Gold and Nickel Extended Thiophenic—TTF Bisdithiolene Complexes

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Supplementary Materials

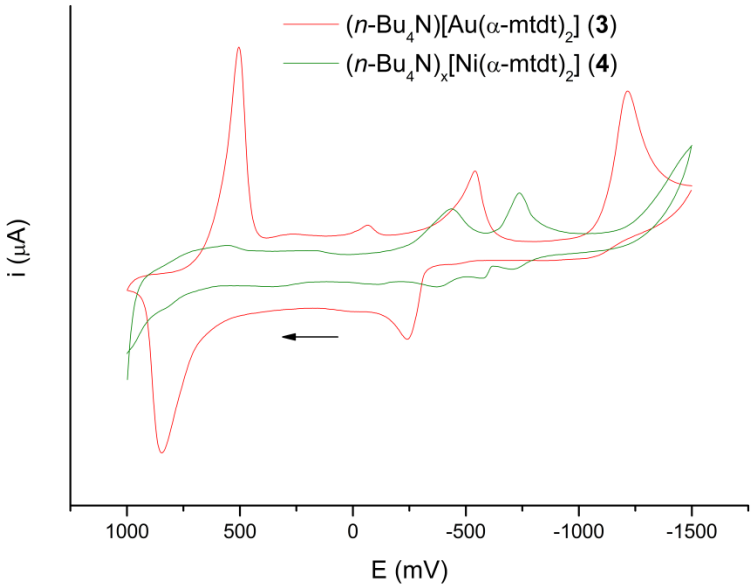

Figure S1. Cyclic voltammetry of (n-Bu$_4$N)[Au(α-mtdt)$_2$] (**3**) and (n-Bu$_4$N)$_x$[Ni(α-mtdt)$_2$] (**4**) vs Ag/AgNO$_3$ (measured in the same conditions the Fc/Fc$^+$ couple has a $E_{1/2}$ = 266 mV).

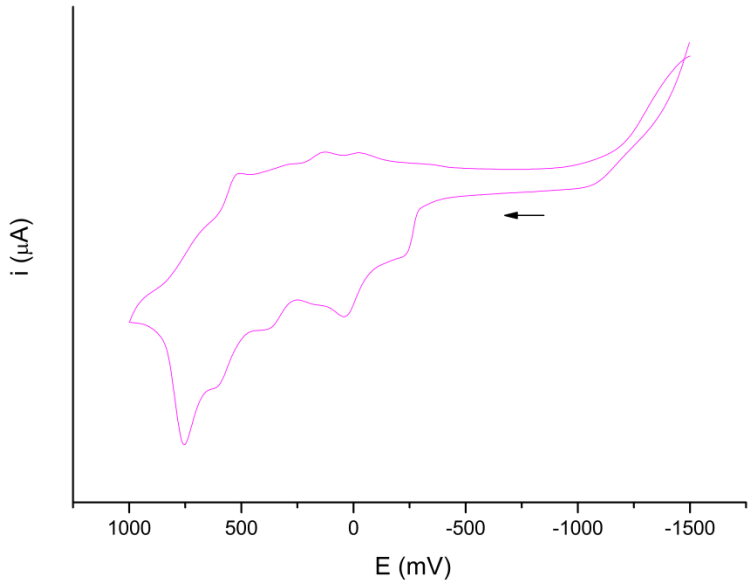

Figure S2. Cyclic voltammetry of (n-Bu$_4$N)$_2$[Au$_2$(α-tbtdt)$_2$] (**5**) vs. Ag/AgNO$_3$ (measured in the same conditions the Fc/Fc$^+$ couple has a $E_{1/2}$ = 266 mV).

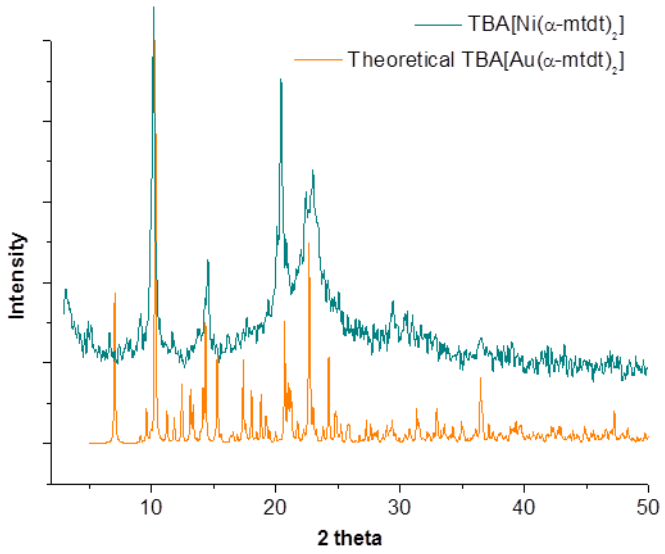

Figure S3. X-ray powder pattern of (n-Bu$_4$N)$_x$[Ni(α-mtdt)$_2$] (**4**, green line) and X-ray powder pattern simulation from (n-Bu$_4$N)[Au(α-mtdt)$_2$] (**3**, orange line) crystal structure.

X-Ray Structural Analysis of Ligand Precursor 1

Here we will report the crystal structure of ligand precursor **1**, which its preparation and characterization was previously reported however no X-ray structure could be determined [1].

Ligand precursor **1** crystallizes in the monoclinic system, space group $P2_1$. The asymmetric unit cell contains two independent neutral α-mtdt molecules, both at general positions. These two α-mtdt molecules are essentially planar, with exception of the cyanoethyl groups, and present disorder in the thiophenic ring with sulphur atoms over two possible positions with occupation factors of 44–56 % (S1/C3-S1A/C3A) for one molecule while the other has 53–47 % (S8/C18-S8A/C18A).

Ligand precursor **1** crystallizes as fibers with very small dimensions severely limiting the X-ray diffraction analysis. Nevertheless, and although the quality of the data collected did not allow a good structural refinement it is consistent with other extended thiophenic-TTF fused dithiolene ligands like the unsubstituted non-aromatic dtdt [2] and aromatic α-tdt [2] and *tert*-butyl-substituted pre-α-tbtdt [1]. Compound **1** crystallizes in the monoclinic system, space group $P2_1$, and it is composed of layers of side-by-side A-B-A-B chains of molecules, running parallel to *c* (Figure S4a). Within the chain the molecules are connected by several S···S short contacts and arranged in a head-to-tail fashion where the cyanoethyl group points outside the chain and the mean plane of adjacent molecules is rotated by about 50°. Along *a*, the chains are regularly packed and connected by C-H···S and C-H···N hydrogen bonds (Figure S4b). Between layers, molecules are connected by several C-H···N hydrogen bonds.

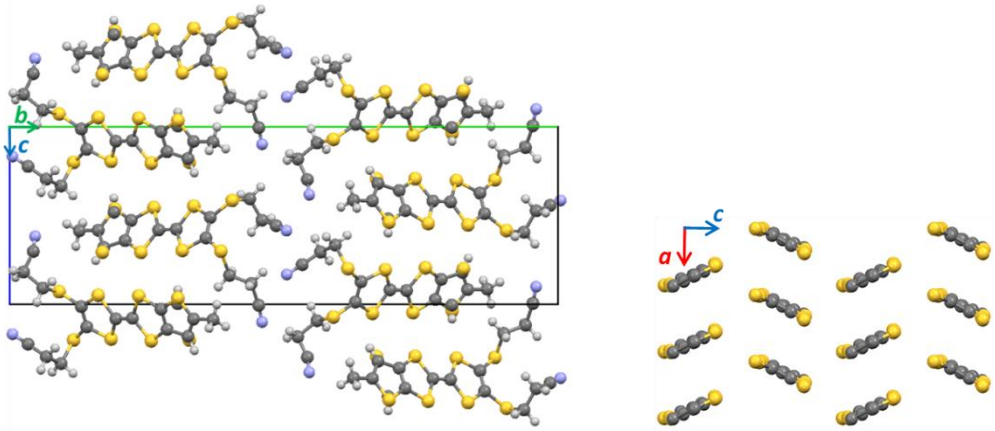

Figure S4. Crystal structure of compound **1**: (**a**) View along the *a* axis; (**b**) partial view along *b* of a layer showing the tilt between the molecules relatively to the chain axis *a* (the cyanoethyl group and hydrogen atoms were omitted for clarity).

Crystallographic data for compound 1: $C_{30}H_{24}N_4S_{14}$, M=889.37 g.mol^{-1}, monoclinic, space group $P2_1$, *a* = 5.1144(3)Å, *b* = 33.259(2)Å, *c* = 10.7953(7)Å, β = 90.104(4)°, V = 1836.3(2)Å^3, Z = 2, ρ_{calc} = 1.608 g.cm^{-3}, μ(Mo *K*α) = 0.859 mm^{-1}, 12015 reflections measured, 6023 unique [R_{int}=0.0511], θ_{max} = 25.026°, R1 = 0.0983 using 4256 Refl.>2σ(I), *ω*R2 = 0.2661, T = 150(2) K. CCDC 1817867.

1. Silva, R. A. L.; Vieira, B. J. C.; Andrade, M. A.; Santos, I. C.; Rabaça, S.; Belo, D.; Almeida, M. TTFs nonsymmetrically fused with alkylthiophenic moieties. *Beilstein J. Org. Chem.* **2015**, *11*, 628-637, DOI: 10.3762/bjoc.11.71.
2. Belo, D.; Figueira, M. J.; Nunes, J. P. M.; Santos, I. C.; Almeida, M.; Crivillers, N.; Rovira, C. Synthesis and characterization of the novel extended TTF-type donors with thiophenic units. *Inorg. Chim. Acta* **2007**, *360*, 3909-3914, DOI: 10.1016/j.ica.2007.03.041.

Table S1. Bond lengths in the crystal structure of (*n*-Bu_4N)[Au(α-mtdt)$_2$] (**3**).

(*n*-Bu_4N)$^+$	**d (Å)**	**[Au(α-mtdt)$_2$]$^-$**	**d (Å)**
C19-C20	1.530(10)	Au1-S8	2.3069(18)
C19-H19A	0.99	Au1-S2	2.3071(17)
C19-H19B	0.99	Au1-S9	2.326(2)
C20-C21	1.492(10)	Au1-S1	2.3262(19)
C20-H20A	0.99	S1-C1	1.764(6)
C20-H20B	0.99	S2-C2	1.753(7)
C21-C22	1.508(11)	S3-C1	1.764(7)
C21-H21A	0.99	S3-C3	1.767(7)
C21-H21B	0.99	S4-C2	1.756(6)
C22-H22A	0.98	S4-C3	1.769(7)
C22-H22B	0.98	S5-C6	1.743(7)
C22-H22C	0.98	S5-C4	1.770(7)
C23-C24	1.525(10)	S6-C5	1.742(8)
C23-H23A	0.99	S6-C4	1.757(7)
C23-H23B	0.99	S8-C10	1.748(8)
C24-C25	1.502(10)	S9-C11	1.752(7)
C24-H24A	0.99	S10-C12	1.766(8)
C24-H24B	0.99	S10-C10	1.781(6)
C25-C26	1.527(10)	S11-C11	1.759(7)
C25-H25A	0.99	S11-C12	1.772(7)
C25-H25B	0.99	S12-C15	1.759(8)
C26-H26A	0.98	S12-C13	1.780(7)
C26-H26B	0.98	S13-C14	1.748(7)
C26-H26C	0.98	S13-C13	1.754(8)
C27-C28	1.537(11)	N1-C23	1.511(9)
C27-H27A	0.99	N1-C27	1.511(10)
C27-H27B	0.99	N1-C19	1.518(9)
C28-C29	1.482(12)	N1-C31	1.533(10)
C28-H28A	0.99	C1-C2	1.326(9)
C28-H28B	0.99	C3-C4	1.337(9)
C29-C30	1.503(12)	C5-C6	1.360(10)
C29-H29A	0.99	C5-C7A	1.428(19)
C29-H29B	0.99	C5-S7	1.766(8)
C30-H30A	0.98	C6-C7	1.498(18)
C30-H30B	0.98	C6-S7A	1.722(9)
C30-H30C	0.98	C8-C7	1.321(18)
C31-C32A	1.492(16)	C8-C7A	1.37(2)
C31-C32	1.564(15)	C8-C9	1.507(9)
C31-H31A	0.99	C8-S7	1.703(9)
C31-H31B	0.99	C8-S7A	1.720(9)

Table S1. Bond lengths in the crystal structure of (*n*-Bu$_4$N)[Au(α-mtdt)$_2$] (**3**). (cont.)

(*n*-Bu$_4$N)$^+$	d (Å)
C34-C33	1.441(13)
C34-H34A	0.98
C34-H34B	0.98
C34-H34C	0.98
C33-C32	1.255(15)
C33-C32A	1.406(17)
C33-H33A	0.99
C33-H33B	0.99
C32-H32B	0.99
C32A-H32C	0.99
C32A-H32D	0.99

[Au(α-mtdt)$_2$]$^-$	d (Å)
C9-H9A	0.98
C9-H9B	0.98
C9-H9C	0.98
C10-C11	1.305(9)
C12-C13	1.333(9)
C14-C15	1.333(10)
C14-C16A	1.63(2)
C14-S14	1.695(10)
C15-S14A	1.643(10)
C15-C16	1.643(19)
C17-C16	1.48(2)
C17-C18	1.522(11)
C17-S14	1.556(11)
C17-C16A	1.557(19)
C17-S14A	1.567(12)
C18-H18A	0.98
C18-H18B	0.98
C18-H18C	0.98
C7-H7	0.95
C16-H16	0.95
C7A-H7A	0.95
C16A-H16A	0.95
C32-H32A	0.99

Table S2. Short S···S and hydrogen bonds in the crystal structure of (*n*-Bu$_4$N)[Au(α-mtdt)$_2$] (**3**).

	Symm. op.*	Length (Å)	Contact type
S1···S6	x,-1+y,z	3.603(2)	M-M C
S8···S4	x,-1+y,z	3.540(2)	M-M C
S8···S6	x,-1+y,z	3.652(3)	M-M C
S10···S2	x,-1+y,z	3.553(2)	M-M C
S12···S2	x,-1+y,z	3.691(3)	M-M C
S12···S9	x,-1+y,z	3.555(3)	M-M C
S11···S13	-x,-y,-z	3.547(3)	M-M C
S13···S13	-x,-y,-z	3.542(3)	M-M C
S3···S3	-x,1-y,1-z	3.619(2)	M-M C
S4···H9A-C9	-x,2-y,1-z	2.968 (150.72 °)	M-M W
S4···H19A-C19	1-x,1-y,1-z	3.021 (123.52 °)	M-TBA
S5···S7	-x,2-y,1-z	3.605(5)	M-M W
C5···H9C-C9	1-x,2-y,1-z	2.821 (83.09 °)	M-M L

Table S2. Short S···S and hydrogen bonds in the crystal structure of (*n*-Bu$_4$N)[Au(α-mtdt)$_2$] (**3**). (cont.)

	Symm. op.*	Length (Å)	Contact type
S13···H34B-C34	-1+x,y,-1+z	3.012 (162.78 °)	M-TBA
S10···H25B-C25	-x,-y,1-z	3.032 (127.34 °)	M-TBA
S12···H27A-C27	-x,-y,1-z	2.922 (152.17 °)	M-TBA
S4···H25A-C25	-x,1-y,1-z	3.034 (160.39 °)	M-TBA
S10···H31A-C31	1-x,-y,1-z	3.078 (107.21 °)	M-TBA
S2···H31A-C31	1-x,1-y,1-z	2.953 (160.10 °)	M-TBA

C - Between chains in the same layer; L - Between chains in different layers; M - Monoanion [Au(α-mtdt)$_2$]; TBA - Cation (*n*-Bu$_4$N); W - Along a chain.

Table S3. Bond lengths relative to tetrabutylammonium molecules A and B in the crystal structure of (*n*-Bu$_4$N)$_2$[Au$_2$(α-tbtdt)$_2$] (**5**).

A	d (Å)	B	d (Å)
N1-C33	1.509(10)	N2-C45	1.503(10)
N1-C29	1.511(10)	N2-C53	1.504(10)
N1-C25	1.526(11)	N2-C49	1.509(10)
N1-C37	1.526(10)	N2-C41	1.516(9)
C25-C26	1.523(12)	C41-C42	1.505(12)
C25-H25A	0.9900	C41-H41A	0.9900
C25-H25B	0.9900	C41-H41B	0.9900
C26-C27	1.515(13)	C42-C43	1.476(14)
C26-H26A	0.9900	C42-H42A	0.9900
C26-H26B	0.9900	C42-H42B	0.9900
C27-C28	1.453(15)	C43-C44	1.451(17)
C27-H27A	0.9900	C43-H43A	0.9900
C27-H27B	0.9900	C43-H43B	0.9900
C28-H28A	0.9800	C44-H44A	0.9800
C28-H28B	0.9800	C44-H44B	0.9800
C28-H28C	0.9800	C44-H44C	0.9800
C29-C30	1.498(12)	C45-C46	1.502(12)
C29-H29A	0.9900	C45-H45A	0.9900
C29-H29B	0.9900	C45-H45B	0.9900
C30-C31	1.472(13)	C46-C47	1.502(13)
C30-H30A	0.9900	C46-H46A	0.9900
C30-H30B	0.9900	C46-H46B	0.9900
C31-C32	1.490(14)	C47-C48	1.508(14)
C31-H31A	0.9900	C47-H47A	0.9900
C31-H31B	0.9900	C47-H47B	0.9900
C32-H32A	0.9800	C48-H48A	0.9800
C32-H32B	0.9800	C48-H48B	0.9800
C32-H32C	0.9800	C48-H48C	0.9800

Table S3. Bond lengths relative to tetrabutylammonium molecules A and B in the crystal structure of (n-$Bu_4N)_2[Au_2(\alpha$-tbtdt$)_2]$ (**5**). (cont.)

A	d (Å)
C33-C34	1.487(13)
C33-H33A	0.9900
C33-H33B	0.9900
C34-C36A	1.41(3)
C34-C35	1.61(3)
C34-H34A	0.9900
C34-H34B	0.9900
C37-C38	1.522(12)
C37-H37A	0.9900
C37-H37B	0.9900
C38-C39	1.538(12)
C38-H38A	0.9900
C38-H38B	0.9900
C39-C40	1.523(14)
C39-H39A	0.9900
C39-H39B	0.9900
C40-H40A	0.9800
C40-H40B	0.9800
C40-H40C	0.9800
C35-C36	1.488(17)
C35-H35A	0.9900
C35-H35B	0.9900
C36-H36A	0.9800
C36-H36B	0.9800
C36-H36C	0.9800
C35A-C36A	1.44(4)
C35A-H35C	0.9800
C35A-H35D	0.9800
C35A-H35E	0.9800
C36A-H36A	0.9900
C36A-H36B	0.9900

B	d (Å)
C49-C50	1.519(11)
C49-H49A	0.9900
C49-H49B	0.9900
C50-C51	1.504(12)
C50-H50A	0.9900
C50-H50B	0.9900
C51-C52	1.512(12)
C51-H51A	0.9900
C51-H51B	0.9900
C52-H52A	0.9800
C52-H52B	0.9800
C52-H52C	0.9800
C53-C54	1.530(12)
C53-H53A	0.9900
C53-H53B	0.9900
C54-C55	1.505(14)
C54-H54A	0.9900
C54-H54B	0.9900
C55-C56	1.517(16)
C55-H55A	0.9900
C55-H55B	0.9900
C56-H56A	0.9800
C56-H56B	0.9800
C56-H56C	0.9800

Table S4. Bond lengths of [$Au_2(\alpha\text{-tbtdt})_2$] molecules Au1 and Au2 in the crystal structure of (n-$Bu_4N)_2[Au_2(\alpha\text{-tbtdt})_2]$ (**5**).

Au1	d (Å)	Au2	d (Å)
Au1-S2	2.272(2)	Au2-S8	2.279(2)
Au1-S1	2.284(2)	Au2-S9	2.279(2)
Au1-Au1	3.0929(7)	Au2-Au2	3.0137(6)
S1-C1	1.755(9)	S8-C13	1.769(8)
S2-C2	1.723(10)	S9-C14	1.747(8)
S2-Au1	2.272(2)	S9-Au2	2.279(2)
S3-C3	1.748(9)	S10-C13	1.744(8)
S3-C1	1.766(11)	S10-C15	1.750(7)
S4-C3	1.754(10)	S11-C15	1.738(9)
S4-C2	1.769(9)	S11-C14	1.778(7)
S5-C5	1.734(10)	S12-C16	1.766(9)
S5-C4	1.761(9)	S12-C17	1.778(8)
S6-C6	1.742(11)	S13-C18	1.753(9)
S6-C4	1.761(9)	S13-C16	1.764(8)
C1-C2	1.345(13)	C13-C14	1.335(11)
C3-C4	1.348(12)	C15-C16	1.342(11)
C5-C6	1.368(14)	C17-C18	1.316(11)
C5-C7	1.405(18)	C17-C19A	1.438(18)
C5-S7A	1.734(19)	C17-S14	1.677(11)
C6-S7	1.666(11)	C18-C19	1.53(2)
C6-C7A	1.95(3)	C18-S14A	1.749(9)
C8-C7	1.307(18)	C19-H19	0.9500
C8-C7A	1.52(3)	C19A-H19A	0.9500
C8-C9	1.505(13)	C20-C19	1.34(2)
C8-S7A	1.737(18)	C20-C19A	1.393(17)
C8-S7	1.756(11)	C20-C21	1.490(11)
C9-C11	1.515(14)	C20-S14A	1.684(10)
C9-C10	1.535(13)	C20-S14	1.688(10)
C9-C12	1.548(13)	C21-C23A	1.35(3)
C10-H10A	0.9800	C21-C24	1.388(19)
C10-H10B	0.9800	C21-C22	1.538(18)
C10-H10C	0.9800	C21-C24A	1.58(3)
C11-H11A	0.9800	C21-C23	1.635(17)
C11-H11B	0.9800	C21-C22A	1.79(2)
C11-H11C	0.9800	C22-H22A	0.9800

Table S4. Bond lengths of [$Au_2(\alpha\text{-tbtdt})_2$] molecules Au1 and Au2 in the crystal structure of (n-$Bu_4N)_2[Au_2(\alpha\text{-tbtdt})_2$] (**5**). (cont.)

Au1	d (Å)
C12-H12A	0.9800
C12-H12B	0.9800
C12-H12C	0.9800
C7-H7	0.9500
C7A-H7A	0.9500

Au2	d (Å)
C22-H22B	0.9800
C22-H22C	0.9800
C23-H23A	0.9800
C23-H23B	0.9800
C23-H23C	0.9800
C24-H24A	0.9800
C24-H24B	0.9800
C24-H24C	0.9800
C22A-H22D	0.9800
C22A-H22E	0.9800
C22A-H22F	0.9800
C23A-H23D	0.9800
C23A-H23E	0.9800
C23A-H23F	0.9800
C24A-H24D	0.9800
C24A-H24E	0.9800
C24A-H24F	0.9800

Table S5. Short S···S and hydrogen bonds in the crystal structure of (n-$Bu_4N)_2[Au_2(\alpha\text{-tbtdt})_2$] (**5**).

	Symm. op.*	Length (Å)	Contact type
S4···S7	-x,-y,1-z	3.669(6)	Au1-Au1 W
S4···H7A-C7A	-x,-y,1-z	2.89 (149.35 °)	Au1-Au1 W
S6···S6	-x,-y,1-z	3.542(4)	Au1-Au1 W
S3···S7A	1-x,-y,1-z	3.5858	Au1-Au1 W
S3···H29B-C29	x,y,z	2.895 (144.73 °)	Au1-TBA
S3···H31A-C31	x,y,z	2.989 (153.64 °)	Au1-TBA
S1···H27A-C27	x,y,z	2.977 (162.09 °)	Au1-TBA
S7A···H31A-C31	x,1+y,z	2.886 (130.44 °)	Au1-TBA
S3···H53A-C53	x,y,z	2.992 (133.18 °)	Au1-TBA
S5···H53B-C53	x,y,z	2.912 (139.13 °)	Au1-TBA
S7A···H56A-C56	x,1+y,z	2.815 (108.68 °)	Au1-TBA
S7A···H56B-C56	x,1+y,z	2.827 (107.86 °)	Au1-TBA
S8···S12	-x,-y,-z	3.563(3)	Au2-Au2 W
S8···S14	-x,-y,-z	3.631(6)	Au2-Au2 W
S10···S12	-x,-y,-z	3.650(3)	Au2-Au2 W
C22A-H22F···S9	-1+x,y,z	2.881 (107.27 °)	Au2-Au2 W
S13···H23D-C23	-x,1-y,-z	2.992 (149.64 °)	Au2-Au2 W

Table S5. Short S···S and hydrogen bonds in the crystal structure of (n-Bu_4N)$_2$[Au_2(α-tbtdt)$_2$] (**5**). (cont.)

	Symm. op.*	**Length (Å)**	**Contact type**
Au2···H49B-C49	x,y,-1+z	2.873 (144.53 °)	Au2-TBA
S10···H49A-C49	x,y,-1+z	2.888 (158.65 °)	Au2-TBA
S11···H41A-C41	x,y,-1+z	2.834 (160.03 °)	Au2-TBA
Au2···H41B-C41	x,y,-1+z	2.831 (154.47 °)	Au2-TBA
S8···H54A-C54	x,y,-1+z	3.019 (146.95 °)	Au2-TBA
S14···H51B-C51	1+x,y,-1+z	2.941 (116.77 °)	Au2-TBA

TBA - Cation (n-Bu_4N); W - Along a chain