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A tetrathiafulvalene–perylene diimide conjugate prepared via click chemistry

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ABSTRACT

A new tetrathiafulvalene (TTF)–perylene diimide (PDI) conjugate is prepared from an azide-functionalized TTF and an acetylenic PDI employing a Cu(I)-catalyzed Huisgen-Meldal-Sharpless reaction (‘click chemistry’). Thus, the TTF donor and PDI acceptor units are linked together by a 1,2,3-triazole unit. The molecules are found to assemble on a mica surface, forming fibrilar structures.

Perylene diimides (PDI, Fig. 1) have attracted wide interest as candidates for organic solar cells and artificial photosynthesis owing to their high fluorescence quantum yields and thermal chemical and photochemical persistencies.[1] Recent interest has emerged in preparing donor–acceptor conjugates between PDI and the good electron donor tetrathiafulvalene (TTF).[2] TTF has been widely exploited as a redox-active unit in both materials and supramolecular chemistries.[3] Hudhomme and co-workers[2a] showed that the fluorescence emission intensity of the PDI unit can be reversibly tuned by the oxidation states of the TTF unit. We became interested in developing a new synthetic route to obtain such dyads by taking advantage of ready access to the acetylenic PDI **1**, recently prepared by us[4] and in parallel by Langhals and Obermeier.[5] We have shown that this alkyne can be subjected to an oxidative homo coupling reaction under Glaser-Hay conditions to provide a PDI dimer,[4] while Langhals and Obermeier[5] have shown that the alkyne unit of the PDI can be subjected to the Cu(I)-catalyzed Huisgen-Meldal-Sharpless reaction[6] (‘click chemistry’) with azides to furnish triazoles. Click chemistry has also been shown to tolerate the presence of a TTF unit.[7] Here, we explore click chemistry for successfully linking TTF and PDI units.

Construction of TTF–PDI dyads from **1** using click chemistry requires an azide-functionalized TTF, the synthesis of which is shown in Scheme 1. TTF compound **2** containing a cyanoethyl-protected thiolate group was prepared according to the procedure of Becher and co-workers.[8] Base-promoted elimination of acrylonitrile followed by alkylation allows for ready functionalization of the thiolate. Thus, the cyanoethyl group was removed using cesium hydroxide, and the resulting thiolate was then alkylated by treatment with 2-chloroethanol to provide compound **3**. This alcohol was subsequently treated with diphenylphosphoryl azide (DPPA) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry *N*,*N*-dimethylformamide (DMF) for 4 h followed by the addition of sodium azide, which produced the TTF-azide **4**.

Next, we subjected the TTF-azide **4** to click reactions in DMF solution. First, compound **4** was treated with phenylacetylene and $CuSO_4$/ascorbic acid, generating the Cu(I) catalyst in situ, which resulted in formation of the TTF-triazole derivative **5** in good yield (Scheme 2). The same conditions were employed in the reaction between **4** and the PDI-alkyne **1**, which furnished the TTF–PDI dyad **6** as a dark-red solid, isolated in a somewhat lower 31% yield (Scheme 2). The product was purified by column chromatography followed by precipitation from dichloromethane by addition of methanol.

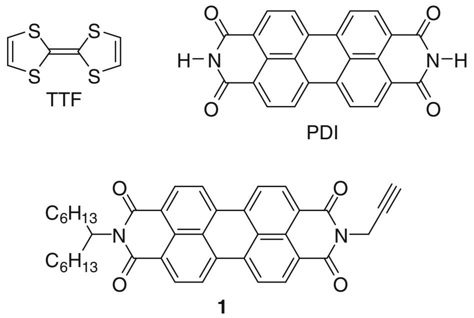

Figure 1.

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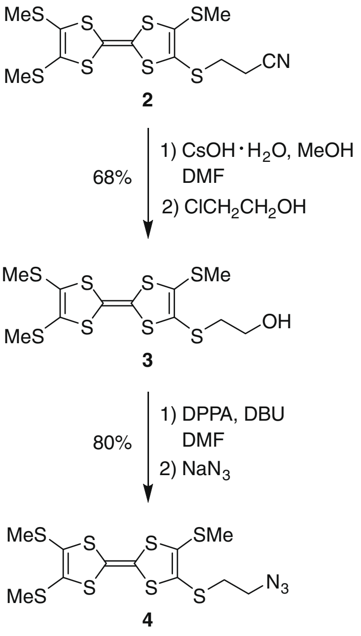
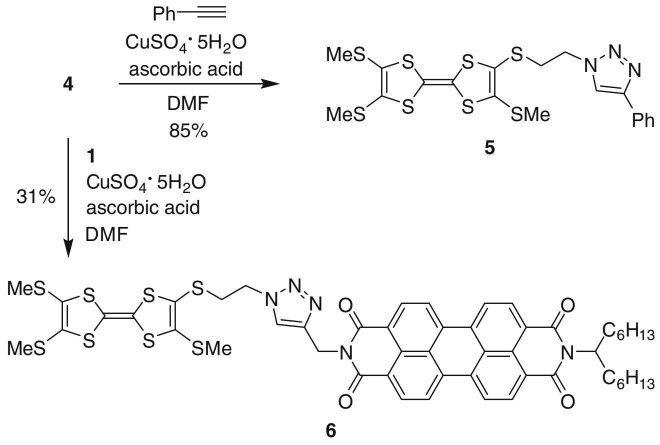


Scheme 1.



Scheme 2.

TTF–PDI dyad **6** was subjected to cyclic voltammetry studies in dichloromethane (containing 0.1 m Bu_4PF_6), which confirmed the presence of both a donor group and an acceptor group (Fig. 2). Thus, the dyad showed two reversible oxidations at half-wave potentials $E_{1/2}$ = +0.08 and +0.40 V versus Fc^+/Fc (Fc = ferrocene) corresponding to two one-electron oxidations of the TTF unit. In addition, two reversible one-electron PDI reductions were observed at $E_{1/2} = -1.05$ and -1.26 V versus Fc^+/Fc, which are close to those observed for other PDI derivatives.[4] The dyad showed characteristic PDI UV–vis absorptions at 458, 489, and 525 nm in CH_2Cl_2.

The TTF–PDI **6** was subjected to Atomic Force Microscopy (AFM) studies on a mica surface. A solution of the dyad was prepared by dissolving a few micrograms in toluene. A single drop was allowed to dry on the mica substrate. The dried sample was then studied using an optical microscope (Fig. 3A). The film formed small wires, created by the receding solvent during evaporation. An image from close-up inspection of the wires is displayed in Figure 3B, the height of the wires is about 30 nm and the width is about 1–2 μm. This image and the AFM image of a thin film obtained by deposition from chloroform (Fig. 3C) reveal that the molecules form treads lying in a net-like texture. As indicated by the color coding (Fig. 3C) and the cross-section (Fig. 3D), the treads in the film have a uniform thickness of about 2 nm. The widths of the treads are difficult to determine. They seem to range from a few nanometers up to 10 s of nanometers. However, this is probably not the true width, since in the image, there is a convolution effect with the AFM probe tip. The formation of the treads suggests that there is some loose ordering of the molecules. We speculate that the PDI section of the molecule controls the packing of the molecules so that one PDI is π-π stacked with a neighboring PDI. The TTF unit and the alkyl chains would then be connected to the backbone of the stacked PDI in more or less disordered packing. The molecules, standing edge on, would then give rise to the 2 nm thick wires observed in the AFM image.

In conclusion, we have expanded the synthetic scope of the acetylenic PDI **1**. Thus, click chemistry using this building block provides a new method for preparing donor–acceptor dyads comprised of TTF and PDI units. The molecules assemble into small wires on a mica surface. Future work will be aimed at exploring the triazole group as a site for metal ion complexation and not merely as a synthetically convenient spacer group. Complexation of a suitable metal ion may provide a triad system for light-induced charge separation.

2-(2-Hydroxyethylthio)-3,6,7-tris(methylthio)tetrathiafulvalene (**3**): The cyanoethyl-protected TTF thiolate **2** (5.43 g, 12.7 mmol) was dissolved in dry DMF (250 mL) and argon was passed through the solution for 0.5 h. An argon-degassed solution of $CsOH{\cdot}H_2O$ (2.34 g,

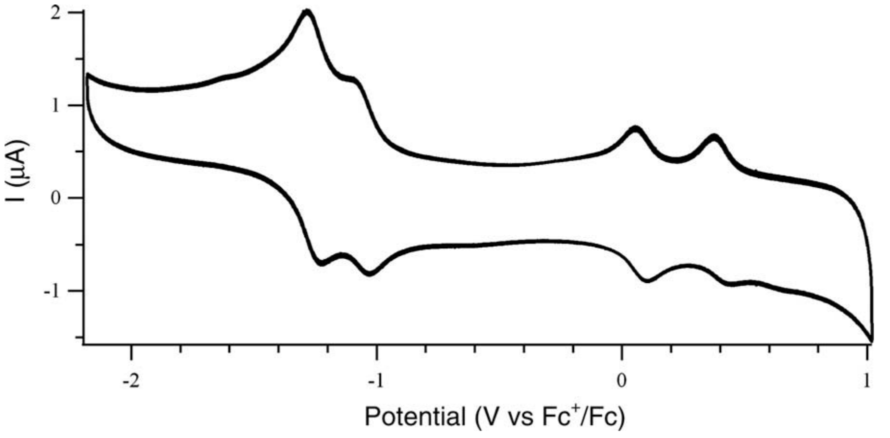


Figure 2. Cyclic voltammogram of TTF–PDI **6** in CH_2Cl_2 and 0.1 M Bu_4PF_6. Reference electrode: Ag/Ag^+; counter electrode: Pt; working electrode: glassy carbon; scan rate: 0.1 V/s.

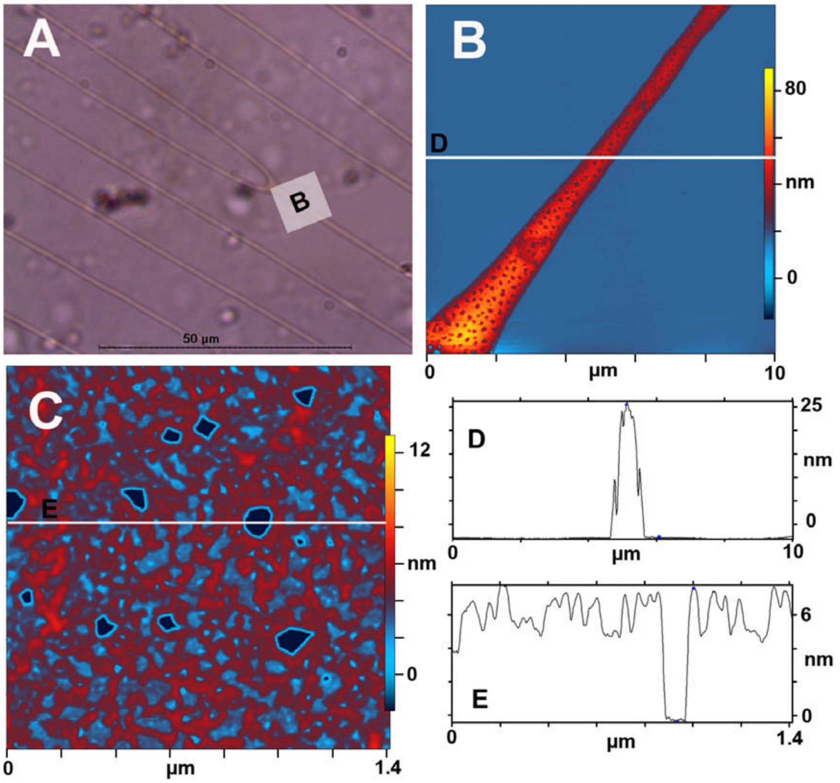


Figure 3. Structure of dropcast samples. (A) Optical microscope image showing small wires of TTF–PDI **6**, created by the receding of the drop of toluene during evaporation. (B) AFM image of a single wire. (C) The structure of a film dropcast from a chloroform solution. The white lines in B and C denote the locations of the height profile cross-sections shown in D and E, respectively.

13.9 mmol) in dry MeOH (30 mL) was added via syringe over 0.5 h. The reaction mixture was stirred for another 0.5 h, then 2-chloroethanol (3.32 mL, 49.5 mmol) was added and stirring was continued overnight. The mixture was evaporated to dryness, and the residue was subjected to column chromatography (SiO_2, gradient elution: $CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH, 95:5), affording **3** (3.6 g, 68%) as a dark-red semi-solid. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.39$ (s, 6H, $2\times SCH_3$), 2.43 (s, 3H, SCH_3), 2.52 (br s t, J = ca. 6 Hz, 1H, CH_2OH), 2.91 (t, $J = 5.9$ Hz, 2H, SCH_2), 3.69 (br s dt, $J = 5.9$ Hz, ca. 6 Hz, 2H, CH_2OH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.3$ (two overlapping), 19.4, 39.3, 60.1, 110.3, 111.7, 122.7, 127.5, 127.7, 133.4; MS (FAB): m/z 418 [M^+]; HRMS (FAB): found: m/z 417.8795 [M^+], $C_{11}H_{14}OS_8$ requires: m/z 417.8810.

2-(2-Azidoethylthio)-3,6,7-tris(methylthio)tetrathiafulvalene (**4**): TTF-alcohol **3** (300 mg, 0.716 mmol) was dissolved in dry DMF (20 mL), and then diphenyl phosphoryl azide (DPPA) (0.77 mL, 3.58 mmol) was added. The mixture was cooled on an ice bath, and DBU (0.11 mL, 0.72 mmol) was added. After stirring for 4 h under nitrogen at rt, sodium azide (0.23 g, 3.58 mmol) was added. The reaction mixture was stirred at rt for another 24 h then washed with water, and the organic layer dried (Na_2SO_4), filtered, and concentrated in vacuo. Column chromatography (SiO_2, CH_2Cl_2) of the residue afforded **4** (254 mg, 80%) as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.43$ (s, 6H, $2\times SCH_3$), 2.45 (s, 3H, SCH_3), 2.95 (t, $J = 6.8$ Hz, 2H, SCH_2), 3.51 (t, $J = 6.8$ Hz, 2H, CH_2N_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.3$ (three overlapping), 35.2, 50.8, 110.3, 112.1, 122.3, 127.6, 127.8, 133.1; one overlapping signal; MS (FAB): m/z 443 [M^+]; HRMS (FAB): found: m/z 442.8900 [M^+], $C_{11}H_{13}N_3S_8$ requires: m/z 442.8875.

2,3,6-Tris(methylthio)-7-[2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethylthio]tetrathiafulvalene (**5**): TTF-azide **4** (100 mg, 0.23 mmol) and phenylacetylene (0.03 mL, 0.27 mmol) were dissolved in DMF (2 mL) at rt, after which $CuSO_4{\cdot}5H_2O$ (3.0 mg, 0.012 mmol) and ascorbic acid (4.2 mg, 0.024 mmol) were added. The solution was stirred at rt for 12 h followed by evaporation of the solvent in vacuo. Column chromatography (SiO_2, CH_2Cl_2 followed by 5% v/v MeOH in CH_2Cl_2) gave the product **5** as an orange solid (100 mg, 85%). Mp 113–114.5 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.43$ (s, 6H, $2 \times SCH_3$), 2.48 (s, 3H, SCH_3), 3.33 (t, $J = 6.6$ Hz, 2H, SCH_2), 4.62 (t, $J = 6.6$ Hz, 2H, CH_2N), 7.34 (m, 1H, Ph), 7.43 (m, 2H, Ph), 7.84 (m, 2H, Ph), 7.97 (s, 1H, triazole-*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.4$ (three overlapping), 35.9, 49.9, 109.5, 112.8, 120.6, 121.1, 125.9, 127.6, 127.7, 128.4, 129.0, 130.7, 134.0, 147.9; MS (FAB): m/z 545 [M^+]; HRMS (FAB): found: m/z 544.9328 [M^+], $C_{19}H_{19}N_3S_8$ requires: m/z 544.9345.

TTF–PDI dyad (**6**): The TTF-azide **4** (40 mg, 0.090 mmol) and alkyne-functionalized PDI **1** (50.0 mg, 0.082 mmol) were dissolved in DMF (5 mL) at rt to afford a deep-red-colored suspension. Then $CuSO_4{\cdot}5H_2O$ (1.0 mg, 0.004 mmol) and ascorbic acid (1.4 mg, 0.008 mmol) were added. The mixture was stirred at rt for 12 h, after which the solvent was removed in vacuo. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2 followed by 5% v/v MeOH in CH_2Cl_2). A red solid was isolated and redissolved in CH_2Cl_2 (3 mL). The pure product was precipitated from this solution by addition of MeOH. TTF–PDI **6** was isolated as a dark-red solid (27 mg, 31%). Mp >150 °C (decomp.). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.83$ (t, $J = 6.7$ Hz, 6H, $CH((CH_2)_5CH_3)_2$), 1.23–1.39 (m, 16H, $CH(CH_2(CH_2)_4CH_3)_2$), 1.84–1.89 and 2.22–2.34 ($2\times$m, $2\times$2H, $CH(CH_2(CH_2)_4CH_3)_2$), 2.36 (s, 3H, SCH_3), 2.37 (s, 3H, SCH_3), 2.44 (s, 3H, SCH_3), 3.26 (t, $J = 6.7$ Hz, 2H, SCH_2), 4.75 (t, $J = 6.7$ Hz, 2H, SCH_2CH_2N), 5.13–5.21 (m, 1H, $NCH(C_6H_{13})_2$), 5.53 (s, 2H, NCH_2), 7.93 (s, 1H, triazole-*H*), 8.29–8.54 (m, 8H, PDI-*H*); MS (FAB): m/z 1053 [$M+H^+$]; HRMS (FAB): found: m/z 1053.1715 [$M+H^+$], $C_{51}H_{51}O_4N_5S_8$ requires: m/z 1053.1707.

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