of 10 (361 mg, 0.25 mmol) and Buⁿ₄NF (1 M in THF, 0.50 mL) in THF (25 mL) was stirred at rt for 15 min, whereupon Et₂O (300 mL) was added. The mixture was washed with H_2O (2 \times 200 mL), dried (MgSO₄) and concentrated in vacuo. Column chromatography (SiO₂, CH₂Cl₂-cyclohexane 1 : 1) afforded 11 (204 mg, 73%) as a red unstable oil that turned greenish after prolonged standing at rt. IR (KBr): $v/cm^{-1} = 3307$ (m), 2924 (s), 2854 (s), 2085 (w), 1724 (s), 1582 (s), 1519 (s), 1466 (s), 1403 (w), 1386 (w), 1249 (s), 1098 (m), 1017 (m), 836 (w), 798 (w), 761 (w), 724 (w); ¹H NMR (300 MHz, CDCl₃): δ /ppm = 0.88 (m, 8 H), 1.26 (br s, 56 H), 1.56-1.70 (m, 8 H), 3.76 (s, 2 H), 4.21 (t, 6.8 Hz, 4 H), 4.25 (t, 6.5 Hz, 4 H), 7.54 (s, 4 H); ¹³C NMR (75 MHz, CDCl₃): δ/ppm = 14.1, 22.7, 25.7, 25.8, 26.9, 28.3, 28.5, 29.2 (x 2), 29.3, 29.5, 31.9, 67.0, 67.1, 82.3, 86.8, 105.6, 126.6, 126.7, 130.2, 132.4, 135.4, 142.8, 159.1, 159.6; MALDI-TOF-MS (DHB): m/z = 1091 (M⁺); HR-FT-MALDI-MS (DHB): m/z =1090.5474 (M⁺, calc. for C₆₂H₉₀O₈S₄: 1090.5519), 1113.5374 $([M+Na]^+, calc. for C_{62}H_{90}NaO_8S_4: 1113.5416).$

1,4-Bis[1-{4,5-bis(decyloxycarbonyl)-1,3-dithiol-2-ylidene}-3-(4-nitrophenyl)-2-propynyl]benzene 13. A mixture of 11 (209 mg, 0.16 mmol) and 4-iodonitrobenzene (490 mg, 1.97 mmol) in THF (10 mL) was Ar-degassed thoroughly. Then [PdCl₂(PPh₃)₂] (10 mg, 0.014 mmol) and diisopropylamine (1.5 mL) were added under Ar-degassing. Finally, CuI (3 mg, 0.02 mmol) was added, and the mixture was stirred at rt for 3 h. Then Et₂O (300 mL) was added and the organic phase was washed with H₂O (250 mL) and sat. aq. NH₄Cl (250 mL), dried (MgSO₄) and concentrated in vacuo. Column chromatography (SiO₂, CH₂Cl₂-cyclohexane 2 : 1) afforded 13 (74 mg, 29%) as an oily orange solid. IR (KBr): $v/cm^{-1} = 2924$ (s), 2854 (s), 2183 (m), 1737 (s), 1714 (s), 1590 (s), 1517 (s), 1469 (m), 1403 (w), 1377 (w), 1339 (s), 1253 (s), 1107 (m), 1013 (w), 973 (w), 855 (m) 802 (w), 749 (m), 722 (w), 687 (w), 622 (w); ¹H NMR (300 MHz, CDCl₃): δ /ppm = 0.88 (m, 12 H), 1.27 (br s, 56 H), 1.70-1.76 (m, 8 H), 4.24 (t, 6.8 Hz, 4 H), 4.29 (t, 6.5 Hz, 4 H), 7.62 (s, 4 H), 7.63 (d, 8.8 Hz, 4 H), 8.21 (d, 8.8 Hz, 4 H); 13 C NMR (75 MHz, CDCl₃): δ /ppm = 14.1, 22.7, 25.7, 25.8, 28.3, 29.2 (\times 2), 29.3, 29.5 (\times 3), 31.9, 67.1, 67.3, 93.4, 97.3, 105.8, 123.7, 126.9, 129.8, 130.6, 131.6, 132.7, 135.5, 144.3, 146.9, 158.9, 159.5; HR-FT-MALDI-MS (DHB): m/z = 1332.5833 (M⁺, calc. for $C_{74}H_{96}N_{20}O_{12}S_4$: 1332.5846), 1355.5634 ($[M+Na]^+$, calc. for $C_{74}H_{96}N_2NaO_{12}S_4$: 1355.5744). Anal. calc. for C74H96N20O12S4 (1333.82): C 66.64, H 7.25, N 2.10, S 9.61; found: C 66.84, H 7.33, N 2.15, S 9.55.

1,4-Bis{3-[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]propynyl}benzene 16. To a solution of 14^{6c} (100 mg, 0.39 mmol) in Ar-degassed THF (10 mL) was added 1,4-diiodobenzene 15 (51.5 mg, 0.156 mmol) and [Pd(PPh₃)₂Cl₂] (8 mg, 0.01 mmol). Then Ar-degassed triethylamine (1.5 mL) and CuI (2 mg, 0.01 mmol) were added. The mixture was stirred at rt for 2.5 h. Then CH₂Cl₂ (200 mL) was added, and the organic phase was washed with sat. aq. NH₄Cl, dried (MgSO₄) and concentrated in vacuo. Column chromatography (SiO₂, CH₂Cl₂) afforded 16 as an orange powder that was recrystallized from CH₂Cl₂-MeOH. Yield: 72 mg (79%). m.p. 182-184 °C. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: $\delta/\text{ppm} = 3.85$ (s, 6 H), 3.87 (s, 6 H), 5.62 (s, 2 H), 7.35 (s, 4 H); ¹³C NMR (75 MHz, CDCl₃): δ /ppm = 53.4 (two overlapping), 88.5, 93.3, 99.7, 122.8, 130.9, 131.0, 131.4, 145.4, 159.5, 159.8; MALDI-TOF-MS (DHB): m/z = 586 (M^+) ; HR-FT-MALDI-MS (DHB): $m/z = 585.9857 (M^+, calc.)$ for C₂₆H₁₈O₈S₄: 585.9884), 608.9777 (M+Na⁺, calc. for C₂₆H₁₈NaO₈S₄: 608.9782).

Crystal structure determination of compound 4

Crystal data. C₁₆H₁₁NO₆S₂, M = 377.38, monoclinic, a = 16.5249(19), b = 5.6048(6), c = 17.472(2) Å, $\beta = 99.608(2)^{\circ}$, U = 1595.5(3) Å³, T = 120(2) K, space group $P2_1/n$ (no. 14), Z = 4, μ (Mo K α) = 0.368 mm⁻¹, 16 297 reflections measured, 3251 unique ($R_{\text{int}} = 0.0877$). The final $R(F^2)$ was 0.0959 (all data) and R(F) was 0.0420 (for $F^2 > 2\sigma(F^2)$).‡

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