Synthesis of Novel 1,4-Benzoquinone-Containing 1,2,3-Triazoles: An Entry Into a New Library

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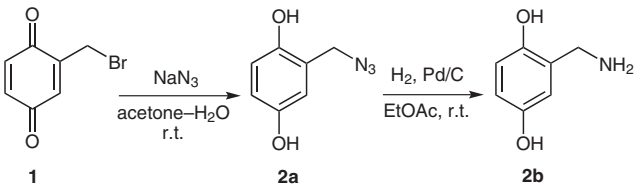
Abstract: A heretofore unexplored library of 1,4-benzoquinone-containing 1,2,3-triazoles was prepared by the application of a highly regioselective copper(I)-catalyzed process. Furthermore, the utilization of this novel triazole–1,4-benzoquinone system as an interesting class of extended, branched molecules for the construction of new supramolecular architectures is presented.

Key words: benzoquinones, azides, triazoles, copper(I) catalysis, regioselectivity

Triazoles, attractive constructs because of their unique chemical properties and structure, have found broad use in agrochemicals and industrial applications such as dyes and dyestuffs, fluorescent compounds, corrosion inhibitors, and photostabilizers, and have been regarded an interesting unit in terms of biological activity.[1,2] In particular, 1,2,3-triazoles have recently become popular as a means for establishing reliable and stable connections in organic synthesis and materials science. Several synthetic methods in which azide[3] plays a prominent role have been developed recently,[4–6] with the discovery that copper(I) catalyzes[6] the 1,3-dipolar cycloaddition reaction between azides and alkynes a particular milestone, opening a myriad of applications.

On the other hand, we have recently turned our attention to benzoquinones,[7] which are ubiquitous in living systems and represent important cofactors in electron transfer in photosynthesis and respiration. In addition, they have found widespread use in medicine as antitumor, antifungal, and antiparasitic drugs, as well as antibiotics.[8–10] We have speculated, perhaps counterintuitively, that molecules in which these structures are combined, that is, molecules that consist of a triazole ring on one side and the quinone moiety on the other, would display the intriguing features of both of these functional groups. Furthermore, such compounds would be interesting in terms of electron- and/or energy-transfer (ET) systems.[11] In this regard, we have initiated a program aimed at introducing a new library of 1,4-benzoquinone-containing 1,2,3-triazoles. Herein, we wish to report the results of our research concerning the regioselective synthesis of such compounds with a variety of substituents at the 4-position of the triazole moiety. Furthermore, the utilization of this novel triazole–quinone system as an interesting class of extended, branched molecules for the construction of new supramolecular architectures is presented here.

Our initial exploratory efforts involved the synthesis of the valuable 2-(azidomethyl)-substituted hydroquinone (**2a**) scaffold (see Scheme 1) which bears both the masked triazole functionality, obtainable through a copper(I)-catalyzed 1,3-dipolar cycloaddition, and the benzoquinone moiety, accessible through oxidation.



Scheme 1

We found that 2-(bromomethyl)-1,4-benzoquinone (**1**) could be converted into the 2-(azidomethyl)-substituted hydroquinone (**2a**) by the action of sodium azide (Scheme 1).[12] Azide **2a** was easily converted into the corresponding amine **2b** by catalytic hydrogenation.

To further explore the reactivity, an initial attempt was made by the treatment of azide **2a** with phenylacetylene in the presence of copper(I) iodide as catalyst at room temperature (Scheme 2; Table 1, entry 3).[6c] We noticed that the reaction provided the corresponding 1,2,3-triazole **3c** with remarkable regioselectivity, favoring the 1,4-regioisomer, albeit in low yield (ca. 10%, by NMR, after 16 h). Increasing the temperature (80 °C) caused a dramatic increase in both the rate of the reaction and the yield (85%). These optimizations were chosen as the standard conditions for testing the scope of this route. Thus, a variety of mono- and disubstituted alkynes including acetoxymethyl-, trimethylsilyl-, aryl-, ferrocenyl-, and thienylacetylenes, as well as dimethyl acetylenedicarboxylate were subjected to the reaction with hydroquinone **2a** under these conditions, to afford the corresponding 1,2,3-triazoles **3a–g** in moderate to good yields (Scheme 2, Table 1). The compounds were characterized by spectroscopy (^{1}H, ^{13}C, DEPT, COSY, HMBC, and HMQC NMR and FTIR) and combustion analysis.

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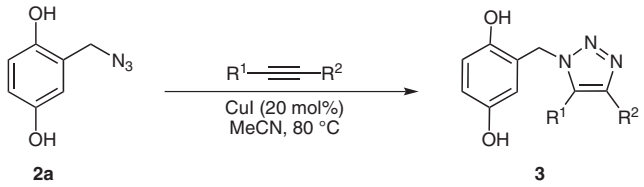
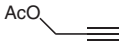
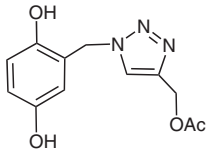
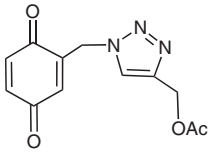
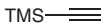
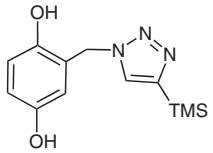
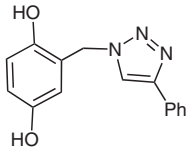
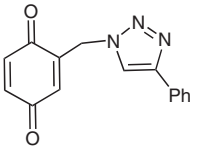
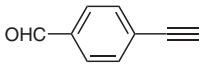
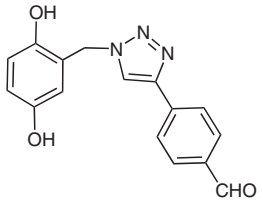
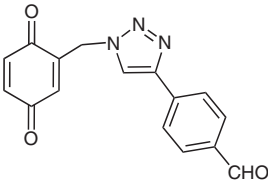
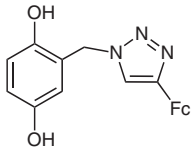
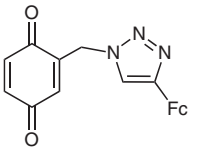
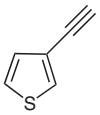
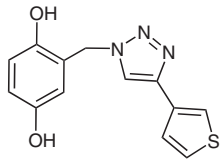
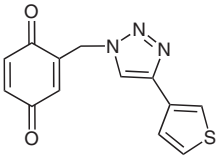
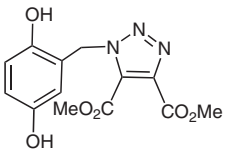
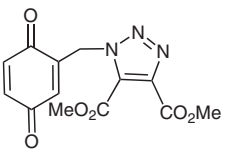


Scheme 2

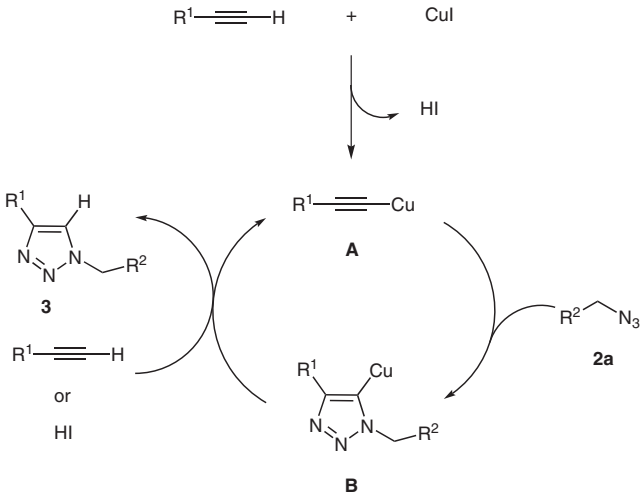
A proposed mechanism for the formation of 1,2,3-triazoles in the presence of the copper catalyst is depicted in Scheme 3.[6c] At the initial stage of the catalytic cycle, the reaction of an alkyne with copper(I) iodide produces acetylide **A**. The [3+2] cycloaddition between the C–C triple bond of copper acetylide **A** and azide **2a** takes place readily to form intermediate **B**. Protonolysis of the C–Cu bond of intermediate **B** affords 1,2,3-triazole **3**.

The following points are worthy of comment. First of all, it appears as if a variation in the steric environment around

Table 1 Synthesis of Novel 1,2,3-Triazoles **3** and 1,4-Benzoquinones **4**

Entry	Acetylene	Triazole[a]	**3**	1,4-Benzoquinone[b]	**4**	Yield[c] (%)
1			**3a**		**4a**	85
2			**3b**[d]	–	–[e]	65 (for **3b**)
3			**3c**		**4c**	85
4			**3d**		**4d**	90
5			**3e**		**4e**	60
6			**3f**		**4f**	90[f]
7			**3g**		**4g**	100[g]

[a] Reagents and conditions: **2a** (2 mmol), $R^1C{\equiv}CR^2$ (3 mmol), MeCN (50 mL), CuI (20 mol%), reflux, 12–26 h.
[b] Reagents and conditions: **3** (1 mmol), MnO_2 (5 equiv), CH_2Cl_2, r.t., 16–32 h.
[c] Isolated and unoptimized yield of **4** over two steps.
[d] The reaction was run at r.t.
[e] Decomposed during oxidation (see text).
[f] Trace amount of 1,5-isomer was also observed.
[g] The reaction was run at r.t. without catalyst.

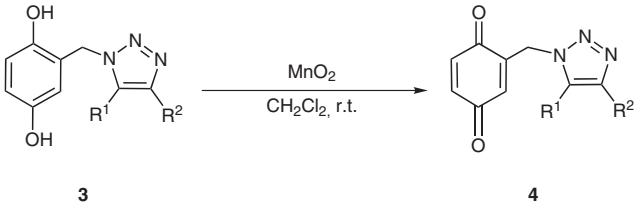


Scheme 3

the alkyne, at least to the extent represented by the cases investigated, had no effect on the regioselectivity of the process, even though it caused a somewhat detrimental effect on the yield; since the lower yield values were obtained with acetylenes substituted with trimethylsilyl (Table 1, entry 2), and ferrocenyl (Table 1, entry 5).

1,2,3-Triazoles **3** were converted into the corresponding 1,4-benzoquinones **4** by treatment with manganese(IV) oxide (Scheme 4, Table 1); the reactions proceeded almost quantitatively, except in the case of the trimethylsilyl derivative (Table 1, entry 2), where the product could not be isolated, probably due to decomposition.

Finally, we explored the use of this novel triazole–1,4-benzoquinone system as an interesting class of extended, branched molecules for the construction of new supramolecular architectures. For this purpose, we investigated the incorporation of the triazole–1,4-benzoquinone system into porphyrinogenic dipyrromethene (dipyrrin) units,



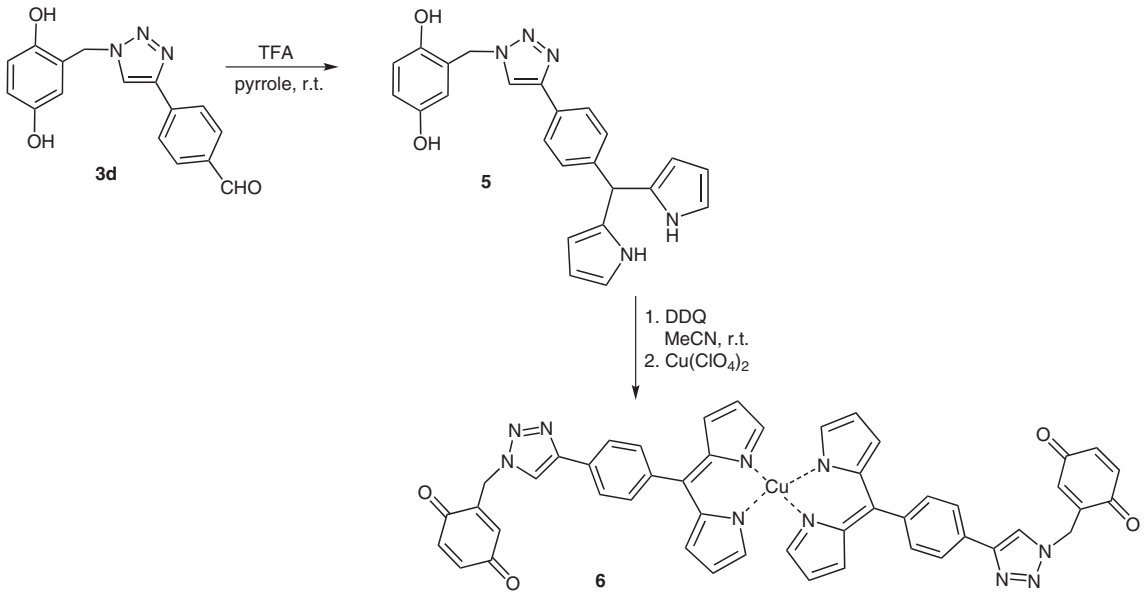
Scheme 4

since dipyrrins offer a number of desirable features, such as ease of purification by conventional flash chromatography over silica gel, intense optical absorptions, and a propensity to form stable, neutral complexes with metal ions.[13]

The synthesis of the bis(ligand)–metal complex **6** was achieved through a two-step reaction sequence: acid-catalyzed condensation of pyrrole with **3d** gives the dipyrromethene-appended ligand precursor **5**, which was subsequently complexed with the metal after oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (Scheme 5). Unfortunately, the ^{1}H NMR spectrum of **6** does not provide useful information, because the metal ion (Cu^{II}) is paramagnetic.

However, absorption spectroscopy of the combination of the 1,2,3-triazole–1,4-benzoquinone system and copper(II) with the dipyrrin chelators was valuable, although no significant emission was observed. The salient feature of bis(ligand)–copper complex **6** was that a new broad absorption band (with a shoulder), ascribed to a metal–ligand charge-transfer process, appeared at around 496 nm (Figure 1). These spectral features are consistent with those of similar compounds reported in the literature.[13]

The electrochemical behavior of bis(ligand)–copper complex **6** was also examined. The cyclic voltammogram exhibited one reversible reduction peak with a half wave potential of –0.41 V, as well as one irreversible reduction



Scheme 5

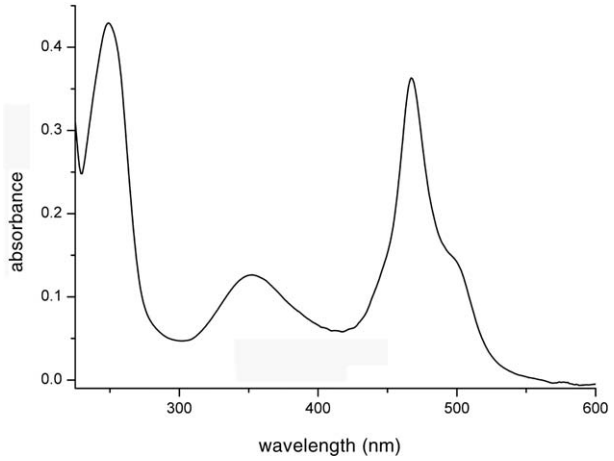


Figure 1 UV/vis absorption spectrum of **6** (10^{-3} M) in dichloromethane

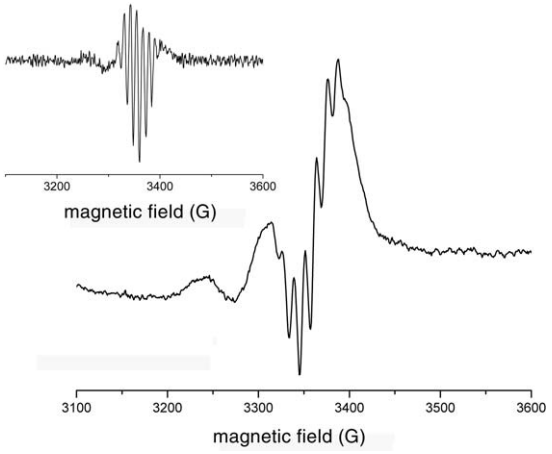


Figure 3 ESR spectrum of **6** (10^{-3} M) in dichloromethane; inset: second derivative of ESR spectrum

peak at –0.84 V (Figure 2), which can be attributed to reduction of 1,4-benzoquinone units and the metal center in complex **6**, respectively.

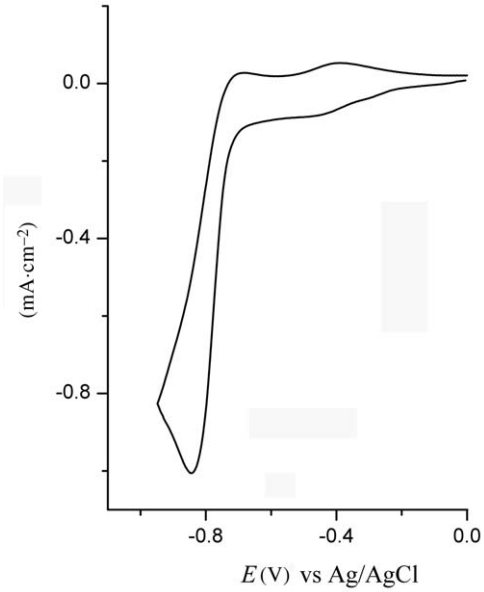


Figure 2 Cyclic voltammogram of **6** in a 0.1 M solution of tetrabutylammonium perchlorate in acetonitrile (scan rate, 100 mV·s^{-1})

The ESR spectrum of **6** also confirmed the presence of copper(II) in the complex. As shown in Figure 3, the unpaired electron of copper(II) interacts with the nuclear spins of nitrogen (I = 1), leading to an ESR signal with some hyperfine lines. Seven superhyperfine lines with equally spaced coupling constants (12 G) for four nitrogen atoms can be attributed to the square planar, rather than tetrahedral, structure of complex **6**.[14]

In summary, a heretofore unexplored library of 1,4-benzoquinone-containing 1,2,3-triazoles was prepared by the application of a highly regioselective copper(I)-catalyzed process. Furthermore, the utilization of this novel triazole–1,4-benzoquinone system as an interesting class of extended, branched molecules for the construction of new supramolecular architectures was presented. Considering the multitude of choices in metal selection, we are confident that this approach can be extended to a variety of novel supramolecular architectures with practical applications in many fields. Efforts to elucidate the versatility of 1,4-benzoquinones **4** reported herein in expanded structures, and applications to electron- and/or energy-transfer (ET) systems are currently underway in our laboratories.

Melting points were determined on a Buchi model 530 apparatus and are uncorrected. IR spectra were recorded on a Mattson model 1000 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on an Avance-Bruker 400 MHz NMR spectrometer, operating at 400 and 100 MHz, respectively. Electroanalytical measurements were performed on a Gamry PCI4/300 potentiostat–galvanostat. A Pt disk (0.02 cm^2) and a Pt wire were used as working and counter electrodes, respectively, as well as Ag/AgCl, which was used in 3 M aq NaCl soln as a reference. UV/vis spectra were recorded on a Hewlett–Packard 8453A diode array spectrometer. ESR spectra were recorded on a Varian E12 ESR spectrometer. Column chromatography was performed on silica gel (Merck, 60–200 mesh). TLC was carried out on Merck 0.2-mm silica gel 60 F254 analytical aluminum plates.

2-(Aminomethyl)benzene-1,4-diol (2b)

A 100-mL, two-necked round-bottomed flask was charged with Pd/C (50 mg, 10 mol%) and azide **2a**[12] (0.33 g, 2 mmol) in EtOAc (50 mL). One of the necks was attached to H_2 gas by a three-way stopcock, and the other neck was capped with a rubber septum. The reactants were degassed and flushed with H_2 gas, while the contents of the flask was stirred magnetically. After 3 h (TLC), the soln was filtered through a short pad of Celite 545 to remove the catalyst, and the solvent was evaporated to give **2b**.

Yield: 0.25 g (89%); dark red oil.

IR (acetone): 3390, 3370, 2930, 2905, 2840, 1650, 1510, 1430, 1350, 1240, 1180, 1100, 863, 803 cm^{-1}.

^{1}H NMR (400 MHz, acetone-d_6): δ = 6.65–6.58 (m, 2 H), 6.50 (m, 1 H), 3.87 (s, 2 H), 2.81 (br s, 4 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 150.9, 147.4, 122.2, 118.2, 115.2, 112.7, 41.2.

Anal. Calcd for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.16; H, 6.29; N, 10.01.

1,2,3-Triazoles 3; General Procedure

CuI (76 mg, 0.4 mmol) was added to a soln of azide **2a**[12] (0.33 g, 2 mmol) and the appropriate alkyne (3 mmol) in MeCN (50 mL), and the homogeneous mixture was heated under reflux. After completion of the reaction (12–26 h, TLC), the mixture was allowed to cool to r.t. and filtered through a short pad of Celite 545, and the solvent was removed under reduced pressure. The residue was chromatographed (silica gel, EtOAc–hexane, 1:4); this gave pure, solid **3**.

[1-(2,5-Dihydroxybenzyl)-1*H*-1,2,3-triazol-4-yl]methyl Acetate (3a)

White solid; mp 152–154 °C.

IR (acetone): 3267, 3031, 2969, 2727, 2129, 2055, 1739, 1712, 1661, 1611, 1509, 1458, 1366, 1227, 115, 1126, 1093, 1041, 1000, 968, 921, 872, 822, 765, 736, 684, 627, 605 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 8.22 (br s, 1 H), 7.84 (s, 1 H), 7.83 (s, 1 H), 6.80 (d, *J* = 9.3 Hz, 1 H, A part of AB system), 6.70–6.68 (m, 2 H), 5.49 (s, 2 H), 5.14 (s, 2 H), 2.01 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 170.2, 150.4, 147.9, 142.5, 124.1, 122.0, 116.7, 116.6, 116.5, 57.4, 49.0, 20.3.

Anal. Calcd for $C_{12}H_{13}N_3O_4$: C, 54.75; H, 4.98; N, 15.96. Found: C, 54.60; H, 5.11; N, 15.68.

2-{[4-(Trimethylsilyl)-1*H*-1,2,3-triazol-1-yl]methyl}benzene-1,4-diol (3b)

White solid; mp 178–180 °C.

IR (acetone): 2996, 2970, 2926, 2854, 2105, 1739, 1661, 1588, 1454, 1367, 1214, 1094, 1016, 844, 761, 633 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 8.24 (s, 1 H), 7.92 (s, 1 H), 7.83 (s, 1 H), 6.80 (d, *J* = 8.5 Hz, 1 H, A part of AB system), 6.68 (dd, *J* = 8.5, 2.9 Hz, 1 H, B part of AB system), 6.63 (d, *J* = 2.9 Hz, 1 H), 5.54 (s, 2 H), 0.27 (s, 9 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 152.1, 149.4, 147.0, 131.3, 124.4, 121.9, 118.0, 117.8, 49.7, 0.0.

Anal. Calcd for $C_{12}H_{17}N_3O_2Si$: C, 54.73; H, 6.51; N, 15.95. Found: C, 55.01; H, 6.48; N, 15.78.

2-[(4-Phenyl-1*H*-1,2,3-triazol-1-yl)methyl]benzene-1,4-diol (3c)

White solid; mp 216–217 °C (dec).

IR (acetone): 3220, 3138, 3064, 3026, 2970, 2948, 2852, 2224, 2122, 1739, 1658, 1609, 1579, 1508, 1456, 1366, 1292, 1214, 1154, 1081, 1055, 1030, 1000, 978, 898, 876, 819, 765, 745, 694, 655, 619 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 8.14 (s, 1 H), 8.13 (br s, 1 H) 7.75 (d, *J* = 7.8 Hz, 2 H), 7.69 (br s, 1 H), 7.27 (t, *J* = 7.6 Hz, 2 H), 7.16 (t, *J* = 7.3 Hz, 1 H), 6.66 (d, *J* = 8.5 Hz, 1 H, A part of AB system), 6.54 (dd, *J* = 8.5–2.9 Hz, 1 H, B part of AB system), 6.50 (d, *J* = 2.9 Hz, 1 H), 5.43 (s, 2 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 150.6, 147.7, 146.9, 131.4, 128.6, 127.6, 125.3, 122.8, 120.6, 116.3, 116.1, 116.0, 48.7.

Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.49; H, 4.96; N, 15.84.

4-[1-(2,5-Dihydroxybenzyl)-1*H*-1,2,3-triazol-4-yl]benzaldehyde (3d)

White solid; mp 236–237 °C.

IR (acetone): 3424, 3137, 3101, 3040, 2969, 2075, 1740, 1696, 1670, 1609, 1574, 1508, 1461, 1365, 1306, 1264, 1212, 1171, 1115, 1076, 1055, 1009, 982, 879, 832, 818, 772, 744, 706, 683, 656, 616 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 10.02 (s, 1 H, CHO), 8.15 (s, 1 H), 8.03–7.90 (AA′BB′ system, 4 H, aromatic), 6.81 (d, *J* = 9.4 Hz, 1 H, A part of AB system), 6.74–6.72 (m, 2 H), 5.57 (s, 2 H).

^{13}C NMR (100 MHz, CD_3OD): δ = 193.5, 151.4, 149.5, 147.4, 137.7, 137.4, 131.3, 127.0, 123.7, 123.2, 117.7, 117.4, 117.3, 50.6.

Anal. Calcd for $C_{16}H_{13}N_3O_3$: C, 65.08; H, 4.44; N, 14.23. Found: C, 65.15; H, 4.50; N, 14.08.

2-[(4-Ferrocenyl-1*H*-1,2,3-triazol-1-yl)methyl]benzene-1,4-diol (3e)

Brownish-red solid; mp 244–246 °C (dec).

IR (acetone): 3451, 3084, 3017, 2969, 2945, 2927, 2855, 2114, 1739, 1618, 1580, 1504, 1451, 1367, 1226, 1215, 1154, 1105, 1092, 1058, 1002, 899, 879, 819, 769, 740, 669 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 8.09 (br s, 1 H), 7.79 (s, 1 H), 7.68 (br s, 1 H), 6.65 (d, *J* = 8.5 Hz, 1 H, A part of AB system), 6.54 (dd, *J* = 8.5–2.7 Hz, 1 H, B part of AB system), 6.45 (d, *J* = 2.7 Hz, 1 H), 5.38 (s, 2 H), 4.61–4.56 (m, 2 H), 4.15–4.12 (m, 2 H), 3.89 (s, 5 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 151.1, 149.4, 148.7, 128.5, 123.9, 120.9, 117.0, 116.8, 70.1, 69.0, 67.3, 55.5, 49.4.

Anal. Calcd for $C_{19}H_{17}FeN_3O_2$: C, 60.82; H, 4.57; N, 11.20. Found: C, 60.90; H, 4.37; N,11.14.

2-{[4-(3-Thienyl)-1*H*-1,2,3-triazol-1-yl]methyl}benzene-1,4-diol (3f)

Brownish solid; mp 242–243 °C (dec).

IR (acetone): 3442, 3014, 2969, 2948, 2857, 2129, 1739, 1609, 1507, 1454, 1366, 1228, 1217, 1152, 1090, 967, 891, 858, 820, 785, 740, 710, 668, 621 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 8.06 (br s, 1 H), 7.95 (s, 1 H), 7.70 (br s, 1 H), 7.67 (d, *J* = 2.2 Hz, 1 H), 7.46 (d, *J* = 4.9 Hz, 1 H), 7.39 (dd, *J* = 4.9, 3.0 Hz, 1 H), 6.79 (d, *J* = 8.5 Hz, 1 H, A part of AB system), 6.69 (dd, *J* = 8.5–2.7 Hz, 1 H, B part of AB system), 6.66 (d, *J* = 2.7 Hz, 1 H), 5.53 (s, 2 H).

^{13}C NMR (100 MHz, CD_3OD): δ = 151.2, 149.5, 145.2, 132.7, 127.7, 126.9, 122.9, 122.4, 121.9, 118.2, 117.9, 117.7, 55.8.

Anal. Calcd for $C_{13}H_{11}N_3O_2S$: C, 57.13; H, 4.06; N, 15.37; S, 11.73. Found: C, 57.00; H, 3.89; N, 15.20; S, 11.56.

Dimethyl 1-(2,5-Dihydroxybenzyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate (3g)

White solid; mp 94–96 °C.

IR (acetone): 3443, 3031, 3010, 2957, 2924, 2852, 2112, 1735, 1658, 1558, 1509, 1458, 1364, 1317, 1229, 1149, 1103, 1095, 1063, 964, 824, 793, 766, 737, 696, 605 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 8.21 (s, 1 H), 7.83 (s, 1 H), 6.74 (d, *J* = 8.7 Hz, 1 H, A part of AB system), 6.67 (dd, *J* = 8.7, 2.8 Hz, 1 H, B part of AB system), 6.55 (d, *J* = 2.8 Hz, 1 H), 5.76 (s, 2 H), 3.91 (s, 3 H), 3.90 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 161.3, 159.9, 151.4, 148.6, 139.8, 132.1, 122.6, 117.2, 117.0, 116.8, 53.6, 52.5, 49.6.

Anal. Calcd for $C_{13}H_{13}N_3O_6$: C, 50.82; H, 4.26; N, 13.68. Found: C, 50.99; H, 4.39; N, 13.61.

2-(1*H*-1,2,3-Triazol-1-ylmethyl)-1,4-benzoquinones 4; General Procedure

Activated MnO_2 (5 equiv) was added to a soln of **3** (1 mmol) in CH_2Cl_2. The heterogeneous mixture was vigorously stirred at r.t. until all the starting material was consumed (16–32 h, TLC). After

completion, the mixture was filtered through a short pad of Celite 545 and the solvent was removed under pressure to give **4**.

{1-[(3,6-Dioxocyclohexa-1,4-dienyl)methyl]-1*H*-1,2,3-triazol-4-yl}methyl Acetate (4a)
Brownish oil.

IR (acetone): 3125, 3015, 2969, 2955, 2866, 2120, 1739, 1664, 1610, 1584, 1549, 1508, 1455, 1366, 1214, 1154, 1110, 1094, 1061, 1017, 968, 897, 845, 762, 742, 697, 656, 633 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 7.89 (s, 1 H), 6.75 (dd, *J* = 10.1, 1.4 Hz, 1 H, A part of AB system), 6.70 (dd, *J* = 10.1, 1.6 Hz, 1 H, B part of AB system), 6.24 (br s, 1 H), 5.37 (s, 2 H), 5.09 (s, 2 H), 1.95 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 187.5, 186.6, 171.2, 143.2, 137.7, 137.2, 134.0, 126.2, 117.6, 58.2, 48.4, 21.3.

Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.24; N, 16.09. Found: C, 55.40; H, 4.12; N, 16.22.

2-[(4-Phenyl-1*H*-1,2,3-triazol-1-yl)methyl]-1,4-benzoquinone (4c)
Brownish solid; mp 133–135 °C.

IR (acetone): 3028, 2969, 2928, 2855, 2115, 2058, 1739, 1660, 1613, 1509, 1457, 1366, 1226, 1217, 1154, 1125, 1091, 1044, 969, 898, 874, 821, 766, 739, 694, 650, 605 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 8.44 (s, 1 H), 7.91 (d, *J* = 7.6 Hz, 2 H), 7.45 (t, *J* = 6.0 Hz, 2 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 6.94 (d, *J* = 10.1 Hz, 1 H, A part of AB system), 6.87 (dd, *J* = 10.1–1.9 Hz, 1 H, B part of AB system), 6.45 (br s, 1 H), 5.56 (s, 2 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 187.7, 186.8, 148.2, 143.6, 137.6, 137.4, 134.0, 132.0, 129.6, 128.7, 126.3, 122.4, 48.3.

Anal. Calcd for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84. Found: C, 68.08; H, 4.21; N, 15.56.

4-{1-[(3,6-Dioxocyclohexa-1,4-dienyl)methyl]-1*H*-1,2,3-triazol-4-yl}benzaldehyde (4d)
Brownish solid; mp 160–161 °C.

IR (acetone): 3005, 2968, 2929, 2856, 2739, 2115, 1737, 1701, 1660, 1609, 1574, 1454, 1423, 1365, 1284, 1214, 1170, 1121, 1075, 1046, 1013, 974, 899, 834, 743, 684, 653, 609 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 10.03 (s, 1 H, CHO), 8.48 (s, 1 H), 8.09–7.94 (AA′BB′ system, 4 H, aromatic), 6.90 (d, *J* = 10.1 Hz, 1 H, A part of AB system), 6.83 (dd, *J* = 10.1, 2.2 Hz, 1 H, B part of AB system), 6.49 (br s, 1 H), 5.55 (s, 2 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 192.2, 187.5, 186.6, 168.2, 147.3, 143.1, 137.7, 137.3, 136.8, 134.3, 131.0, 126.8, 123.8, 48.5.

Anal. Calcd for $C_{16}H_{11}N_3O_3$: C, 65.53; H, 3.78; N, 14.33. Found: C, 65.60; H, 3.65; N, 14.09.

2-[(4-Ferrocenyl-1*H*-1,2,3-triazol-1-yl)methyl]-1,4-benzoquinone (4e)
Reddish oil.

IR (acetone): 3006, 2969, 2925, 2853, 2127, 1739, 1659, 1587, 1443, 1367, 1215, 1092, 1057, 879, 817, 668 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 7.78 (s, 1 H), 6.83 (d, *J* = 10.1 Hz, 1 H, A part of AB system), 6.72 (dd, *J* = 10.1, 2.1 Hz, 1 H, B part of AB system), 6.25 (br s, 1 H), 5.35 (s, 2 H), 4.63 (m, 2 H), 4.19 (m, 2 H), 3.95 (s, 5 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 185.7, 185.0, 146.2, 141.8, 135.9, 135.5, 132.2, 119.6, 74.4, 68.6, 67.7, 65.7, 46.6.

Anal. Calcd for $C_{19}H_{15}FeN_3O_2$: C, 61.15; H, 4.05; N, 11.26. Found: C, 61.21; H, 4.18; N, 11.09.

2-{[4-(3-Thienyl)-1*H*-1,2,3-triazol-1-yl]methyl}-1,4-benzoquinone (4f)
Brownish solid.

IR (acetone): 3067, 3014, 2969, 2948, 2855, 2130, 1739, 1685, 1601, 1507, 1450, 1366, 1284, 1226, 1217, 1120, 1089, 1061, 1000, 965, 897, 855, 820, 785, 712, 618 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 8.14 (s, 1 H), 7.71 (br s, 1 H), 7.47–7.41 (m, 2 H), 6.86 (d, *J* = 9.9 Hz, 1 H, A part of AB system), 6.79 (d, *J* = 9.9 Hz, 1 H, B part of AB system), 6.37 (s, 1 H), 5.46 (s, 2 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 191.7, 190.9, 149.2, 147.6, 141.9, 141.5, 138.3, 137.1, 131.4, 130.9, 126.3, 126.0, 53.9.

Anal. Calcd for $C_{13}H_9N_3O_2S$: C, 57.55; H, 3.34; N, 15.49; S, 11.82. Found: C, 57.63; H, 3.29; N, 15.38; S, 11.56.

Dimethyl 1-[(3,6-Dioxocyclohexa-1,4-dienyl)methyl]-1*H*-1,2,3-triazole-4,5-dicarboxylate (4g)
White solid; mp 90–92 °C.

IR (acetone): 3011, 2968, 2956, 2848, 2126, 2024, 1881, 1738, 1661, 1603, 1556, 1456, 1364, 1320, 1277, 1226, 1220, 1152, 1097, 1064, 964, 944, 899, 845, 826, 797, 772, 740, 712, 693, 670, 617 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 6.79 (d, *J* = 10.1 Hz, 1 H, A part of AB system), 6.72 (d, *J* = 10.1 Hz, 1 H, B part of AB system), 6.24 (s, 1 H), 5.58 (s, 2 H), 3.82 (s, 3 H), 3.78 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 187.5, 186.5, 161.3, 159.4, 142.9, 141.0, 137.7, 137.3, 133.9, 131.2, 53.8, 52.8, 48.5.

Anal. Calcd for $C_{13}H_{11}N_3O_6$: C, 51.15; H, 3.63; N, 13.77. Found: C, 51.22; H, 3.48; N, 13.61.

2-({4-[4-(Di-1*H*-pyrrol-2-ylmethyl)phenyl]-1*H*-1,2,3-triazol-1-yl}methyl)benzene-1,4-diol (5)
Aldehyde **3d** (0.154 g, 0.52 mmol) was dissolved in neat pyrrole (10 mL), and the soln was degassed by bubbling with N_2 for 20 min. TFA (0.01 mL, 0.09 mmol) was added, and the soln was stirred for 10 min. It was then diluted with CH_2Cl_2 (50 mL), washed with 0.1 N aq NaOH (50 mL) and H_2O (50 mL), and subsequently dried ($MgSO_4$). The $MgSO_4$ was removed by vacuum filtration and the filtrate was evaporated to remove the CH_2Cl_2. The remaining pyrrole was removed by vacuum distillation with gentle heating. The product was purified by column chromatography (silica gel, hexanes–CH_2Cl_2, 1:1, then MeOH–CH_2Cl_2, 5:95).

Yield: 83%; yellow solid; mp 238–239 °C.

IR (KBr): 3828, 3752, 3427, 2923, 2859, 2378, 1627, 1501, 1455, 1394, 1356, 1282, 1206, 1089, 931, 810, 728, 612, 482 cm^{-1}.

^1H NMR (400 MHz, CD_3OD): δ = 8.16 (s, 1 H), 7.70 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 8.2 Hz, 2 H), 6.73 (d, *J* = 8.5 Hz, 1 H), 6.67–6.62 (m, 4 H), 6.00 (t, *J* = 3.0 Hz, 2 H), 5.75 (bd, *J* = 2.0 Hz, 2 H), 5.54 (s, 2 H), 5.44 (s, 1 H).

^{13}C NMR (100 MHz, CD_3OD): δ = 151.4, 149.4, 148.8, 145.2, 134.2, 130.1, 129.7, 125.5, 123.4, 122.1, 118.0, 117.6, 117.3, 108.1, 107.6, 50.4, 45.2.

UV/Vis (CH_2Cl_2): λ_{max} = 250, 297 nm.

Anal. Calcd for $C_{24}H_{21}N_5O_2$: C, 70.06; H, 5.14; N, 17.02. Found: C, 70.16; H, 5.08; N, 16.97.

Bis(ligand)–Copper Complex 6
A soln of DDQ (0.170 g, 0.69 mmol) in MeCN (20 mL) was added dropwise to a stirred soln of pyrrole **5** (0.284 g, 0.69 mmol) in MeCN (10 mL) at r.t. The reaction mixture turned dark red, and the stirring was continued for another 30 min. Then $Cu(ClO_4)_2$ was added to the mixture, which was stirred overnight. The solvent was re-

moved and the residue was purified by column chromatography (silica gel, $CHCl_3$); this afforded a dichroic red/green film.

Yield: 0.381 g (63%); mp >300 °C.

UV/Vis (CH_2Cl_2): λ_{max} = 251, 268, 496.

Calcd for $C_{48}H_{32}CuN_{10}O_4$: C, 65.78; H, 3.68; N, 15.98. Found: C, 65.85; H, 3.61; N, 16.04.

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