Preparation of Linear Aromatic Disulfonic Acids: New Linker Molecules for Metal-Organic Frameworks

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Abstract: Four linear aromatic disulfonic acids were prepared, which are structurally similar to dicarboxylic acids commonly used as linker molecules for metal-organic frameworks. 4,4′-Biphenyldisulfonic acid was prepared in three steps from 4,4′-dibromobiphenyl (54% overall yield). Direct sulfonation of terphenyl gave the respective all-*para*-constituted disulfonic acid in 73% yield. Tolane-4,4′-disulfonic acid was obtained by a three-step sequence consisting of Sonogashira coupling, oxidative degradation of a thioester, and hydrolysis in 20% overall yield. By using a Glaser coupling, the bis(4-sulfophenyl)butadiyne was analogously prepared in 30% overall yield.

Key words: alkynes, arenes, sulfur, cross coupling, metal-organic frameworks

At the end of the era of crude oil, the use of alternative energy sources becomes more and more urgent. Primarily for use in vehicles, the application of hydrogen fuel cells is an attractive option. However, this alternative is today far from being used routinely because of problems with the storage of hydrogen gas.[1] In this context, a new class of organic-inorganic hybrid materials, the so-called metal-organic frameworks (MOFs),[2] has recently entered the focus of scientific interest, since MOFs can be applied as storage media for gases, in particular for hydrogen.[3] The majority of the so far reported MOFs are based on carboxylic acids as linker molecules. This is also the case for the probably most prominent representative of this class of compounds, $[Zn_4O](bdc)_3$, the so called MOF-5.[4] This material is outstanding because of its excellent gas-storage properties on the one hand. On the other hand, the organic linker molecule, the dianion of terephthalic acid (**1**) (Figure 1), 1,4-benzenedicarboxylate (BDC^{2-}), is readily available in large quantities and at low costs.[5]

The aim of our research is the synthesis of metal-organic frameworks (MOFs) with oligosulfonic acids as linker molecules.[6] Compared to so far known MOF materials based on carboxylates, the main advantage of sulfonate-MOFs is their enhanced thermal stability, which is an essential requirement for applications in catalysis and as storage media for gases. We have, for example, prepared the sulfo analogue of terephthalic acid, the 1,4-benzenedisulfonic acid (**2**), H_2BDS, as well as its Cu(II) and Zn(II) salts. Compound $[Cu(bds)(H_2O)_4]$ decomposed at 400 °C,[7] which is about 200 K above the values observed for analogous copper(II) terephthalate.[8] The compound $[Zn(bds)(dmf)_2]$ is (after desolvation) actually stable up to

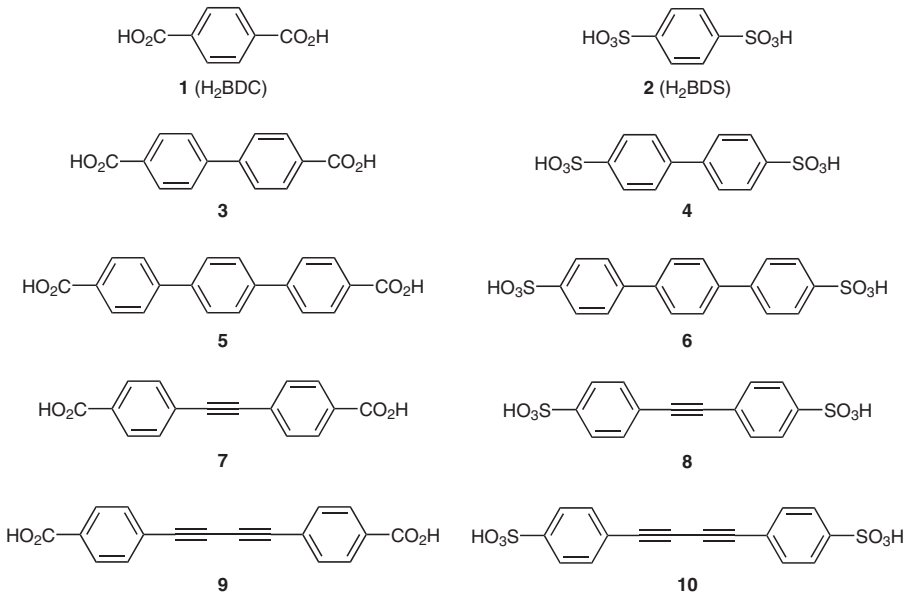

Figure 1 Linear, aromatic dicarboxylic and disulfonic acids as linker molecules for metal-organic frameworks

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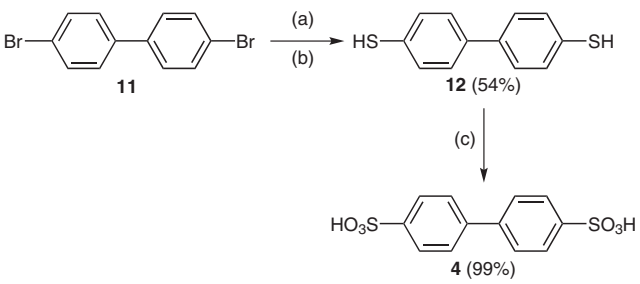
600 °C.[9] Beside their thermal stability, the acidity of sulfonic acids is several orders of magnitude higher than that of carboxylic acids, which allows for the application of more Brønsted-basic inorganic precursor compounds, such as metal oxides and carbonates. Furthermore, sulfonates hold more donor atoms than carboxylates, therefore, they should have a significantly different coordination behavior and we expect to observe new and so far unknown framework structures.

Apart from H_2BDC (**1**), other linear dicarboxylic acids with elongated carbon backbones have been used as linker molecules in MOFs: Bi- and terphenyl dicarboxylic acids (**3** and **5**),[10,11] tolane dicarboxylic acid (**7**),[12] and diphenylbutadiyne dicarboxylic acid (**9**)[13] (Figure 1). The variation of the distance of the coordinating functional groups by the organic spacer allows to adjust the pore sizes and therefore to tune the materials' properties. In contrast to the widespread use of carboxylic acids, most constitutionally similar sulfonic acids have been unknown so far and new synthetic routes need to be developed. In order to fill this gap, we report on the preparation of disulfonic acids **4**, **6**, **8**, and **10**. Compound **4** could be prepared by direct sulfonation of biphenyl,[14] but it was obtained as a mixture of regioisomers, which made separation necessary and lowered the yield. Compound **6** was mentioned once as an intermediate for the production for dihydroxyterphenyl,[15] but it was not characterized. Compounds **8** and **10** are new.

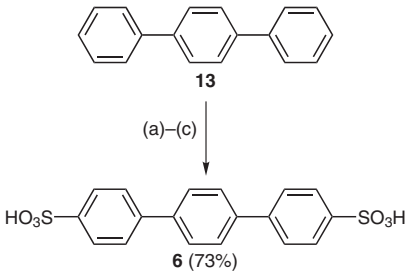
The synthesis of organic oligosulfonic acids is limited by the regioselectivity as well as the deactivating nature of sulfo groups. In the case of direct sulfonation of biphenyl, a hardly separable mixture of regioisomers was obtained.[14] Therefore, it was decided to follow our route published for H_2BDS (**2**)[7] and oxidize dithiol **12** in order to prepare 1,4-disulfonic acid **4**. As the purification of the reaction product **4** turned out to be very tedious, the use of hydrogen peroxide in a mixture of water–methanol–chloroform was beneficial for the oxidation of dithiol **12**. All other components of the reaction mixture could be removed in high vacuum after full conversion was achieved and the disulfonic acid **4** as the only nonvolatile material was obtained in high purity and quantitative yield (Scheme 1). Dithiol **12**[16] has been prepared before by multi-step procedures. We herein report on a sequential



Scheme 1 Synthesis of 4,4′-biphenyldisulfonic acid (**4**). *Reagents and conditions*: (a) *i*-PrSNa (6 equiv), DMA, 100 °C, 18 h; (b) Na (15 equiv), DMA, 100 °C, 20 h; (c) H_2O_2 (14 equiv), H_2O, MeOH, $CHCl_3$, 23 °C, 20 h.

one-pot protocol for the scalable synthesis of intermediate **12** from commercially available dibromobiphenyl **11**. First, a nucleophilic aromatic substitution with *i*-PrSNa takes place in dimethylacetamide (DMA) under formation of the dithioether. Subsequently, an excess of sodium was added to the reaction mixture and the isopropyl groups are reductively cleaved. Acidic workup afforded the product **12** in good yield (54%).

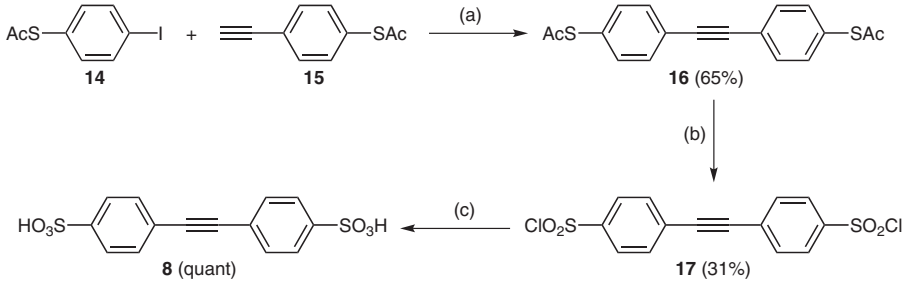
In contrast to the preparation of biphenyl derivative **4**, the direct sulfonation of terphenyl **13** proceeded with high regioselectivity to give disulfonic acid **6**. However, the isolation and purification of this product turned out to be very tedious. For this reason, we first prepared the disodium salt, which was crystallized from water and then protonated by means of a column of cationic ion exchange resin to yield the diacid **6** in good yield (Scheme 2).



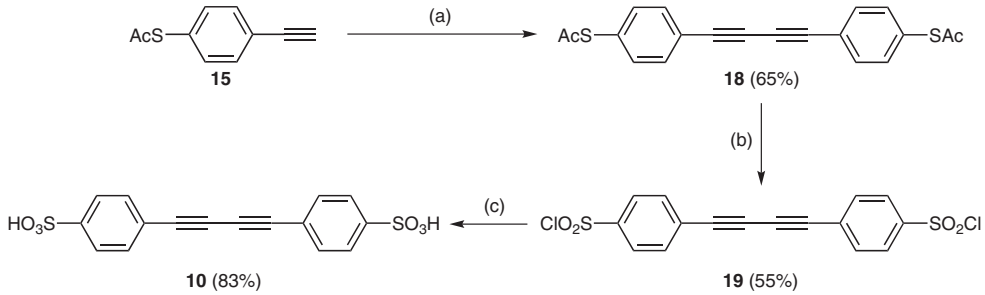
Scheme 2 Synthesis of terphenyldisulfonic acid **6**. *Reagents and conditions*: (a) concd H_2SO_4 (7.5 equiv), 160 °C, 4 h; (b) NaOH (excess), H_2O; (c) Amberlyst 15, H_2O.

In order to prepare tolanedisulfonic acid **8**, the initial plan was to convert 4,4′-dibromotolane in a nucleophilic aromatic substitution reaction with *i*-PrSNa in a straightforward manner as for the preparation of disulfonic acids **2** and **4**. Addition reactions to the triple bond were, however, observed, which gave significant amounts of by-products. Therefore, the disulfonyl dichloride **17** (Scheme 3) was prepared first by oxidative degradation of a thiol derivative with *N*-chlorosuccinimide (NCS) and HCl (for generation of Cl_2 in situ), as was successfully realized in the preparation of cyclohexanedisulfonic acid.[6b] For this reason, the *S*-acetyliodothiophenol **14** and the respective phenylacetylene derivative **15** were prepared according to literature protocols.[17] Alkyne **15** was actually accessed from compound **14** by Sonogashira coupling reaction. Conversion of these two starting materials **14** and **15** in another Sonogashira coupling reaction gave the bis(thioacetyl) derivative **16** in good yield (65%). Dithioester **16** was then oxidatively degraded to its respective bis(sulfonyl) chloride **17** with NCS/HCl. The crude material **17** contained several impurities, which made successive chromatography and recrystallization necessary. Therefore, the yield remained not fully satisfying. Final hydrolysis of compound **17** with hot water gave the disulfonic acid **8** in quantitative yield.

In order to prepare the butadiyne derivative **10** along an analogous route as above, phenylacetylene derivative **15** was submitted to a copper- and nickel-catalyzed variant[18]



Scheme 3 Synthesis of tolanedisulfonic acid **8**. *Reagents and conditions*: (a) *i*-Pr_2NEt (2.5 equiv), $[Pd(PPh_3)_2Cl_2]$ (0.06 equiv), CuI (0.19 equiv), THF, 23 °C, 18 h; (b) NCS (8 equiv), MeCN, HCl, H_2O, 10–23 °C, 2 h; (c) THF, H_2O, 100 °C, 23 h.



Scheme 4 Synthesis of diphenylbutadiyne disulfonic acid **10**. *Reagents and conditions*: (a) TMEDA (0.2 equiv), CuI (0.05 equiv), $NiCl_2 \cdot 6H_2O$ (0.05 equiv), air, THF, 23 °C, 60 h; (b) NCS (8 equiv), MeCN, HCl, H_2O, 10–23 °C, 4.5 h; (c) THF, H_2O, 100 °C, 28 h.

of the Glaser coupling reaction in air (Scheme 4). Bisthioester **18** was obtained in good yield (65%) and then submitted to oxidative degradation of the thioester with NCS/HCl. Again after subsequent chromatography and crystallization, the bis(sulfonyl) chloride **19** was obtained in moderate yield (55%). As above, the final hydrolysis of compound **19** with hot water gave the disulfonic acid **10** in 83% yield.

In contrast to carboxylic acids, which are ubiquitous linker molecules in the field of metal-organic frameworks, sulfonic acids are extraordinarily rare in this context. We have prepared four linear aromatic disulfonic acids, which are structurally similar to frequently used dicarboxylic acids. Terphenyldisulfonic acid **6** was obtained as a single regioisomer by direct sulfonation of terphenyl **13** (one step, 73% yield). Impurities and other regioisomers were separated by crystallization of its sodium salt. In contrast, direct sulfonation of biphenyl was known to yield several regioisomers. Therefore, dibromobiphenyl **11** was used with predefined constitution and converted in three steps by nucleophilic substitution with *i*-PrSNa, reductive cleavage of the *i*-Pr groups via the dithiol **12** and final oxidation to the respective disulfonic acid **4** (54% overall yield). Tolanedisulfonic acid **8** was obtained by a three-step sequence of Sonogashira coupling, oxidative degradation of thioester groups with NCS/HCl, and hydrolysis of the bis(sulfonyl) chloride **17** (20% yield over three steps). Preparation bis(4-sulfophenyl)butadiyne (**10**) followed the same strategy as for the tolane derivative **8**, but by replacing the Sonogashira with a Glaser coupling reaction. Compound **10** was obtained in 30% yield over three steps.

Preparative column chromatography was carried out using Merck SiO_2 (0.035–0.070 mm, type 60 A) with hexane, EtOAc, *tert*-butyl methyl ether (MTBE), or CH_2Cl_2 as eluent. TLC was performed on Merck SiO_2 F_{254} plates on aluminum sheets. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500. Multiplicities of carbon signals were determined with DEPT experiments. MS and HRMS spectra were obtained with a Finnigan MAT 95 (EI and CI) and a Waters Q-TOF Premier (ESI, negative mode) spectrometer. IR spectra were recorded on a Bruker Tensor 27 spectrometer equipped with a 'GoldenGate' diamond ATR unit. Elemental analyses were measured with a Euro EA-CHNS from HEKAtech. DTA/TG measurements were performed with a thermal analyzer (TGA/SDTA 851^E, Mettler-Toledo). These measurements did not only reveal the melting points of the sulfonic acids **4**, **6**, **8**, and **10**, but also their contents of crystal water. A column of ion exchange resin Amberlyst 15 (Fluka) was used; capacity: 12 mmol/g. This column was regenerated with 100 mL of half concd HCl after each preparation and reused. All starting materials were commercially available.

4,4′-Biphenyldithiol (12)

A suspension of 4,4′-dibromobiphenyl (**11**; 3.12 g, 10.0 mmol, 1 equiv) and *i*-PrSNa (4.91 g, 50.0 mmol, 5 equiv) in DMA (30 mL) was stirred under N_2 for 18 h at 100 °C. The conversion was monitored by GLC; if incomplete, more *i*-PrSNa (1.00 g, 10.2 mmol, 1 equiv) was added and the mixture was stirred at 100 °C until full conversion was achieved. Subsequently, Na (1.72 g, 75.0 mmol, 7.5 equiv) and DMA (10 mL) were added, and the resulting mixture was stirred for 20 h at 100 °C under N_2. The conversion was monitored by GLC; if incomplete, more Na (1.72 g, 75.0 mmol, 7.5 equiv) and DMA (10 mL) were added and the mixture further stirred at 100 °C, until full conversion was achieved. The mixture was diluted with MTBE (100 mL) and H_2O (100 mL), and concd HCl (ca. 50 mL) was added, until pH <1 was reached. After phase separation, the aqueous layer was extracted with MTBE (2 × 100 mL). The combined organic layers were washed with H_2O (2 × 100 mL), dried ($MgSO_4$), and evaporated after filtration. The residue was chromatographed twice (SiO_2, 1. hexane–MTBE, 1:1; 2. hexane–MTBE gradient elution from 5:1 to 1:1) to give the title com-

pound **12** (1.18 g, 5.41 mmol, 54%) as a yellow solid; mp 185 °C; R_f = 0.38 (hexane–MTBE, 1:1).

IR (ATR): 2958 (w), 2551 (w), 1633 (m), 1591 (m), 1474 (m), 1394 (m), 1259 (w), 1103 (m), 998 (w), 915 (w), 804 (s), 697 (w) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.49 (s, 2 H, SH), 7.33 (d, ^3J = 8.4 Hz, 4 H), 7.43 (d, ^3J = 8.4 Hz, 4 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 127.4 (CH), 129.8 (CH), 129.9 (C), 137.8 (C).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{12}H_{10}S_2$ [M^+]: 218.0224; found: 218.0218.

4,4′-Biphenyldisulfonic Acid Sesterhydrate (4)

Aq H_2O_2 (30%, 1.0 mL, 8.0 mmol, 33 equiv) was added to a suspension of dithiol **12** (77 mg, 0.24 mmol, 1 equiv) in MeOH (3 mL) and $CHCl_3$ (3 mL) and the resulting mixture was stirred for 16 h at r.t. Subsequently, all volatile materials were removed in high vacuum, the residue was redissolved in H_2O (4 mL) and treated again with aq H_2O_2 (30%, 1 mL, 8.0 mmol, 33 equiv). After stirring for 4 h at 23 °C, all volatile materials were removed in high vacuum to yield the title compound **4** (85 mg, 0.24 mmol, 99%) as a colorless solid; mp 235 °C (dec., DTA/TG).

IR (ATR): 2921 (br, m), 1694 (br, m), 1596 (m), 1484 (w), 1386 (w), 1121 (s), 1029 (s), 1015 (s), 860 (m), 837 (m), 816 (s), 721 (s) cm^{-1}.

^1H NMR (300 MHz, D_2O): δ = 7.32 (d, ^3J = 8.4 Hz, 4 H), 7.59 (d, ^3J = 8.4 Hz, 4 H).

$^{13}C\{^1H\}$ NMR (75 MHz, D_2O): δ = 125.9 (CH), 127.4 (CH), 141.7 (C), 141.8 (C).

MS (ESI, neg. mode): *m*/*z* = 313 [M – H^+], 156 [M – 2 H^+].

[1,1′:4′,1″-Terphenyl]-4,4″-disulfonic Acid Dihydrate (6) Disodium Salt of 6

Terphenyl (**13**; 4.60 g, 20.0 mmol, 1 equiv) was added in small portions at 110 °C to concd H_2SO_4 (8.20 mL, 149 mmol, 7.5 equiv). The resulting mixture was stirred for 4 h at 160 °C, then cooled to r.t., and poured into H_2O (100 mL). After filtration through a pad of Celite (2 × 3 cm, rinsed with H_2O), aq NaOH (1.75 mol/L, ca. 125 mL) was added, until pH 5–6 was obtained. The mixture was heated to ca. 95 °C and H_2O (ca. 900 mL) was added, until the precipitate was completely dissolved. After cooling to r.t., the precipitate was collected on a glass frit and dried in high vacuum to yield the disodium salt of the title compound (6.90 g, 15.3 mmol, 76%) as the hemihydrate and as a colorless solid; mp >300 °C.

IR (ATR): 3068 (w), 1597 (w), 1568 (w), 1484 (m), 1393 (w), 1236 (m), 1182 (s), 1128 (s), 1047 (s), 1012 (m), 999 (m), 814 (s), 755 (s), 723 (m), 645 (s) cm^{-1}.

^1H NMR (300 MHz, D_2O): δ = 7.79–7.87 (m).

Anal. Calcd for $C_{18}H_{12}Na_2O_6S_2 \cdot 0.5\ H_2O$ (443.40): C, 48.76; H, 2.96. Found: C, 48.92; H, 2.90.

Compound 6

An aqueous solution (250 mL) of part of the disodium salt (300 mg, 0.67 mmol) was transferred on top of a column (19.5 g Amberlyst 15). The acid was eluted with H_2O until the pH of the eluent was neutral. After removal of the water by rotary evaporation and drying of the residue in high vacuum, product **6** (273 mg, 0.64 mmol, 96%) was obtained as a colorless solid; mp 286 °C (dec., DTA/TG).

IR (ATR): 2599 (br, m), 2165 (br, m), 1660 (br, m), 1594 (m), 1568 (m), 1480 (m), 1390 (w), 1105 (s), 1030 (s), 993 (s), 812 (s), 756 (s), 723 (m), 627 (s) cm^{-1}.

^1H NMR (300 MHz, D_2O): δ = 7.21 (s, 4 H), 7.35 (d, *J* = 8.1 Hz, 4 H), 7.66 (d, *J* = 8.1 Hz, 4 H).

$^{13}C\{^1H\}$ NMR (125 MHz, D_2O): δ = 126.3 (CH), 127.4 (CH), 127.7 (CH), 138.8 (C), 141.6 (C), 142.8 (C).

MS (ESI, neg. mode): *m*/*z* = 389 [M – H^+], 194 [M – 2 H^+].

HRMS (ESI, neg. mode): *m*/*z* calcd for $C_9H_6O_3S^{2-}$ [M – 2 H^+]: 194.0043; found: 194.0042.

4,4′-Di(acetylthio)tolane (16)

i-Pr_2NEt (2.05 g, 15.9 mmol, 2.5 equiv) was added under a N_2 atmosphere to a solution of iodobenzene derivative **14** (1.77 g, 6.36 mmol, 1.0 equiv). and alkyne **15** (1.40 g, 7.94 mmol, 1.25 equiv) in THF (12.7 mL). After stirring for 5 min at 23 °C, [$Pd(PPh_3)_2Cl_2$] (279 mg, 0.40 mmol, 0.06 equiv) and CuI (227 mg, 1.19 mmol, 0.19 equiv) were added together with THF (3.3 mL). The resulting mixture was stirred at r.t., until complete conversion was observed by GLC (18 h). CH_2Cl_2 (60 mL) and H_2O (50 mL) were added, and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were washed with H_2O (50 mL), dried ($MgSO_4$), and evaporated after filtration. The residue was chromatographed (SiO_2, gradient elution from hexane via hexane–MTBE, 10:1 and 2:1 to MTBE) to yield the title compound **16** (1.35 g, 4.13 mmol, 65%) as a light-yellow solid; mp 122 °C; R_f = 0.44 (hexane–MTBE, 2:1).

IR (ATR): 2921 (w), 1913 (w), 1697 (s), 1587 (w), 1498 (m), 1397 (m), 1354 (m), 1112 (s), 1087 (s), 1014 (m), 955 (s), 820 (s), 658 (m), 615 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 6 H), 7.41 (d, *J* = 8.5 Hz, 4 H), 7.55 (d, *J* = 8.5 Hz, 4 H).

$^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ = 30.3 (CH_3), 90.2 (C), 124.2 (C), 128.5 (C), 132.2 (2 CH), 134.2 (2 CH), 193.2 (C).

HRMS (ESI, pos. mode): *m*/*z* calcd for $C_{18}H_{14}O_2S_2$ + Na [M + Na^+]: 349.0333; found: 349.0336.

Anal. Calcd for $C_{18}H_{14}O_2S_2$ (326.43): C, 66.23; H, 4.32; S, 19.65. Found: C, 66.08; H, 4.31; S, 19.50.

Tolane-4,4′-disulfonyl Chloride (17)

Bisthioester **16** (707 mg, 2.17 mmol, 1 equiv) was dissolved in MeCN (6.3 mL) with gentle warming. After cooling to 0 °C, NCS (2.32 g, 17.4 mmol, 8 equiv) and aq HCl (2 mol/L, 2.4 mL, 4.8 mmol, 2.2 equiv) were added and the resulting mixture was stirred for 45 min at 10–15 °C, then for 1 h at 23 °C. After dilution with CH_2Cl_2 (60 mL) and H_2O (60 mL), the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were washed with H_2O (60 mL), dried ($MgSO_4$), and evaporated after filtration. The residue was chromatographed (SiO_2, hexane–CH_2Cl_2, 1:1) to yield a crude material (280 mg), which was further purified by recrystallization from hexane–$CHCl_3$ (1:1, 10 mL) to yield the title compound **17** (254 mg, 0.68 mmol, 31%) as light-yellow crystals; mp 235–236 °C; R_f = 0.90 (CH_2Cl_2).

IR (ATR): 3092 (w), 3065 (w), 2360 (w), 1933 (w), 1588 (m), 1496 (w), 1371 (s), 1285 (w), 1174 (s), 1104 (w), 1075 (m), 1012 (w), 962 (w), 833 (s), 715 (w), 663 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.5 Hz, 4 H), 8.07 (d, *J* = 8.5 Hz, 4 H).

$^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ = 91.8 (C), 127.2 (2 CH), 129.3 (C), 132.8 (2 CH), 144.2 (C).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{14}H_8Cl_2O_4S_2$ [M^+]: 373.9241; found: 373.9250.

Anal. Calcd for $C_{14}H_8Cl_2O_4S_2$ (375.25): C, 44.81; H, 2.15; S, 17.09. Found: C, 44.85; H, 1.96; S, 17.31.

Tolane-4,4′-disulfonic Acid Dihydrate (8)

A suspension of dichloride **17** (94 mg, 0.25 mmol) in H_2O (10 mL) was heated to reflux for 18 h. Then THF (5 mL) was added to the mixture and it was heated to reflux for further 5 h. Subsequently, it was filtered through a pad of cotton (rinsed with H_2O) and the filtrate was evaporated in high vacuum to yield the title compound **8** (96 mg, 0.25 mmol, quant) as a light-grey solid; mp 158–160 °C (DTA/TG).

IR (ATR): 2704 (br, m), 1666 (br, m), 1596 (m), 1499 (w), 1395 (w), 1114 (br, s), 1101 (s), 996 (br, s), 829 (s), 685 (s) cm^{-1}.

^1H NMR (500 MHz, D_2O): δ = 7.60 (d, *J* = 8.4 Hz, 4 H), 7.72 (d, *J* = 8.4 Hz, 4 H).

$^{13}C\{^1H\}$ NMR (500 MHz, D_2O): δ = 90.3 (C), 125.3 (C), 125.8 (2 CH), 132.2 (2 CH), 142.6 (C).

MS (ESI, neg. mode): *m/z* = 337 [M – H^+], 168 [M – 2 H^+].

HRMS (ESI, neg. mode): *m/z* calcd for $C_{14}H_8O_6S_2^{2-}$ [M – 2 H^+]: 167.9887; found: 167.9890.

1,4-Bis[4-(acetylthio)phenyl]butadiyne (18)

CuI (28.6 mg, 0.15 mmol, 0.05 equiv) and $NiCl_2 \cdot 6\ H_2O$ (35.7 mg, 0.15 mmol, 0.05 equiv) were added to a solution of TMEDA (70 mg, 0.60 mmol, 0.20 equiv) in THF (12 mL). After stirring the resulting suspension for 2 min at 23 °C, alkyne **15** (529 mg, 3.00 mmol, 1 equiv) and THF (2 mL) were added and the resulting mixture was stirred for 60 h at 23 °C in an atmosphere of air (a reflux condenser was used in order prevent evaporation of the solvent), while following the conversion by GLC. After dilution with H_2O (50 mL) and CH_2Cl_2 (80 mL), the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 80 mL). The combined organic layers were washed with H_2O (80 mL), dried ($MgSO_4$), and the solvent was evaporated after filtration. Chromatography on SiO_2 (gradient elution from hexane–MTBE, 10:1 via 2:1 to hexane–CH_2Cl_2, 2:1 to neat CH_2Cl_2) furnished title compound **18** (344 mg, 0.98 mmol, 65%) as a yellow solid; mp 279–280 °C; R_f = 0.14 (hexane–MTBE, 10:1).

IR (ATR): 3365 (w), 2922 (w), 1900 (w), 1696 (s), 1586 (w), 1480 (m), 1394 (m), 1353 (m), 1267 (w), 1114 (s), 1088 (s), 1012 (m), 9584 (s), 820 (s), 627 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 6 H), 7.39 (d, *J* = 8.2 Hz, 4 H), 7.55 (d, *J* = 8.2 Hz, 4 H).

$^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ = 30.3 (CH_3), 75.3 (C), 81.4 (C), 122.7 (C), 129.5 (C), 133.0 (2 CH), 134.2 (2 CH), 193.0 (C).

HRMS (EI, 70 eV): *m/z* calcd for $C_{20}H_{14}O_2S_2$ [M^+]: 350.0435; found: 350.0444.

Anal. Calcd for $C_{20}H_{14}O_2S_2$ (350.45): C, 68.54; H, 4.03; S, 18.30. Found: C, 68.53; H, 4.11; S, 18.20.

1,4-Bis[4-(chlorosulfonyl)phenyl]butadiyne (19)

NCS (609 mg, 4.56 mmol, 8 equiv) and aq HCl (2 mol/L, 0.63 mL, 1.26 mmol, 2.2 equiv) were added at 0 °C to a suspension of diyne **18** (200 mg, 0.57 mmol, 1 equiv) in MeCN (1.6 mL) and the resulting mixture was stirred for 3 h at 10–15 °C. More of the above HCl (0.20–0.50 mL) was added. If no change of the mixture (clearing) appeared, the reaction temperature was brought to 23 °C and then stirred for further 90 min. Otherwise, the mixture was left for further 30 min at 10–15 °C before stirring for 90 min at 23 °C. After dilution with CH_2Cl_2 (20 mL) and H_2O (20 mL), the layers were separated and the aqueous phase extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with H_2O (40 mL), dried ($MgSO_4$), and evaporated after filtration. The residue was chromatographed (SiO_2, CH_2Cl_2, R_f = 0.75) to yield a crude material (241 mg), which was further purified by recrystallization from $CHCl_3$ (8 mL) to yield the title compound **19** (126 mg, 0.32 mmol, 55%) as a yellow solid; mp 199–201 °C (dec.).

IR (ATR): 3094 (w), 1712 (br, m), 1583 (m), 1484 (w), 1374 (s), 1328 (m), 1282 (w), 1185 (m), 1166 (s), 1075 (m), 1012 (m), 962 (m), 831 (s), 798 (m), 783 (m), 736 (w), 711 (w), 651 (w), 618 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 5.1 Hz, 4 H), 8.04 (d, *J* = 5.1 Hz, 4 H).

$^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ = 77.9 (C), 81.2 (C), 127.1 (2 CH), 128.5 (C), 133.6 (2 CH), 144.3 (C).

HRMS (EI, 70 eV): *m/z* calcd for $C_{16}H_8Cl_2O_4S_2$ [M^+]: 397.9241; found: 397.9233.

Anal. Calcd for $C_{16}H_8Cl_2O_4S_2$ (399.27): C, 48.13; H, 2.02; S, 16.06. Found: C, 47.75; H, 1.83; S, 16.36.

1,4-Bis(4-sulfophenyl)butadiyne Dihydrate (10)

A suspension of acid chloride **19** (40 mg, 0.10 mmol) in H_2O (10 mL) was heated to reflux for 22 h. Subsequently, THF (6 mL) was added and the mixture was heated to reflux for further 6 h. After filtration, all volatile materials were removed in high vacuum to yield the title compound **10** (33 mg, 0.083 mmol, 83%) as a light-grey solid; mp 174–176 °C (DTA/TG).

IR (ATR): 2848 (br, m) 1668 (br, m), 1590 (m), 1557 (w), 1486 (w), 1396 (w), 1356 (m), 1160 (s), 1117 (br, s), 1061 (s), 1030 (s), 1001 (br, s), 894 (br, s), 831 (s), 786 (m), 646 (br, s) cm^{-1}.

^1H NMR (500 MHz, D_2O): δ = 7.14 (d, *J* = 7.3 Hz, 4 H), 7.39 (d, *J* = 7.3 Hz, 4 H).

$^{13}C\{^1H\}$ NMR (500 MHz, D_2O): δ = 75.8 (C), 81.8 (C), 124.2 (C), 125.7 (2 CH), 133.2 (2 CH), 143.1 (C).

HRMS (ESI, neg. mode): *m/z* calcd for $C_{16}H_9O_6S_2^-$ [M – H^+]: 360.9846; found: 360.9850.

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