

C_2 -Symmetric chiral tetrathiafulvalene-bis(oxazolines) (TTF-BOX): new precursors for organic materials and electroactive metal complexes

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SUPPORTING INFORMATION

Experimental section

General comments. Dry CH₂Cl₂ was obtained by distillation over P₂O₅, THF was distilled over sodium and benzophenone, and toluene was distilled over sodium. Nuclear magnetic resonance spectra were recorded on a Bruker Avance DRX 500 spectrometer operating at 500.04 MHz for ¹H and 125.75 MHz for ¹³C. Chemical shifts are expressed in parts per million (ppm) downfield from external TMS. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. MALDI-TOF MS spectra were recorded on a Bruker Biflex-IIIITM apparatus, equipped with a 337nm N₂ laser. Elemental analyses were performed by the "Service d'Analyse du CNRS" at Gif/Yvette, France.

2-(*S*)-N-(1-Hydroxy-propyl)-EDT-TTF-diamide 2a

EDT-TTF-bis(methylcarboxylate) (3.0 g, 7.3 mmol) and (*S*)-alaninol (1.4 mL, 18.3 mmol) were added in a Schlenk flask with 3 mL of toluene. NaH (4 mg, 0.2 mmol; 60% dispersion in mineral oil) was then added into the flask under nitrogen, which was sealed and placed at 70 °C. After 12 h the mixture was filtered, and then washed thoroughly with dichloromethane (50 mL). The remaining solid was dissolved in THF (200 mL) and filtered. After evaporation, we obtained an orange powder (2.7 g, 5.5 mmol, yield 75%) pure enough to be used for the next step without further purification.

mp 148-150 °C. ¹H NMR (DMSO-d₆) δ (ppm) 1.04 (d, ³J = 7.0 Hz, 6H, Me), 3.28 (m, 2H, OCH₂), 3.25 (m, 2H, OCH₂), 3.39 (s, 4H, S(CH₂)₂S), 3.81 (m, 2H, NCH), 4.76 (t, ³J = 5.5 Hz, 2H, OH), 8.54 (d, ³J = 8.0 Hz, 2H, NH); MALDI-TOF-MS m/z = 495.9 (M⁺). Anal. Calc. for C₁₆H₂₀N₂O₄S₆: C 38.69, H 4.06, N 5.64. Found: C 41.98, H 4.49, N 5.21%.

2-(*R*)-N-(1-Hydroxy-propyl)-EDT-TTF-diamide 2b

By the same procedure, from 1 g of EDT-TTF-diester (2.4 mmol) and 0.57 mL of (*R*)-alaninol (7.3 mmol). 830 mg of an orange powder (1.7 mmol, Yield: 70%). Analyses are identical to the previous compound.

EDT-TTF-bis-((*S*)-2-(4-methyl-oxazoline)) 3a

To solution of bis(hydroxyamide) **2a** (1.3 g, 2.7 mmol) and NEt₃ (1.5 mL, 10.8 mmol) in THF (100 mL), methanesulfonyl chloride (MsCl) (0.83 mL, 10.8 mmol) was added and, after 0.5 h of stirring at 0 °C, NEt₃ (6.8 mL, 49 mmol) was further added and the reaction mixture thus obtained was heated at 70 °C for 40 h. After evaporation the product was purified by

chromatography on silica gel (dichloromethane : ethyl acetate 10:1) to obtain 0.6 g (1.3 mmol, yield 48%) of an orange powder.

mp 163-164°C. ^1H NMR (CDCl_3) δ (ppm) 1.30 (d, $^3J = 6.5$ Hz, 6H, Me), 3.29 (s, 4H, $\text{S}(\text{CH}_2)_2\text{S}$), 3.89 (t, $^3J = ^2J = 8$ Hz, 2H, OCH_2), 4.29 (m, 2H, NCH), 4.44 (t, $^3J = ^2J = 9.5$ Hz, 2H, OCH_2); ^{13}C NMR (CDCl_3) δ (ppm) 20.9 (CH_3), 30.1 ($\text{S}(\text{CH}_2)\text{-S}$), 62.2 (CHCH_3), 74.9 (OCH_2), 108.9-112.0-113.9-126.3 ($\text{C}=\text{C}$), 155.5 ($\text{C}=\text{N}$); MALDI-TOF-MS $m/z = 460.0$ (M^+). IR (cm^{-1}) 2957-2917-2888 (C-H), 1710 ($\text{C}=\text{N}$), 1654-1621-1567 ($\text{C}=\text{C}$). Anal. Calc. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{S}_6$: C 41.71, H 3.50, N 6.08. Found: C 41.63, H 3.36, N 5.97%.

EDT-TTF-bis-((*R*)-2-(4-methyl-oxazoline)) **3b**

The same reaction provided, starting from 500 mg of compound **2b** (1.00 mmol), 180 mg of an orange powder (0.39 mmol, yield 39%). Analyses are identical to those obtained for the compound **3a**.

(**3a**) $\text{Mo}(\text{CO})_4$ **4a**

$\text{Mo}(\text{CO})_4(\text{piperidine})_2$ (25 mg, 65 μmol) and **3a** (23 mg, 50 μmol) were dissolved in CH_2Cl_2 (30 ml) and the solution heated to reflux for 1.5 h. The orange solution became dark red. After partial evaporation of the solvent, the product was purified by chromatography on silica gel (dichloromethane) to obtain 29 mg of a brown powder (44 μmol , yield 87%).

^1H NMR (CDCl_3) δ (ppm) 1.50 (d, $^3J = 6.5$ Hz, 6H, Me), 3.32 (s, 4H, $\text{S}(\text{CH}_2)_2\text{S}$), 4.09 (t, $^3J = ^2J = 7.5$ Hz, 2H, OCH_2), 4.28 (m, 2H, NCH), 4.60 (t, $^3J = ^2J = 9.5$ Hz, 2H, OCH_2); MALDI-TOF-MS $m/z = 460.7$ [$\text{M-Mo}(\text{CO})_4$] $^+$, 557.6 [M-4CO] $^+$, 641.5 [M-CO] $^+$; IR (cm^{-1}) 2966-2923 (C-H), 2008-1889-1860-1818 ($\text{C}\equiv\text{O}$), 1630-1621-1577 ($\text{C}=\text{C}$, $\text{C}=\text{N}$).

(**3a**) $\text{W}(\text{CO})_4$ **5a**

The same procedure was repeated with the precursor $\text{W}(\text{CO})_4(\text{piperidine})_2$ (30 mg, 65 μmol) and **3a** (23 mg, 50 μmol) in 30 mL of CH_2Cl_2 . The mixture was concentrated under vacuum and was purified on silica gel (dichloromethane) to afford 32 mg of a brown powder (42 μmol , yield:85%).

^1H NMR (CDCl_3) δ (ppm) 1.52 (d, $^3J = 6.5$ Hz, 6H, Me), 3.32 (s, 4H, $\text{S}(\text{CH}_2)_2\text{S}$), 4.14 (t, $^3J = ^2J = 7.5$ Hz, 2H, OCH_2), 4.34 (m, 2H, NCH), 4.62 (t, $^3J = ^2J = 9.5$ Hz, 2H, OCH_2); ^{13}C NMR (CDCl_3) δ (ppm) 21.1 (CH_3), 30.0 ($\text{S}(\text{CH}_2)\text{-S}$), 68.2 (CHCH_3), 75.4 (OCH_2), 106.5-113.9-114.4-129.6 ($\text{C}=\text{C}$), 160.6 ($\text{C}=\text{N}$), 203.9-212.0 ($\text{C}\equiv\text{O}$); MALDI-TOF-MS $m/z = 460.7$ [M -

$W(CO)_4]^+$, 643.5 $[M-4CO]^+$, 727.5 $[M-CO]^+$; IR (cm^{-1}) 2970-2924 (C-H), 2002-1882-1834-1801 ($C\equiv O$), 1631-1621-1579 (C=C, C=N).

X-Ray Structure Determinations. Details about data collection and solution refinement are given in Table S1. X-ray diffraction measurements were performed on a Bruker Kappa CCD diffractometer for the compounds **3a** and **5a** and on a Stoe Imaging Plate diffractometer system for **4a**, both operating with a Mo-K α ($\lambda = 0.71073$ Å) X-ray tube with a graphite monochromator. The structures were solved (SHELXS-97) by direct methods and refined (SHELXL-97) by full-matrix least-square procedures on F^2 .¹ All non-H atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations but not refined.

Table S1 Crystallographic data, details of data collection and structure refinement parameters.

compound	3a	4a	5a
formula	C ₁₆ H ₁₆ N ₂ O ₂ S ₆	C ₂₀ H ₁₆ MoN ₂ O ₆ S ₆	C ₂₀ H ₁₆ N ₂ O ₆ S ₆ W
mw	460.67	668.65	756.56
cryst. syst.	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1$	$P2_1$
a (Å)	5.0250(3)	7.9794(9)	7.9843(3)
b (Å)	17.6060(12)	12.1549(9)	12.1519(16)
c (Å)	11.9010(12)	13.5558(15)	13.4532(13)
α (deg)	90.00	90.00	90.00
β (deg)	101.87(2)	93.397(13)	93.646(5)
γ (deg)	90.00	90.00	90.00
V (Å ³)	1030.37(14)	1312.5(2)	1302.6(2)
Z	2	2	2
d_{calcd} , g cm ⁻³	1.485	1.692	1.929
μ (mm ⁻¹)	0.677	1.016	4.954
Flack parameter	-0.06(8)	-0.01(5)	-0.020(5)
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
No. of unique refl.	3807	4878	5803
No. of obs. refl.	2687	3963	5335
R_1, wR_2 (obs. data) ^a	0.038, 0.072	0.038, 0.087	0.023, 0.047
R_1, wR_2 (all data) ^a	0.075, 0.081	0.054, 0.097	0.029, 0.051

$$^a R(F_o) = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}; R_w(F_o^2) = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2}.$$

¹ G. M. Sheldrick, *Programs for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1996.

X-Ray structure of 3a

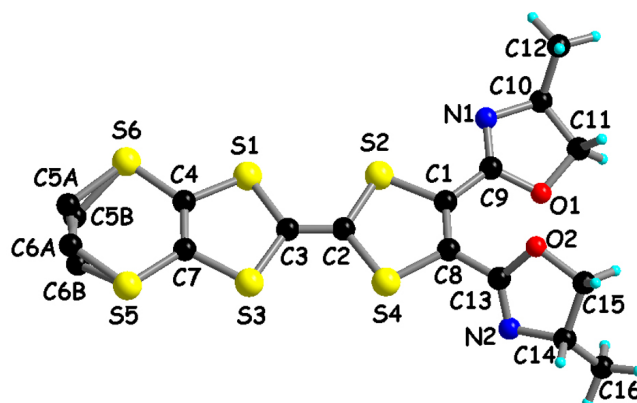


Fig. S1 Molecular structure of **3a** along with the numbering scheme.

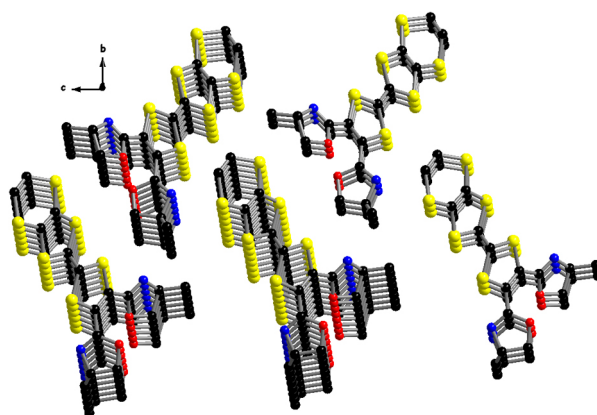


Fig. S2 Packing diagram of **3a**. The disorder on the ethylene bridge is not shown.

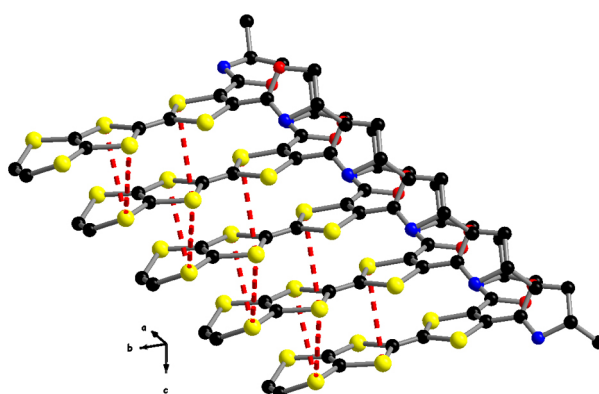


Fig. S3 Uniform stacking of donors along *a* in the structure of **3a**. The S...S contacts shorter than 4 Å are highlighted. The disorder on the ethylene bridge is not shown.

Bond Lengths (Å)

C1 C8 1.342(4)	C1 C9 1.454(4)	C1 S2 1.754(3)	C2 C3 1.346(4)
C2 S4 1.755(3)	C2 S2 1.755(3)	C3 S3 1.749(4)	C3 S1 1.766(3)
C4 C7 1.339(5)	C4 S6 1.748(4)	C4 S1 1.749(3)	C5A C6B 1.44(2)
C5A S6 1.817(16)	C5B C6A 1.585(18)	C5B S6 1.822(16)	C6A S5 1.746(11)
C6B S5 1.839(11)	C7 S5 1.744(3)	C7 S3 1.756(4)	C8 C13 1.468(5)
C8 S4 1.746(3)	C9 N1 1.253(4)	C9 O1 1.358(4)	C10 N1 1.473(4)
C10 C11 1.506(6)	C10 C12 1.522(5)	C11 O1 1.438(4)	C13 N2 1.243(4)
C13 O2 1.352(4)	C14 C16 1.478(5)	C14 N2 1.481(4)	C14 C15 1.495(5)
C15 O2 1.460(4)			

Bond Angles (°)

C8 C1 C9 128.2(3)	C8 C1 S2 117.8(2)	C9 C1 S2 113.9(2)
C3 C2 S4 123.4(3)	C3 C2 S2 121.7(3)	S4 C2 S2 114.9(2)
C2 C3 S3 124.2(3)	C2 C3 S1 120.8(3)	S3 C3 S1 114.93(19)
C7 C4 S6 127.9(3)	C7 C4 S1 117.8(3)	S6 C4 S1 114.24(19)
C6B C5A S6 115.7(11)	C6A C5B S6 106.6(8)	C5B C6A S5 115.7(9)
C5A C6B S5 111.0(10)	C4 C7 S5 126.9(3)	C4 C7 S3 117.4(2)
S5 C7 S3 115.6(2)	C1 C8 C13 127.4(3)	C1 C8 S4 117.2(2)
C13 C8 S4 115.4(2)	N1 C9 O1 118.2(3)	N1 C9 C1 124.4(3)
O1 C9 C1 117.4(3)	N1 C10 C11 103.8(3)	N1 C10 C12 111.1(4)
C11 C10 C12 113.7(3)	O1 C11 C10 104.1(3)	N2 C13 O2 118.7(3)
N2 C13 C8 125.9(3)	O2 C13 C8 115.3(3)	C16 C14 N2 111.2(3)
C16 C14 C15 114.1(4)	N2 C14 C15 103.8(3)	O2 C15 C14 104.9(3)
C9 O1 C11 104.8(3)	C13 O2 C15 104.4(3)	C9 N1 C10 106.5(3)
C13 N2 C14 107.2(3)	C4 S1 C3 94.61(16)	C1 S2 C2 94.64(16)
C3 S3 C7 94.85(17)	C8 S4 C2 95.19(16)	C7 S5 C6A 104.3(4)
C7 S5 C6B 97.1(4)		

X-Ray structure of 4a

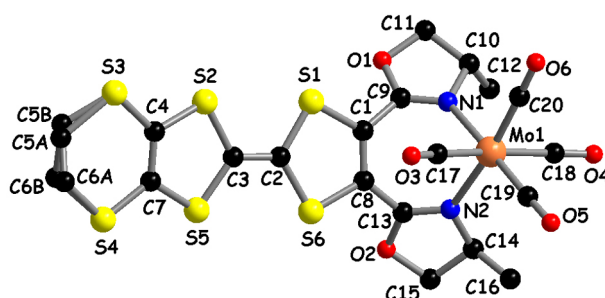


Fig. S4 Molecular structure of **4a** along with the numbering scheme. H atoms are omitted.

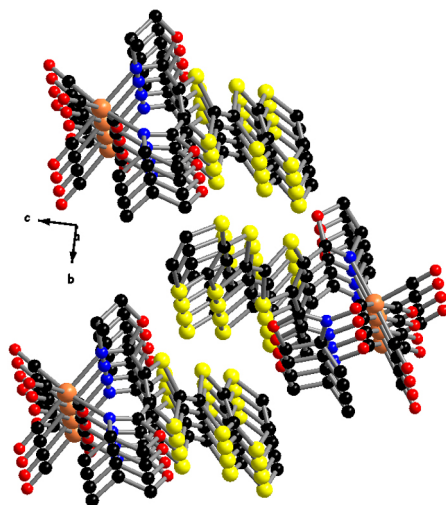


Fig. S5 Packing diagram of **4a**. Short lateral S...S contacts along *b* are measured between 3.6 and 3.8 Å. The disorder on the ethylene bridge is not shown.

Bond Lengths (Å)

Mo1 C20 1.928 (8)	Mo1 C19 1.938 (7)	Mo1 C18 2.018 (5)	Mo1 C17 2.034 (6)
Mo1 N1 2.260 (4)	Mo1 N2 2.277 (4)	S1 C1 1.729 (5)	S1 C2 1.744 (6)
S2 C4 1.744 (5)	S2 C3 1.752 (6)	S3 C5B 1.65 (3)	S3 C4 1.733 (6)
S3 C5A 1.91 (3)	S4 C6B 1.702 (18)	S4 C7 1.724 (6)	S4 C6A 1.739 (18)
S5 C3 1.738 (6)	S5 C7 1.742 (5)	S6 C8 1.748 (5)	S6 C2 1.749 (6)
O1 C9 1.342 (6)	O1 C11 1.463 (6)	O2 C13 1.333 (6)	O2 C15 1.466 (7)
O3 C17 1.130 (7)	O4 C18 1.152 (6)	O5 C19 1.173 (8)	O6 C20 1.182 (9)
N1 C9 1.273 (6)	N1 C10 1.482 (6)	N2 C13 1.291 (6)	N2 C14 1.479 (7)
C1 C8 1.342 (9)	C1 C9 1.465 (7)	C2 C3 1.373 (7)	C4 C7 1.356 (9)
C5A C6B 1.32 (4)	C5B C6A 1.59 (4)	C8 C13 1.460 (7)	C10 C12 1.499 (8)
C10 C11 1.518 (8)	C14 C16 1.494 (10)	C14 C15 1.504 (9)	

Bond Angles (°)

C20 Mo1 C19 88.6 (3)	C20 Mo1 C18 86.7 (3)	C19 Mo1 C18 82.9 (3)
C20 Mo1 C17 87.4 (3)	C19 Mo1 C17 85.8 (3)	C18 Mo1 C17 167.4 (2)
C20 Mo1 N1 93.2 (3)	C19 Mo1 N1 178.1 (2)	C18 Mo1 N1 96.5 (2)
C17 Mo1 N1 94.9 (2)	C20 Mo1 N2 172.3 (3)	C19 Mo1 N2 99.0 (2)
C18 Mo1 N2 95.6 (2)	C17 Mo1 N2 91.7 (2)	N1 Mo1 N2 79.16 (15)
C1 S1 C2 94.9 (3)	C4 S2 C3 94.7 (3)	C5B S3 C4 104.1 (12)
C5B S3 C5A 12 (2)	C4 S3 C5A 99.9 (9)	C6B S4 C7 100.2 (8)
C6B S4 C6A 30.4 (8)	C7 S4 C6A 105.3 (6)	C3 S5 C7 94.7 (3)

C8 S6 C2 94.8(3) C9 O1 C11 105.5(4) C13 O2 C15 105.3(4)
C9 N1 C10 106.7(4) C9 N1 Mo1 127.4(3) C10 N1 Mo1 125.8(3)
C13 N2 C14 106.2(4) C13 N2 Mo1 127.5(3) C14 N2 Mo1 126.2(3)
C8 C1 C9 125.3(4) C8 C1 S1 118.3(4) C9 C1 S1 116.2(4)
C3 C2 S1 121.9(5) C3 C2 S6 122.7(4) S1 C2 S6 115.2(3)
C2 C3 S5 123.7(5) C2 C3 S2 121.2(5) S5 C3 S2 115.1(3)
C7 C4 S3 128.0(4) C7 C4 S2 116.7(4) S3 C4 S2 115.2(3)
C6B C5A S3 120.3(19) C6A C5B S3 117.6(17) C5B C6A S4 117.8(15)
C5A C6B S4 119(2) C4 C7 S4 127.0(4) C4 C7 S5 117.5(4)
S4 C7 S5 115.5(4) C1 C8 C13 127.2(5) C1 C8 S6 116.8(4)
C13 C8 S6 115.9(5) N1 C9 O1 118.0(4) N1 C9 C1 127.5(5)
O1 C9 C1 114.5(4) N1 C10 C12 109.3(5) N1 C10 C11 103.1(4)
C12 C10 C11 112.6(5) O1 C11 C10 103.7(4) N2 C13 O2 118.4(4)
N2 C13 C8 127.8(5) O2 C13 C8 113.8(4) N2 C14 C16 112.9(6)
N2 C14 C15 104.1(4) C16 C14 C15 113.0(7) O2 C15 C14 104.7(5)
O3 C17 Mo1 172.6(6) O4 C18 Mo1 170.0(5) O5 C19 Mo1 178.4(6)
O6 C20 Mo1 178.2(6)

X-Ray structure of 5a

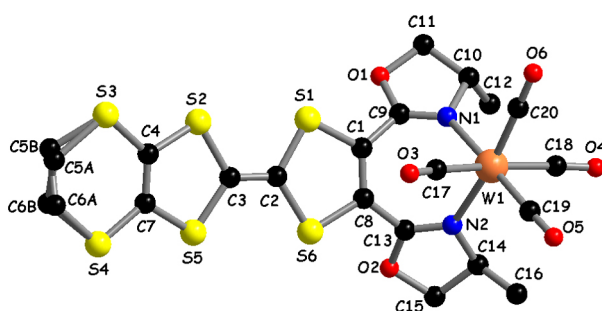


Fig. S6 Molecular structure of **5a** along with the numbering scheme. H atoms are omitted.

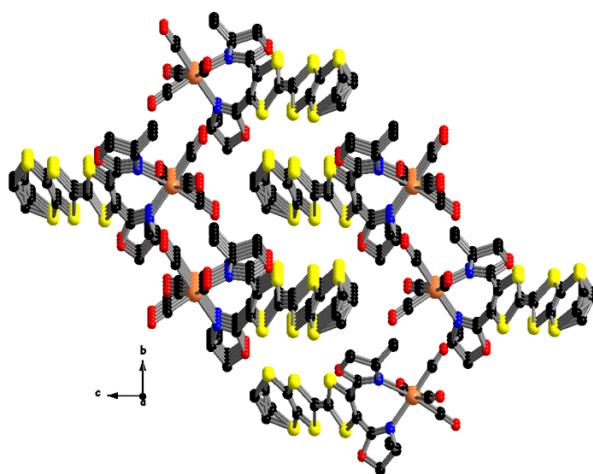


Fig. S7 Packing diagram of **5a**. Short lateral S...S contacts along *b* are measured between 3.6 and 3.8 Å. The disorder on the ethylene bridge is not shown.

Bond Lengths (Å)

W1 C20 1.954 (6)	W1 C19 1.955 (5)	W1 C18 2.012 (4)	W1 C17 2.028 (4)
W1 N1 2.239 (3)	W1 N2 2.250 (4)	S1 C1 1.736 (4)	S1 C2 1.755 (5)
S2 C4 1.748 (4)	S2 C3 1.760 (5)	S3 C5B 1.728 (18)	S3 C4 1.747 (4)
S3 C5A 1.864 (17)	S4 C6B 1.707 (15)	S4 C7 1.740 (5)	S4 C6A 1.753 (16)
S5 C3 1.752 (5)	S5 C7 1.755 (5)	S6 C8 1.754 (5)	S6 C2 1.757 (5)
O1 C9 1.349 (5)	O1 C11 1.464 (5)	O2 C13 1.335 (5)	O2 C15 1.447 (6)
O3 C17 1.135 (6)	O4 C18 1.138 (4)	O5 C19 1.155 (6)	O6 C20 1.148 (7)
N1 C9 1.265 (5)	N1 C10 1.494 (5)	N2 C13 1.282 (5)	N2 C14 1.493 (5)
C1 C8 1.330 (8)	C1 C9 1.465 (5)	C2 C3 1.342 (6)	C4 C7 1.313 (8)
C5A C6B 1.50 (2)	C8 C13 1.474 (6)	C10 C11 1.513 (7)	C10 C12 1.515 (7)
C14 C16 1.483 (9)	C14 C15 1.500 (8)		

Bond Angles (°)

C20 W1 C19 89.3 (3)	C20 W1 C18 87.5 (3)	C19 W1 C18 82.9 (3)	C20 W1 C17 87.1 (3)
C19 W1 C17 86.0 (2)	C18 W1 C17 167.7 (2)	C20 W1 N1 92.7 (2)	C19 W1 N1 177.9 (2)
C18 W1 N1 96.5 (2)	C17 W1 N1 94.77 (19)	C20 W1 N2 171.6 (2)	C19 W1 N2 98.8 (2)
C18 W1 N2 95.53 (17)	C17 W1 N2 91.37 (18)	N1 W1 N2 79.24 (13)	C1 S1 C2 94.9 (2)
C4 S2 C3 94.6 (2)	C5B S3 C4 102.0 (7)	C5B S3 C5A 20.2 (6)	C4 S3 C5A 102.1 (6)
C6B S4 C7 99.1 (6)	C6B S4 C6A 29.8 (6)	C7 S4 C6A 104.7 (6)	C3 S5 C7 94.4 (3)
C8 S6 C2 94.6 (3)	C9 O1 C11 104.8 (3)	C13 O2 C15 104.9 (4)	C9 N1 C10 106.4 (3)
C9 N1 W1 127.9 (3)	C10 N1 W1 125.5 (3)	C13 N2 C14 105.8 (4)	C13 N2 W1 128.4 (3)

C14 N2 W1 125.7(3) C8 C1 C9 125.4(3) C8 C1 S1 118.2(3) C9 C1 S1 116.1(3)
C3 C2 S1 121.9(4) C3 C2 S6 123.3(4) S1 C2 S6 114.8(2) C2 C3 S5 123.8(4)
C2 C3 S2 122.1(4) S5 C3 S2 113.9(2) C7 C4 S3 128.1(3) C7 C4 S2 117.4(3)
S3 C4 S2 114.4(3) C6B C5A S3 114.3(11) C6A C5B S3 113.5(11) C5B C6A S4
117.7(10)
C5A C6B S4 113.1(10) C4 C7 S4 127.7(3) C4 C7 S5 118.0(3) S4 C7 S5 114.2(4)
C1 C8 C13 127.0(4) C1 C8 S6 117.4(3) C13 C8 S6 115.6(5) N1 C9 O1 118.6(4)
N1 C9 C1 127.1(4) O1 C9 C1 114.3(3) N1 C10 C11 102.9(3) N1 C10 C12 108.5(4)
C11 C10 C12 111.8(4) N1 C10 H10 111.1 O1 C11 C10 104.3(4) N2 C13 O2 118.9(4)
N2 C13 C8 127.1(4) O2 C13 C8 114.0(4) C16 C14 N2 113.6(5) C16 C14 C15 114.0(6)
N2 C14 C15 103.2(4) O2 C15 C14 105.8(4) O3 C17 W1 172.1(5) O4 C18 W1 170.4(5)
O5 C19 W1 178.3(5) O6 C20 W1 178.6(6)

Circular dichroism measurements. Circular dichroism spectra were recorded using spectrometric grade solvents in a 1 cm cell at sample concentrations of 10^{-3} to 10^{-5} M using a Jasco J-720 Spectropolarimeter and were analyzed using the associated J700 software.

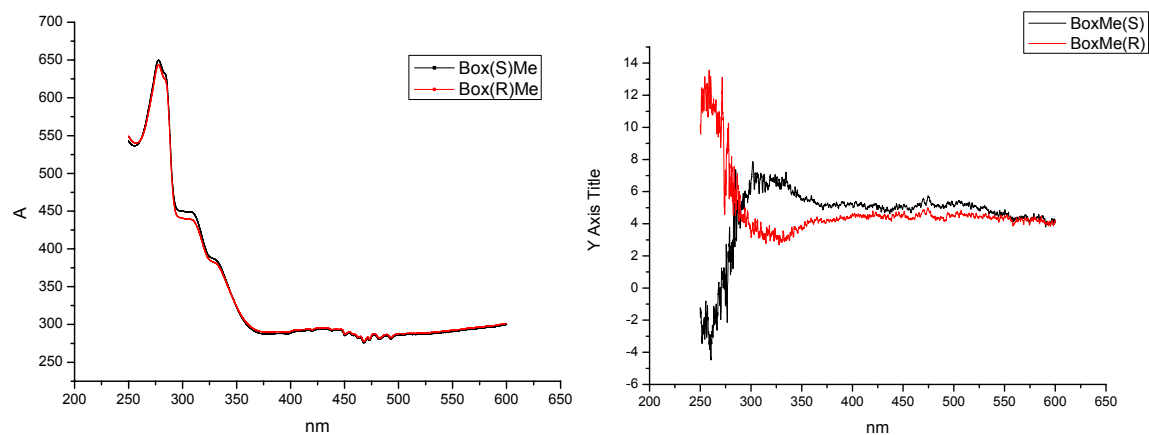


Fig. S8 UV-Visible absorption spectra of **3a-b** in CH₂Cl₂ (left). CD spectra of **3a-b** in CH₂Cl₂ (right). The Cotton effects are centered at $\lambda_{\text{max}} = 313$ nm and 259 nm.

Electrochemical studies. Cyclic voltammetry measurements were performed using a three-electrode cell equipped with a platinum millielectrode of 0.126 cm² area, an Ag/Ag⁺ pseudo-reference and a platinum wire counter-electrode. The potential values were then re-adjusted with respect to the saturated calomel electrode (SCE). The electrolytic media involved a 0.1 mol.L⁻¹ solution of (*n*-Bu₄N)PF₆ in CH₃CN. All experiments have been performed at room temperature at 0.1 V·s⁻¹. Experiments have been carried out with an EGG PAR 273A potentiostat with positive feedback compensation.

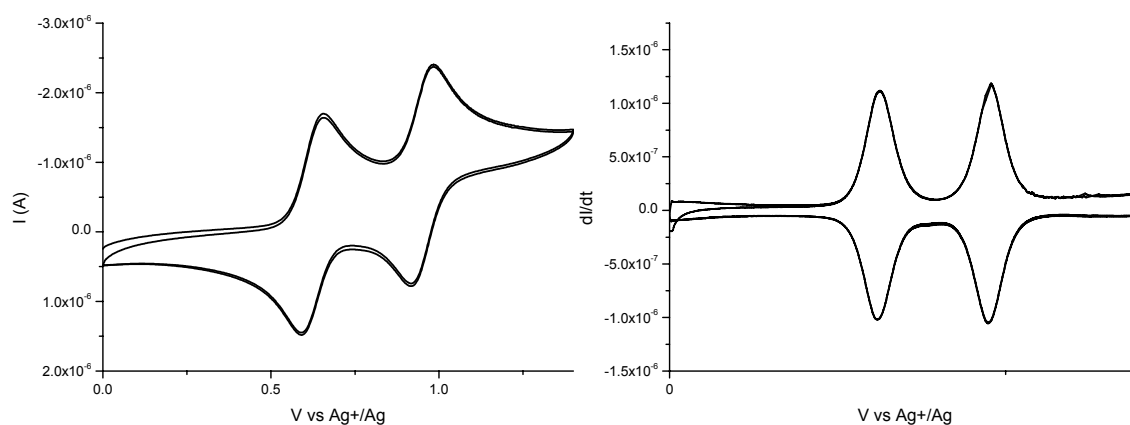


Fig. S9 Cyclic voltammetry of **3a** (normal and deconvoluted curves).

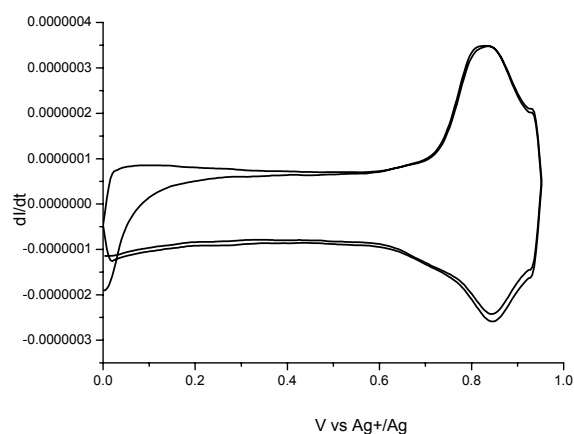


Fig. S10 Cyclic voltammetry of **4a** (deconvoluted curve). Only the first oxidation process is shown.

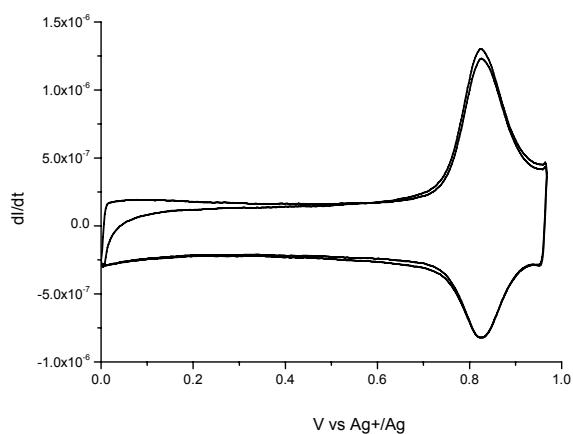


Fig. S11 Cyclic voltammetry of **5a** (deconvoluted curve). Only the first oxidation process is shown.

Table S2 Oxidation potentials from cyclic voltammetry data. Measurements have been performed in MeCN in the presence of (*n*-Bu₄N)PF₆ (0.1 M) at a scan rate of 0.1 V·s⁻¹.

compound	E ¹ _{1/2} (V)	E ² _{1/2} (V)	E ³ _{1/2} (V)	E ⁴ _{1/2} (V)
3a	0.57	0.90		
4a	0.48	0.70 ^a	0.84 ^a	1.01 ^a
5a	0.49	0.73 ^a	1.06 ^a	1.26 ^a

^a Partially reversible process