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Functionalisation reactions of 2,5-diphenyl-1,3,4-oxadiazoles bearing a terminal ethynyl or butadiynyl substituent: X-ray crystal structures of the products

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2-(4-*tert*-Butylphenyl)-5-(4-ethynylphenyl)-1,3,4-oxadiazole **1** and the butadiyne analogue **2** reacted with triethyl orthoformate in the presence of zinc iodide to give the acetal derivatives **3** and **4** which were hydrolysed with Amberlyst-15 in acetone-water to afford the alkynylaldehyde derivatives **5** and **6** in high yields. The reaction of 4,5-bis(methoxycarbonyl)-2-tributylphosphonium-1,3-dithiole tetrafluoroborate salt **7** with **5** (*n*BuLi, THF) gave the Wittig product 2-(3-{4-[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl]phenyl}prop-2-ynylidene)-1,3-dithiole-4,5-dimethyl dicarboxylate **11** (33% yield) whereas other attempted Wittig and Horner–Wadsworth–Emmons reactions led to the unexpected loss of the aldehyde group from compounds **5** and **6** to give **1** and **2**, respectively. The X-ray crystal structures of compounds **3**, **4**, **5** and **11** are reported: the π-systems of all four molecules adopt predominantly planar conformations. A comparison of bond lengths in the structures of **5** and **11** reveals extended π-conjugation in the latter.

Introduction

2,5-Diaryl-1,3,4-oxadiazole derivatives have enjoyed widespread use in organic chemistry due to their high photoluminescence quantum yield and their good thermal and chemical stabilities.[1] These properties, combined with the electron-deficient nature of the oxadiazole ring, have led to their application as electron-transporting/hole-blocking (ECHB) materials in multilayer and blended organic light emitting devices (OLEDs).[2] Low molecular weight diaryloxadiazoles,[3] star-shaped oligomers[4] and polymeric derivatives (with the oxadiazole units as pendant groups or in the main chain)[5] have been studied in this context.

In recent years there has been a renaissance in the chemistry of new alkyne and diyne systems. Their syntheses have been greatly facilitated by developments in organometallic coupling methodology, notably the Sonogashira reaction,[6] and their sp carbon frameworks provide interesting rigid molecular architectures, the structures of which are simplified compared to alkene analogues due to the lack of *E*/*Z* isomerism. The extent of conjugation through sp hybridised carbon frameworks continues to be widely debated among experimentalists[7] and theoreticians,[7,8] and the potential of ethynyl derivatives of arenes and heteroarenes to function as "molecular wires" is a hot topic.[9] For example, ethynyl and butadiynyl derivatives of porphyrins,[10] tetrathiafulvalenes[11] and organometallic complexes[12] have been synthesised as building blocks for studies in this field.

In this paper we combine these two contemporary themes (*i.e.* diaryl-1,3,4-oxadiazole and alkyne/diyne chemistry) and describe reactions involving the terminal ethynyl and butadiynyl units of the new 2,5-diphenyl-1,3,4-oxadiazole derivatives **1** and **2**, along with X-ray crystal structures of four of the products obtained.

Results and discussion

Compounds **1** and **2** have recently been synthesised in our laboratory.[13] Initial attempts at functionalisation of the terminal *sp* carbon atoms in **1** and **2** by deprotonation (with NaH, DBU, LDA or *t*-BuLi) and reaction with 4-ethoxybenzaldehyde or DMF) gave no substituted product. Starting material was recovered in high yields in all cases. However, functionalisation of both **1** and **2** proceeded smoothly using Gorgues' protocol (triethyl orthoformate in the presence of zinc iodide)[14] to afford **3** and **4** in 85% and 77% yields, respectively (Scheme 1). Compounds **3** and **4** were surprisingly resistant to hydrolysis under classical acidic conditions. However, reaction of **3** with pure formic acid in chloroform at <10 °C gave the corresponding aldehyde **5** (57% yield). Under these conditions compound **4** decomposed and **6** could not be isolated. However, the method of choice for this hydrolysis was treatment of **3** or **4** with the ion exchange resin Amberlyst-15 in acetone–water,[15] which gave aldehydes **5** and **6** in >95% yield.

In attempts to extend further the π-electron conjugated system, we explored Wittig and Horner–Wadsworth–Emmons reactions of **5** and **6** with a range of 2-trialkylphosphonium-1,3-dithiole salts **7**–**9** and the related phosphonate ester derivatives **10**, under standard conditions[16] (*n*BuLi or LDA in THF). Numerous reactions were tried [specifically: all the salts **7**–**9** with **5**; and **7**, **8** and **9** (R = Ph and *n*-Bu, R^1 = Me, SC_5H_{11}) and **10** (R^1 = Me, SC_5H_{11} and CH_2OAc) with **6**]. With one exception (see below), the only compounds isolated after chromatographic purification were recovered starting materials **5** or **6** (45–65% yields) and the terminal alkynes **1** or **2** (25–45% yields). The mechanism by which the aldehyde group is lost under these conditions is at present not known. The exception was the isolation of compound **11** (33% yield) from the reaction of salt **7** with **5** (*n*BuLi, THF). Compound **11** is an air-stable, yellow–orange crystalline solid (λ_{max} 384 nm in CH_2Cl_2). The cyclic voltammogram of **11** displays the typical quasi-reversible one-electron oxidation wave of a 1,3-dithiol-2-ylidene unit[17] at E^{ox} +0.95 V (in CH_2Cl_2) or +0.84 V (in MeCN) *vs* Ag/AgCl.

It is known that complexation of alkyne or butadiyne units to $Co_2(CO)_6$ clusters masks the reactivity of the triple bond(s).[18] We sought, therefore, to enhance the reactivity of the aldehyde group of **5** and **6** in Wittig reactions by using the derived cobalt carbonyl complexes **12** and **13** which were readily obtained in high yields. Complex **12** was obtained by reaction of dicobalt octacarbonyl with **5**; compound **13** was obtained *via* the tetracobalt complex **14** of the acetal **4**. However, no reaction was observed between **12** and reagents **7** and **8**, under the conditions described above: starting material **12** was recovered in high

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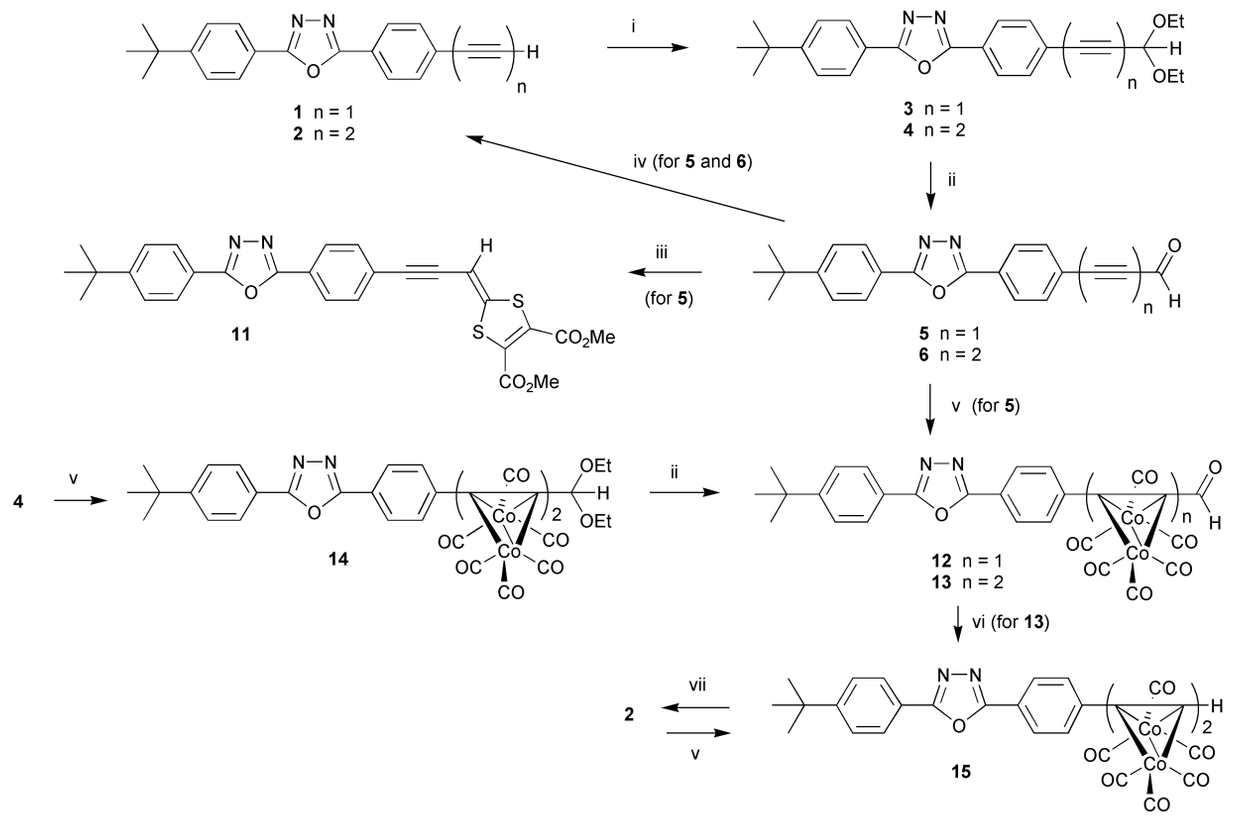
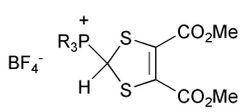
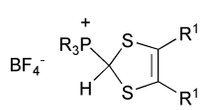


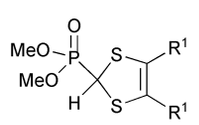
Scheme 1 *Reagents and conditions*: i, triethyl orthoformate, ZnI_2, (and THF for **2**), heat; ii, Amberlyst-15, acetone–water, 20 °C; or (for **3**) formic acid, $CHCl_3$, <10 °C; iii, reagent **7**, *n*-BuLi, THF, −78 °C to 20 °C; iv, reagents **8**–**10**, *n*-BuLi or LDA, THF, −78 °C to 20 °C or reflux; v, $Co_2(CO)_8$, THF, 20 °C; vi, reagents **7** or **8**, *n*-BuLi, THF, −78 °C to 20 °C; vii, trimethylamine oxide, THF, 20 °C.



7 R = *n*-Bu
8 R = Ph



9 R = Ph; R^1 = Me, H, S-nC_5H_{11}
R = *n*-Bu; R^1 = Me, S-nC_5H_{11}
R = *n*-Bu; R^1–R^1 = SCH_2CH_2S



10 R^1 = Me, H, S*n*-C_5H_{11}, CH_2OAc
R^1–R^1 = SCH_2CH_2S

yield. Compound **13** behaved differently: the aldehyde group was lost (as above with compounds **5** and **6**) and compound **15** was obtained in 30–45% yield. Again, no Wittig product was observed. Compound **15** was also obtained directly from **2** in 72% yield. Decomplexation of **12**–**15** to regenerate the corresponding ethynyl or butadiynyl system occurred cleanly (44–66% yields) under standard conditions,[18b] *viz*. trimethylamine oxide in THF.

X-Ray crystal structures of compounds 3, 4, 5 and 11

All four molecules (Fig. 1; Table 1) adopt predominantly planar conformations, with the exception of both OEt groups in **3** and **4**, the keto-oxygen in **5**, one of the CO_2Me groups in **11**, and the *tert*-butyl atoms C(4), C(5) and C(6) in each molecule, all non-hydrogen atoms lie in one plane with the average deviations of 0.08 (**3**, **4**), 0.03 (**5**), 0.06 (**11**) and the maximum deviations of 0.25 (**3**), 0.24 (**4**), 0.08 (**5**) and 0.12 Å (**11**). Benzene rings *A* and *B* are inclined to the oxadiazole ring by 13.0 and 0.9° in **3**, 7.2 and 7.8° in **4** (the dihedral angle between rings *A* and *B* is only 3.3°), 3.2 and 2.1° in **5**, and 6.8 and 3.0° in **11**, respectively.

The geometry of the diethoxy-propyne and -pentadiyne moieties in **3** and **4** are unexceptional[19] and can be compared to $(Ph_3P)(C_5H_5)NiC{\equiv}CCH(OEt)_2$[20] and $\{(MeO)_3P\}_2(OC)_2IFeC{\equiv}CCH(OMe)_2$.[21] In **5**, which to our knowledge is the first structurally characterised alkynylaldehyde, the C(9)=O(2) bond is twisted out of the ring *B* plane by 25.7° and shows no special conjugation with the triple bond, the C(8)–C(9) bond [1.445(3) Å] being marginally longer than the standard C(sp^1)–C(sp^2) bond (1.431 Å).[19] (Unfortunately X-ray quality crystals of **6** could not be obtained). On the contrary, in **11** the dithiole ring is flat and coplanar within 0.7° to the benzene ring *B*, the C(8)–C(9) bond is shortened to 1.419(2) Å, indicating some delocalisation. Similar bond distances have been observed in butadiynyl derivative of tetrathiafulvalene,[11] although the precision of the structure was low. As in the latter, in **11** the methoxycarbonyl substituents at C(17) and C(18) have different orientations, inclined to the dithiole ring by 4.4° and 78.2°.

Molecules of **3** and **11** form continuous stacks in the crystal structures. Adjacent molecules in each stack are inversion-related, hence they overlap in a head-to-tail fashion and their planes are strictly parallel. The mean interplanar separations in **3** alternate between 3.42 and 3.44 Å, in **11** between 3.49 and 3.56 Å. Molecules **4** and **5** are stacked into centrosymmetric (head-to-tail) dimers with interplanar separations of 3.34 (**4**) and 3.36 Å (**5**). However, these dimers do not form infinite stacks, but pack in a herringbone fashion, contacting at a dihedral angle of 34.4° (**4**) and 49.7° (**5**).

Conclusions

We have explored functionalisation of the terminal carbon atoms of the ethynyl and butadiynyl derivatives **1** and **2**. Appropriate reaction conditions have been defined for the efficient two-step conversion of **1** and **2**, *via* acetal derivatives **3** and **4**, into the corresponding alkynylaldehyde derivatives **5** and **6**. The Wittig reaction product **11** has been obtained from **5**. Cobalt carbonyl complexes **12**–**15** are reported, and their

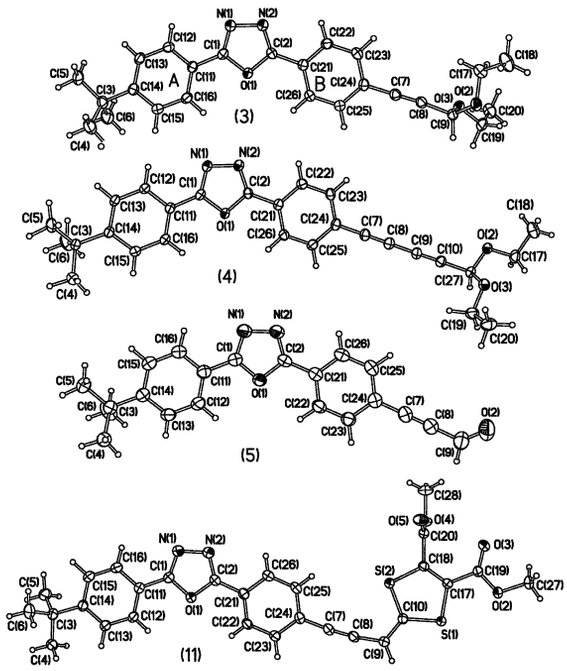


Fig. 1 X-Ray structures of **3**, **4**, **5** and **11**, showing 50% atomic displacement ellipsoids.

Table 1 Bond distances (Å)

	3	**4**	**5**	**11**
C(24)–C(7)	1.441(2)	1.432(2)	1.430(2)	1.433(2)
C(7)–C(8)	1.193(2)	1.200(2)	1.206(3)	1.204(2)
C(8)–C(9)	1.478(2)	1.375(2)	1.445(3)	1.419(2)
C(9)–C(10)	—	1.201(2)	—	1.357(2)
C(10)–C(27)	—	1.476(2)	—	1.357(2)
C(9)–O(2)	1.408(2)	1.393(2)[a]	1.192(3)	—
C(9)–O(3)	1.406(2)	1.420(3)[a]	—	—

[a] Bonds C(27)–O(2) and C(27)–O(3).

decomplexation reactions occur smoothly to regenerate the corresponding alkyne or diyne systems. X-Ray crystal structure analyses reveal that the π-systems of compounds **3**, **4**, **5** and **11** adopt predominantly planar conformations. Further uses of the novel alkynes **1** and **2** as building blocks for the synthesis of extended π-electron systems for advanced materials applications are underway in our laboratory.[13b]

Experimental

General

The details are the same as those reported recently.[3b]

2-(4-*tert*-Butylphenyl)-5-[4-(3,3-diethoxypropyn-1-yl)phenyl]-1,3,4-oxadiazole 3. Compound **1**[13] (1.0 g, 3.3 mmol) and ZnI_2 (100 mg, 0.31 mmol) were dissolved in triethyl orthoformate (30 cm^3). The mixture was stirred under Ar for 5 h (oil-bath temperature 140 °C) then cooled to 20 °C. The solvent was removed *in vacuo* and the residue was chromatographed (silica, DCM–diethyl ether 94 : 6, v/v) and recrystallised from ethanol–ethyl acetate to obtain **3** as white needles (1.2 g, 85%) mp: 82–84 °C. δ_H ($CDCl_3$): 1.30 (t, J = 7.2 Hz, 6H), 1.38 (s, 9H), 3.70 (m, 2H), 3.85 (m, 2H), 5.53 (s, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 8.06 (d, J = 8.0 Hz, 2H), 8.10 (d, J = 8.0 Hz, 2H); δ_C ($CDCl_3$): 15.4, 31.4, 35.4, 61.3, 84.5, 87.4, 91.9, 121.1, 124.3, 125.4, 126.3, 126.9, 127.1, 132.8, 155.8, 164.0, 165.1; MS (EI): *m*/*z* (%): 404 (M^+, 52), 359 (100). UV/Vis (DCM): λ_{max} 305 nm. Anal for $C_{25}H_{28}N_2O_3$ (404.21): calcd C, 74.23; H, 6.98; N, 6.93. Found: C, 74.19; H, 6.95; N, 6.97%.

2-(4-*tert*-Butylphenyl)-5-[4-(5,5-diethoxy-1,3-pentadiyn-1-yl)-phenyl]-1,3,4-oxadiazole 4. Following the method used to prepare **3**, compound **2**[13] (1.0 g, 3.1 mmol), ZnI_2 (105 mg, 0.31 mmol), THF (10 cm^3) and triethyl orthoformate (30 cm^3) were stirred under Ar for 3 h (oil-bath temperature 110 °C). Chromatography (silica, DCM–diethyl ether 92 : 8, v/v) and recrystallisation from ethanol–ethyl acetate gave **4** as white needles (1.0 g, 77%) mp: 141–143 °C. δ_H ($CDCl_3$): 1.28 (t, J = 7.2 Hz, 6H), 1.38 (s, 9H), 3.66 (m, 2H), 3.78 (m, 2H), 5.41 (s, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 8.06 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 8.0 Hz, 2H); δ_C ($CDCl_3$): 15.3, 31.3, 35.4, 61.6, 69.7, 75.7, 78.3, 79.1, 91.8, 121.1, 124.7, 124.8, 126.4, 127.0, 127.1, 133.5, 155.9, 163.9, 165.2; MS (EI): *m*/*z* (%): 428 (M^+, 88), 383 (98), 355 (100). UV/Vis (DCM): λ_{max} 324 nm. Anal for $C_{27}H_{28}N_2O_3$ (428.21): calcd C, 75.68; H, 6.59; N, 6.54. Found: C, 75.66; H, 6.57; N, 6.57%.

{3-[5-(4-*tert*-Butylphenyl)-1,3,4-oxadiazol-2-yl]phenyl}-propynal 5. *Method (a).* Compound **3** (1.0 g, 2.5 mmol) was dissolved in acetone (100 cm^3). Amberlyst-15 resin (1.0 g) and water (1 cm^3) were added and the mixture was stirred vigorously for 36 h at 20 °C. The precipitate was removed by suction filtration and washed with DCM. The filtrate was evaporated *in vacuo* to yield a residue which was chromatographed (silica, DCM–diethyl ether 94 : 6, v/v) and recrystallised from hexane–ethyl acetate to yield **5** as white needles (0.80 g, 97%) mp: 152–155 °C (decomp.). δ_H ($CDCl_3$): 1.38 (s, 9H), 7.57 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 8.8 Hz, 2H), 8.20 (d, J = 8.8 Hz, 2H), 9.47 (s, 1H); δ_C ($CDCl_3$): 31.3, 35.6, 90.0, 93.4, 120.9, 122.7, 126.4, 127.1, 127.2, 134.0, 156.0, 163.6, 165.4, 176.7; MS (EI): *m*/*z* (%): 330 (M^+, 67), 315 (100). UV/Vis (DCM): λ_{max} 316 nm. Anal for $C_{21}H_{18}N_2O_2$ (330.14): calcd C, 76.34; H, 5.49; N, 8.48. Found: C, 76.32; H, 5.47; N, 8.50%.

Method (b). A solution of **3** (1.0 g, 2.5 mmol) in a mixture of chloroform (60 cm^3) and pure formic acid (30 cm^3) was stirred under Ar for 1 h at 10 °C and then stored for 24 h at 6–8 °C. Water was added and the organic phase was washed with water again several times (3 × 100 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by chromatography (silica, DCM–diethyl ether 95 : 5, v/v) to yield **5** (0.47 g, 57%) identical with the sample above.

5-{4-[5-(4-*tert*-Butylphenyl)-1,3,4-oxadiazol-2-yl]phenyl}-penta-2,4-diynal 6. By analogy with the preparation of **5**, compound **9** (0.6 g, 1.4 mmol), acetone (100 cm^3), Amberlyst-15 resin (1 g) and water (1 cm^3) followed by chromatography (silica, DCM–diethyl ether 92 : 8, v/v) gave **6** as a pale yellow solid (0.5 g, 95%) mp: 127–130 °C (decomp.). δ_H ($CDCl_3$): 1.38 (s, 9H), 7.66 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 8.4 Hz, 2H), 8.16 (d, J = 8.4 Hz, 2H), 9.31 (s, 1H); δ_C ($CDCl_3$): 31.3, 35.4, 83.8, 84.5, 87.6, 120.9, 123.2, 126.4, 127.1, 127.2, 132.8, 133.4, 155.9, 156.0, 163.8, 165.4, 175.8; MS (EI): *m*/*z* (%): 354 (M^+, 26), 190 (98), 105 (100). UV/Vis (DCM): λ_{max} 333 nm. Anal for $C_{23}H_{18}N_2O$ (354.14): calcd C, 77.95; H, 5.12; N, 7.90. Found: C, 78.00; H, 5.14; N, 7.89%.

2-(3-{4-[5-(4-*tert*-Butylphenyl)-1,3,4-oxadiazol-2-yl]phenyl}-prop-2-ynylidene)-1,3-dithiole-4,5-dimethyl dicarboxylate 11. To a stirred solution of salt **7**[22] (1.2 g, 2.3 mmol) in dry THF (20 cm^3) under N_2 at −78 °C, was added *n*-butyllithium (1.6 M solution in hexane, 1.5 cm^3, 2.4 mmol). The reaction mixture was stirred for 30 min, then a solution of **5** (0.8 g, 2.3 mmol) in THF (30 cm^3), was added very slowly and the mixture was left to warm to room temperature with stirring overnight. The solvents were removed *in vacuo* and the residue was chromatographed (silica, DCM–diethyl ether 96 : 4, v/v) and recrystallised from hexane–ethyl acetate to yield **11** as yellow–orange needles (0.40 g, 33%) mp: 201–20 °C. δ_H ($CDCl_3$): 1.38 (s, 9H), 3.86 (s, 3H), 3.88 (s, 3H), 5.65 (s, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 8.06 (d, J = 8.5 Hz, 2H), 8.08

Table 2 Crystal data

Compound	**3**	**4**	**5**	**11**
Formula	$C_{25}H_{28}N_2O_3$	$C_{27}H_{28}N_2O_3$	$C_{21}H_{18}N_2O_2$	$C_{28}H_{24}N_2O_5S_2$
Formula weight	404.49	428.51	330.37	532.61
T/K	120	120	120	120
Symmetry	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (# 14)	$P2_1/c$ (# 14)	$P2_1/c$ (# 14)	$P\bar{1}$ (# 2)
a/Å	7.356(2)	14.835(5)	11.945(2)	10.878(1)
b/Å	19.870(5)	6.161(1)	6.183(1)	11.000(1)
c/Å	15.136(4)	25.549(3)	23.460(5)	12.705(1)
α/°	90	90	90	114.87(1)
β/°	91.37(1)	91.14(1)	97.94(1)	105.88(1)
γ/°	90	90	90	97.05(1)
V/Å^3	2211.7(10)	2334.7(9)	1716.0(5)	1276.5(2)
Z	4	4	4	2
μ/mm^{-1}	0.08	0.08	0.08	0.25
Refls collected	24719	19697	19480	15831
Unique refls	5123	6234	3935	6727
R_{int}	0.048	0.055	0.060	0.041
Refls $F^2>2\sigma(F^2)$	3761	4459	2788	5969
$R[F^2>2\sigma(F^2)]$	0.043	0.056	0.053	0.035
w$R(F^2)$, all data	0.105	0.152	0.161	0.095

(d, J = 8.5 Hz, 2H); δ_C ($CDCl_3$): 31.4, 35.4, 53.5, 53.7, 89.8, 93.2, 99.4, 121.2, 123.4, 126.3, 126.7, 127.0, 131.7, 146.8, 155.7, 159.7, 160.0, 164.2, 165.0; MS (EI): *m*/*z* (%): 532 (M^+, 100). UV/Vis (DCM): λ_{max} 384 nm. Anal for $C_{28}H_{24}N_2O_5S_2$ (532.11): calcd C, 63.14; H, 4.54; N, 5.26; S 12.04. Found: C, 63.11; H, 4.52; N, 5.24; S 12.06%. CV ($c = 10^{-3}$ M in DCM–nBu$_4$NPF$_6$, 0.05 M, Pt electrode, scan rate = 100 mV s^{-1}): E^{ox} (V *vs* Ag/AgCl) +0.95; CV (same conditions in CH_3CN): E^{ox} (V *vs* Ag/AgCl) +0.84.

Dicobalt hexacarbonyl complex 12. $Co_2(CO)_8$ (0.30 g, 1.5 eq) was added under Ar to a solution of **5** (0.20 g, 0.6 mmol) in dry tetrahydrofuran (20 cm^3). After stirring for 30 min at 20 °C, the solvent was removed *in vacuo.* The residue was purified by chromatography (silica, DCM–diethyl ether 95 : 5, v/v) to yield **12** as a black–violet solid (180 mg, 88%) mp: > 350 °C. δ_H ($CDCl_3$): 1.39 (s, 9H), 7.58 (d, br, J = 7.5 Hz, 2H), 7.78 (d, br, J = 7.5 Hz, 2H), 8.11 (m, br, 4H), 10.57 (s, 1H); δ_C ($CDCl_3$): 31.4, 35.4, 85.5, 89.7, 121.2, 124.3, 126.4, 127.1, 127.9, 130.5, 140.6, 155.8, 164.1, 165.1, 191.1, 197.7; MS (TOF-ES): *m*/*z* (%): 616 (M^+, 100). UV/Vis (DCM): λ_{max} 310 nm. Anal for $C_{27}H_{18}Co_2N_2O_8$ (615.97): calcd C, 52.62; H, 2.94; N, 4.55. Found: C, 52.64; H, 2.95; N, 4.52%.

Tetracobalt dodecacarbonyl complex 13. Compound **14** (0.40 g, 0.4 mmol) was dissolved in acetone (30 cm^3). Amberlyst-15 resin (0.40 g) and water (1 cm^3) were added. The mixture was stirred vigorously for 36 h at 20 °C. Workup as described for **12** with chromatography (silica, DCM–diethyl ether 95 : 5, v/v) gave **13** as brown black solid (0.21 g, 56%) mp: >350 °C. δ_H ($CDCl_3$): 1.38 (s, 9H), 7.59 (d, br, J = 7.4 Hz, 2H), 7.75 (d, br, J = 7.4 Hz, 2H), 8.03 (m, br, 4H), 10.23 (s, 1H); δ_C ($CDCl_3$): 30.9, 35.2, 85.7, 87.4, 88.0, 89.6, 121.0, 124.2, 126.2, 127.1, 127.8, 130.4, 141.0, 155.1, 164.2, 165.5, 191.0, 197.2; MS (TOF-ES): *m*/*z* (%): 926 (M^+, 18), 354 (100). UV/Vis (DCM): λ_{max} 301 nm. Anal for $C_{35}H_{18}Co_4N_2O_{14}$ (925.81): calcd C, 45.38; H, 1.96; N, 3.02. Found: C, 45.46, H, 2.01; N, 3.00%.

Tetracobalt dodecacarbonyl complex 14. $Co_2(CO)_8$ (0.25 g, 3 eq.) was added under Ar to a solution of **4** (0.1 g, 0.2 mmol) in dry tetrahydrofuran (30 cm^3). After stirring for 1 h, the solvent was removed *in vacuo*. The residue was purified by chromatography (silica, DCM–diethyl ether 95 : 5, v/v) to yield **14** as a brown–black solid (0.15 g, 65%) mp: > 350 °C. δ_H ($CDCl_3$): 1.19 (m, 6H), 1.26 (s, 9H), 3.55 (m, br, 2H), 3.79 (m, br, 2H), 5.40 (s, 1H), 7.30 (s, br, J = 7.5 Hz, 2H), 7.37 (s, br, J = 7.5 Hz, 2H), 7.83 (s, br, J = 7.5 Hz, 2H), 8.13 (s, br, J = 7.5 Hz, 2H); δ_C ($CDCl_3$):15.2, 31.0, 34.9, 61.3, 69.7, 76.1, 78.6, 80.4, 92.0, 125.1, 126.2, 126.8, 127.1, 127.5, 133.2, 155.1, 163.7, 164.9, 197.0; MS (TOF-ES): *m*/*z* (%): 1000 (M^+, 12), 130 (100). UV/Vis (DCM): λ_{max} 305 nm. Anal for $C_{39}H_{28}Co_4N_2O_{15}$ (999.88): calcd C, 46.82; H, 2.82; N, 2.80. Found: C, 46.86; H, 2.88; N, 2.72%.

Tetracobalt dodecacarbonyl complex 15. *Method (a).* $Co_2(CO)_8$ (1.3 g, 3 eq.) was added under Ar to a solution of **2** (0.40 g, 1.2 mmol) in dry tetrahydrofuran (50 cm^3). After stirring for 30 min, the solvent was removed *in vacuo*. The residue was purified by chromatography (silica, DCM–diethyl ether 95 : 5, v/v) to yield **15** as a brown–black solid (0.80 g, 72%) mp: > 350 °C. δ_H ($CDCl_3$): 1.39 (s, br, 9H), 6.69 (s, br, 1H), 7.58 (d, br, J = 7.5 Hz, 2H), 7.73 (d, br, J = 7.5 Hz, 2H), 8.08 (d, br, J = 7.5 Hz, 2H), 8.17 (d, br, J = 7.5 Hz, 2H); δ_C ($CDCl_3$): 31.2, 35.6, 72.9, 126.3, 127.0, 127.7, 129.8, 142.3, 155.9, 199.5; MS (TOF-ES): *m*/*z* (%): 898 (M^+, 100). UV/Vis (DCM): λ_{max} 308 nm. Anal for $C_{34}H_{18}Co_4N_2O_{13}$ (897.81): calcd C, 45.46; H, 2.02; N, 3.12. Found: C, 45.51; H, 2.04; N, 3.11%.

Method (b). Treatment of **13** with reagents **7** or **8** under the conditions described above for the preparation of **11** gave compound **15** in 30–45% yields.

Decomplexation of 12–15: general procedure. Trimethylamine oxide (5 equiv. for **12**; 10 equiv. for **13**–**15**) was added to a solution of **12**–**15** (0.1– 0.2 mmol) in tetrahydrofuran (*ca*. 20 cm^3). After stirring for 1 h at 20 °C, diethyl ether was added and the mixture was extracted with water. The organic layer was separated, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by chromatography to yield **5** (66% yield); **6** (44% yield); **4** (45% yield) and **2** (63% yield).

X-Ray crystallography

Single-crystal diffraction experiments (Table 2) were carried out on a SMART 3-circle diffractometer with a 6 K (for **5**) or 1 K CCD area detector, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[23] Full crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre. CCDC reference numbers 225628–225631. See http://www.rsc.org/suppdata/ob/b3/b315694j/ for crystallographic data in .cif or other electronic format.

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