

Syntheses, crystal structures and electrochemical properties of bis(catechol)s with acetylene group

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Abstract

Three bis(catechol) compounds 5,5'-(buta-1,3-diyne-1,4-diyl) bis(3-*tert*-butylcatechol) (Biscat 1), 5,5'-(2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl)bis(3-*tert*-butylcatechol) (Biscat 2) and 5,5'-(1,3-phenylene)bis(ethyne-2,1-diyl)bis(3-*tert*-butylcatechol) (Biscat 3) were obtained from cross-coupling reactions. Biscat 1 and Biscat 2 were characterized by X-ray crystal analysis and cyclic voltammetry (CV). The results from X-ray crystal analysis shows that Biscat 1 and 2 possess a rod like structure with molecular lengths 14.7 Å for Biscat 1 and 19.3 Å for Biscat 2. In Biscat 1, the two catechol rings are not in the same plane and the dihedral angle of terminal catechol rings is about 25°. CVs for Biscat 1 and 2 were measured under alkaline conditions. An oxidation wave was observed corresponding to Sq-Sq (Sq: semiquinone) → Bq-Bq (Bq: benzoquinone) at around -300 mV. However, the redox waves disappeared when the CV scan was repeated. In contrast, Biscat 3 showed stable redox waves in the range from -1 V to +1.5 V even in alkaline conditions. These results suggest that Biscat 1 and 2 were converted into polymer or oligomer compounds (insoluble materials) through the Bq-Bq structures during repeat of the CV scans.

Key words; bis(catechol), acetylene group, rod like structure, electrochemical behavior

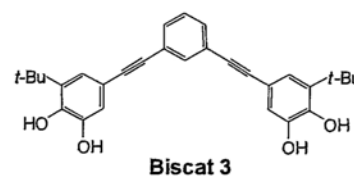
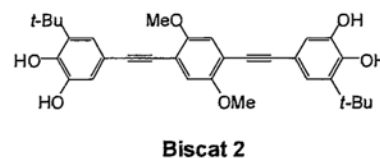
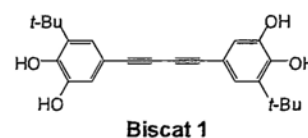
1. Introduction

Catechol oxidase (COs) is familiar as an *o*-diphenol oxidase as it catalyzes the oxidation of catechols to the corresponding quinones, a process known as catecholase activity. Because of this peculiar ability COs may perform a key role in the disease resistance mechanisms of higher plants [1] [2]. In addition, the coordination chemistry of transition metals complexes containing catecholate and semiquinone ligands have shown uniquely interesting properties resulting from the similarity in energy of the quinone π electronic levels with metal d-orbitals [3] [4] [5]. Recently, binuclear metal complexes with unsaturated connections between the dioxolene group have been studied with regard to possible electronic and magnetic coupling properties [6] [7] [8] [9] [10]. Attention has been drawn to these compounds as possible molecular devices in the field of materials science. Thus dioxolene compounds have the able to shuttle through several oxidation states in the sequence *o*-benzoquinone/*o*-benzosemiquinone/catecholate.

2. Experimental Section

Materials and Methods: Preparations were performed using Schlenk techniques. All solvents were dried and distilled by standard methods before use. Reagents were obtained from Wako Chemical Co. and used without further purification. IR spectra were measured as KBr disks on a JASCO IR-8000 FT-IR spectrometer, and $^1\text{H-NMR}$ spectra

Hence the study of catechol chemistry is proving to be valuable for both biology and physics. For the present work, we



have designed a series of new dioxolene ligands with acetylene groups as the linker [11] [12] since it is very important to reveal the properties of the basic bis(catechol) ligands in order to further study their transition metal complexes. These bis(catechol)s have π conjugated structure and also expected to fluoresce. In this work we report the syntheses, characterization, and particularly the electrochemical properties of three bis(catechol)s.

were recorded on a Varian Mercury-300 spectrometer and JEOL-500 spectrometer. UV-visible spectra were recorded on a SHIMADZU UV-2450 spectrometer, and cyclic voltammograms measurements were made under a flow of nitrogen using ALS/CHI 660A instrument. Solutions of the complexes were prepared in CH_3CN containing

(*n*-Bu₄N)(PF₆) (ca. 0.1 M) as supporting electrolyte. Platinum wire working and counter electrode were used with Ag/AgNO₃ reference electrode. The Fc⁺/Fc couple appeared at +0.08 V ($\Delta E = 65$ mV) vs. Ag/AgNO₃ with this experimental arrangement, and the ferrocene couple was used as an internal reference.

3-*tert*-butyl-4,5-bis(tetrahydro-2H-

pyranoxy)bromobenzene (2) [14]: Solution of dry dichloromethane (150 ml) **1** [12] [13] (10.8 g, 0.04 mol) and pyridinium-*p*-toluenesulfonate (**Care!** Known carcinogen, 0.22 g, 0.88 mmol) was ice cooling under Argon. 3,4-dihydro-2H-pyran (24 ml, 0.26 mol) added dropwise with ice cooling and stirring continued for 1 h until H₂ evolution had ceased. The solution washed with saturated NaHCO₃ aqueous solution (3 times, 50 ml), and the organic phase dried (MgSO₄) and concentrated in vacuum. The resulting oil was purified by column chromatography (hexane/ethyl acetate=5/1) to afford **2** as yellow oil (14.6 g, 80 %). R_f (benzene)=0.55; IR (KBr, cm⁻¹) 2956s, 1584s, 1567s, 1467s, 1437s, 1395s, 1361m, 1280s, 1260s, 1167s, 1084s, 1009s, 957s, 939s, 854s, 765m, 574w; ¹H NMR (300 MHz, CDCl₃, ppm) 1.36 (9 H, s), 1.39 (4H, s), 1.66 (4H, m), 1.89 (4H, m), 3.63 (2 H, m), 3.90 (2 H, m), 6.24 (1H, s), 6.34 (1H, s), 7.03 (1 H, s), 7.14 (1 H, s).

3-*tert*-butyl-4,5-bis(tetrahydro-2H-

pyranoxy)ethynylbenzene (3) [15]: Trimethylsilylacetylene (8.00 ml, 57.8 mmol) was added by syringe to a 300 ml round bottomed flask containing a well stirred mixture of **2** (15.9 g,

0.039 mol), Pd(PPh₃)₂Cl₂ (1.08 g, 1.54 mmol), CuI (0.146 g, 0.770 mmol) and triethylamine (50 ml). The resultant mixture was stirred at reflux for 12 h. The solvent was removed and the residue was placed on silica (400 ml) and eluted with hexane/ethyl acetate=5/1. Compound was obtained as reddish yellow oil (12.7 g, 77%). Also these compound dissolved in chloroform (100 ml) was stirred with aqueous 2M-KOH (20 ml) for 30 min at room temperature. The aqueous phase as then extracted with chloroform (3 times, 20 ml), and the organic phase dried (MgSO₄) and concentrated in vacuum. The resulting oil was purified by column chromatography (hexane/benzene=1/3) to afford **3** as reddish yellow oil (8.95 g, 92 %). R_f (hexane/ethyl acetate=4/1)=0.65; IR (KBr, cm⁻¹) 3527m, 3310m, 2951s, 2868m, 2103w, 1585m, 1468s, 1448s, 1359s, 1255s, 1200s, 1180s, 1119s, 1073s, 1034s, 981s, 872m, 736m; ¹H NMR (300 MHz, CDCl₃, ppm) 1.37 (4H, s), 1.39 (9H, s), 1.64 (4H, m), 1.87 (4H, m), 2.92 (1H, s), 3.63 (2H, m), 3.90 (2H, m), 6.34 (1H, s), 6.49 (1H, s), 6.93 (1H, m), 6.98 (1H, m).

5,5'-(buta-1,3-diyne-1,4-diyl) bis(3-*tert*-butylcatechol) (Biscat 1):

In 300 ml round bottomed flask containing a well stirred mixture of **3** (1.00 g, 2.79 mmol), Pd(PPh₃)₂Cl₂ (0.087 g, 0.122 mmol), CuI (0.012 g, 0.061 mmol) and triethylamine (50 ml). The resultant mixture was stirred under reflux for 12 h. The solvent was removed and the residue was placed on silica gel and eluted with hexane/benzene=1/1. Compound was obtained as reddish brown oil (0.48 g, 48%). Also the compound dissolved in chloroform (10

ml) was stirred with aqueous 2M-HCl (2 ml) for 30 min at room temperature. The aqueous phase as then extracted with chloroform (3 times, 20 ml), and the organic phase dried (MgSO_4) and concentrated in vacuum. The resulting oil was purified by column chromatography (silica gel, hexane/ethyl acetate=5/1) to afford **Biscat 1** as reddish brown powder (0.21 g, 40%). IR (KBr, cm^{-1}) 3483s, 2958s, 2135m, 1589s, 1501s, 1482s, 1419s, 1368s, 1296s, 1257s, 1176s, 1131m, 980s, 857m, 800m, 754m, 690m, 649m, 527m; ^1H NMR (300 MHz, CDCl_3 , ppm) 1.37 (9H, s), 5.48 (1H, s), 5.95 (1H, s), 6.86 (1H, s), 7.07 (1H, s); EI-Mass $m/z=378$; (*Anal.* Calc. for $\text{C}_{24}\text{H}_{26}\text{O}_4 \cdot 3\text{H}_2\text{O}$: C, 66.65; H, 7.46. Found: C, 66.51; H, 6.58 %). UV-Vis (acetone, $\lambda_{\text{max}}(\text{nm})$) 326 ($\lambda = 4.51 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 350 ($\lambda = 3.86 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

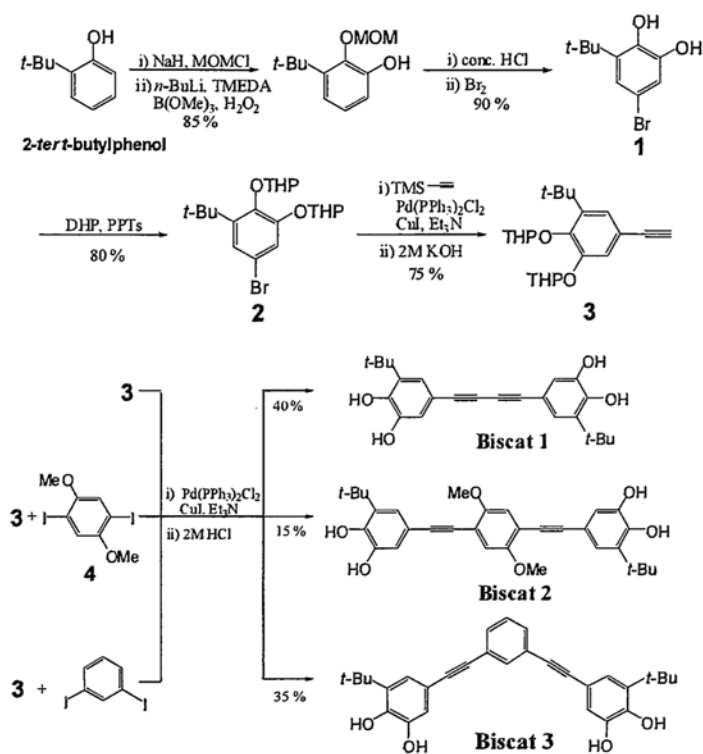
1,4-diiodo-2,5-dimethoxybenzene (4) [16]: A 500 ml flask was charged with iodine (4.59 g, 36.2 mmol), 1,4-dimethoxy benzene (5.00 g, 36.2 mmol), iodic acid (3.82 g, 21.7 mmol), CCl_4 (11 ml), glacial acetic acid (72 ml), 10.0 ml 30% H_2SO_4 . The resulting mixture was heated to 75°C for 3 days. After this time, 150 ml water was added and this solution was extracted three times with 100 ml diethyl ether. This diethyl ether solution was washing three times with 10% sodium thiosulfate (100 ml) to remove any unreacted iodine. Also organic solution was washing two times with a 5% NaOH solution (100 ml), followed by washing three times with saturated NaCl aqueous solution. The organic layer was dried over MgSO_4 and the solvent removed under reduced pressure. The product, 2,5-dimethoxy-1,4-diiodobenzene, was

isolated by crystallization step from methanol to give an overall yield of 38%. IR (KBr, cm^{-1}) 3448m, 2958s, 2930m, 1484s, 1433s, 1217s, 1063s; ^1H NMR (300 MHz, CDCl_3 , ppm) 3.81 (6H, s), 7.17 (2H, s).

5,5'-(2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl)bis(3-tert-butyl-catechol) (Biscat 2): 4 (1.00 g, 2.56 mmol) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.431 g, 0.614 mmol), CuI (0.058 g, 0.307 mmol) and triethylamine (50 ml) were added to a 500 ml round bottomed flask and a well stirred. Dry THF solution of **3** (2.75 g, 7.68 mmol) was added to this reactants. The resultant mixture was stirred for 12 h. The solvent was removed and the residue was placed on silica gel and eluted with benzene. Compound was obtained as reddish brown oil (794 mg, 36%). Also the compound dissolved in chloroform (10 ml) was stirred with aqueous 2M-HCl (2 ml) for 30 min in methanol at room temperature. The aqueous phase as then extracted with chloroform (3 times, 20 ml), and the organic phase dried (MgSO_4) and concentrated in vacuum. The resulting oil was purified by column chromatography (silica gel, hexane/ethyl acetate=5/1) to afford **Biscat 2** as reddish brown crystals (0.149 g, 15%). IR (KBr, cm^{-1}) 3449s, 2955m, 2201w, 1590m, 1509m, 1420s, 1312s, 1215m, 1034m, 989m, 867m, 755w, 637w; ^1H NMR (300 MHz, CDCl_3 , ppm) 1.39 (9H, s), 3.87 (3H, s), 6.91 (1H, d), 6.98 (1H, s), 7.09 (1H, d); EI-Mass $m/z=514$; (*Anal.* Calc. for $\text{C}_{32}\text{H}_{34}\text{O}_6 \cdot \text{CHCl}_3/\text{C}_6\text{H}_{14}$: C, 65.04; H, 6.86. Found: C 65.52; H 6.32 %). UV-Vis (acetone, $\lambda_{\text{max}}(\text{nm})$) 370 ($\lambda = 4.64 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

5,5'-(1,3-phenylene)bis(ethyne-2,1,1-diyl)bis(3-*tert*-butylcatechol)

(Biscat 3): Dry THF solution of **3** (1.86 g, 5.20 mmol) was added to a 500 ml round bottomed flask containing a well stirred mixture of 1,3-diodobenzene (0.85 g, 2.60 mmol), Pd(PPh₃)₂Cl₂ (0.431 g, 0.614 mmol), CuI (0.058 g, 0.307 mmol) and triethylamine (50 ml). The resultant mixture was stirred for 12 h. The solvent was removed and the residue was placed on silica gel and eluted with benzene. Compound was obtained as reddish brown oil. Also the compound dissolved in chloroform (50 ml) was stirred with aqueous 2M-HCl (2 ml) for 1 h in methanol at room temperature. The aqueous phase as then extracted with chloroform (3 times, 30 ml), and the organic phase dried (MgSO₄) and concentrated in vacuum. The resulting oil was purified by column chromatography (silica gel, hexane/ethyl acetate=2/1) to afford **Biscat 3** as reddish brown oil (0.48 g, 35 %). IR (KBr, cm⁻¹) 3511s, 2958m, 2208w, 1590m, 1509m, 1482m, 1420s, 1312s, 1215m, 1034m, 989m, 867m, 755w, 637w; ¹H NMR (300 MHz, CDCl₃, ppm) 1.39 (18H, s), 5.09 (2H,s), 5.87 (2H, s), 6.89 (2H, s), 7.07 (2H, s), 7.38 (1H, t), 7.40 (2H, d), 7.63 (1H, s); EI-Mass m/z=454; (Anal. Calc. for C₃₀H₃₀O₄ · H₂O: C, 76.25; H, 6.83. Found: C 76.65; H 7.45 %). UV-Vis (acetone, λ_{max}(nm)) 326 (λ = 2.72 × 10⁴ M⁻¹cm⁻¹).



Scheme 1

Crystallography

Crystal data for Biscat 1 and Biscat 2: Single crystals of **Biscat 1** and **Biscat 2** were grown by slowly diffusion solvent hexane (**Biscat 1**) or acetone (**Biscat 2**) from the saturated chloroform solution. A crystal suitable for crystallographic data collection was coated with an amorphous resin and cooled in the nitrogen stream of a Rigaku/MSM Mercury CCD diffractometer. A full sphere of intensity data was measured, and the structure was solved using direct methods. Crystallographic data are summarized in Table 1. Selected bond length and angles are in Table 2. CIF data have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 697743 (**Biscat 1**), CCDC No. 697744 (**Biscat 2**). Copies of this information

may be obtained free charge from The Director,
CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK
(fax: +44-1223-336-033); email:

deposit@ccdc.cam.ac.uk or [www:
http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

Table 1. Crystallographic data for **Biscat 1** and **Biscat 2**.

| | Biscat 1 | Biscat 2 |
|------------------------|--|--|
| Formula | C ₂₄ H ₂₆ O ₄ | C ₃₈ H ₄₆ O ₈ |
| Fw | 378.47 | 630.78 |
| Crystal system | triclinic | triclinic |
| Space group | P-1(#2) | P-1(#2) |
| Z | 2 | 2 |
| a, Å | 6.929(7) | 11.989(11) |
| b, Å | 9.542(9) | 12.786(9) |
| c, Å | 15.30(2) | 13.230(10) |
| α, deg | 91.10(1) | 61.171(18) |
| β, deg | 98.46(2) | 87.54(3) |
| γ, deg | 91.08(2) | 84.95(3) |
| V / Å ³ | 1000(1) | 1770(2) |
| T / K | 170 | 170 |
| d / g cm ⁻³ | 1.256 | 1.184 |
| μ, cm ⁻¹ | 0.84 | 0.819 |
| R(Rw) | 0.066(0.157) | 0.0890(0.1114) |
| GOF | 1.08 | 1.002 |

^a Data were collected using Mo Kα radiation with a wavelength of 0.71073 Å.

^b Discrepancy indices are defined as: $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ and $R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}}$.

Table 2. Selected bond lengths(Å) and angles(deg) for **Biscat 1** and **Biscat 2**.

| Biscat 1 | | | |
|-----------------|----------|-------|----------|
| O1-C1 | 1.373(2) | O2-C3 | 1.381(3) |

| | | | |
|-----------------|------------|-------------|------------|
| O3-C16 | 1.358(2) | O4-C17 | 1.389(2) |
| C1-C2 | 1.403(3) | C1-C6 | 1.398(3) |
| C1-C7 | 1.536(3) | C2-C3 | 1.399(3) |
| C3-C4 | 1.380(3) | C4-C5 | 1.395(3) |
| C5-C6 | 1.4000(3) | C5-C11 | 1.434(3) |
| C7-C8 | 1.544(3) | C7-C9 | 1.530(3) |
| C7-C11 | 1.529(3) | C11-C12 | 1.204(3) |
| C12-C13 | 1.379(3) | C13-C14 | 1.202(3) |
| C14-C19 | 1.436(3) | C15-C16 | 1.406(2) |
| C15-C20 | 1.392(3) | C15-C21 | 1.539(3) |
| C16-C17 | 1.394(3) | C17-C18 | 1.378(3) |
| C18-C19 | 1.401(3) | C19-C20 | 1.399(3) |
| C21-C22 | 1.533(3) | C21-C23 | 1.540(3) |
| C21-C24 | 1.537(3) | | |
| O1-C2-C1 | 121.5(2) | O1-C2-C3 | 117.3(2) |
| O2-C3-C2 | 114.9(2) | O2-C3-C4 | 123.6(2) |
| C5-C11-C12 | 176.5(2) | C11-C12-C13 | 176.2(2) |
| C12-C13-C14 | 175.5(2) | C13-C14-C19 | 175.1(2) |
| Biscat 2 | | | |
| O1-C115 | 1.376(2) | O1-C16 | 1.428(2) |
| O2-C6 | 1.385(2) | O3-C7 | 1.365(2) |
| C1-C2 | 1.544(2) | C1-C3 | 1.531(2) |
| C1-C4 | 1.526(2) | C1-C5 | 1.538(2) |
| C5-C6 | 1.397(2) | C5-C9 | 1.406(2) |
| C6-C7 | 1.396(2) | C7-C8 | 1.386(2) |
| C8-C10 | 1.393(2) | C9-C10 | 1.399(2) |
| C10-C11 | 1.441(2) | C11-C12 | 1.200(2) |
| C12-C13 | 1.435(2) | C13-C14 | 1.400(2) |
| C13-C15 | 1.406(2) | C14-C15 | 1.390(2) |
| O2-C6-C5 | 121.14(15) | O2-C6-C7 | 116.64(14) |
| O3-C7-C8 | 124.34(16) | O3-C7-C6 | 114.80(18) |
| C10-C11-C12 | 178.07(12) | C12-C13-C14 | 178.39(16) |

3. Results and Discussion

Synthesis of Biscat

The synthetic schemes for the Biscats are shown in scheme 1. The synthesis of the desired bis(catechol) in general required diiodide analogues of compounds and monofunctionalized catechol. As spacer units, we chose an ethynyl group, because we required a rod type molecular wire structure with redox functionality. Protection of the OH groups of the catechol made use of tetrahydro-2H-pyran (THP) during the course of the syntheses of these compounds. The THP groups can be cleaved easily by traces of HCl in methanol. Therefore, we synthesized THP-protected catechol **2** by applying an adapted protocol for the introduction of the THP groups. The same reaction sequence that was used for the synthesis of monofunctional derivatives including the iodination, Sonogashira cross-coupling reaction, and cleavage of the THP functionality was then applied again and led to 3-*tert*-butyl-4,5-bis(tetrahydro-2H-pyranoxy) ethynylbenzene **3** over four steps (Scheme 1). Again, a twofold Sonogashira reaction of **3** and **4** (or 1,3-diiodobenzene) yielded **Biscat 2** and **Biscat 3** (Scheme 1). **3** was subsequently dimerised by the Sonogashira reaction with use of [Pd(PPh₃)₂]Cl₂ as the palladium source and CuI to yield a precursor with THP protected OH groups for the synthesis of **Biscat 1**. The three Biscats are identified by IR, ¹H-NMR, EI-Mass and EA as described in the experimental section. Interestingly, the emission spectrum of **Biscat 2**

in CHCl₃ displays a sharp band with a maximum at 400 nm. The quantum yield of **Biscat 2** was also measured as 59.2% at room temperature in CHCl₃ solution.

Molecular structure of Biscat 1 and Biscat 2

The structure of **Biscat 1** and **Biscat 2** were determined to identify features that might be significant in propagating electronic coupling between the catechol regions at either end of the di-ethynylene bridge and that might promote exchange between metal ions chelated by the catecholate groups. **Biscat 1** is shown in Figure 1. Two *tert*-butyl groups into catechol moiety put on the same side for the di-ethynylene bridge. Also, the two catechol rings are not planar, since there is a dihedral angle between two catechol rings of 25°. The two ethynyl groups forms slightly bent structures, not linear chains. The bond lengths between the carbon atoms within the catechol ring are consistent with typical values for catechols and catecholate ligands. The C-C length across the center is shorter than a single bond value with a distance of 1.379(3) Å, and the two C≡C triple bonds of the bridge have localized triple bond values of 1.204(3) and 1.202(3) Å (Table 2). There is no weak interaction with the nearest molecule. The molecular length for **Biscat 1** is 14.7 Å. The structure of **Biscat 2** is shown in Figure 2. Both terminal catechol rings are located at centers of inversion symmetry. At the conclusion of the

refinement on the **Biscat 2** molecule an acetone was located and added to the refinement as a solvent of crystallization. The three aromatic rings are not in the same plane. The dihedral angle between terminal catechol ring and center

dimethoxyphenyl ring is about 18°. The C-C triple bond of the bridge has a localized triple bond value of 1.200(2) Å (Table 2). There is no weak interaction with the nearest molecule. The molecular length for **Biscat 2** is 19.3 Å.

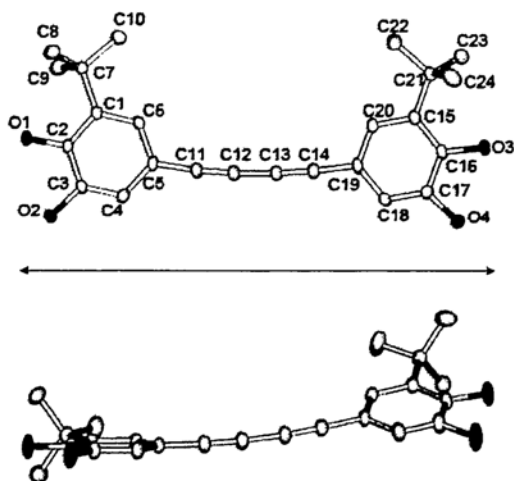


Figure 1. Molecular structure of **Biscat 1**

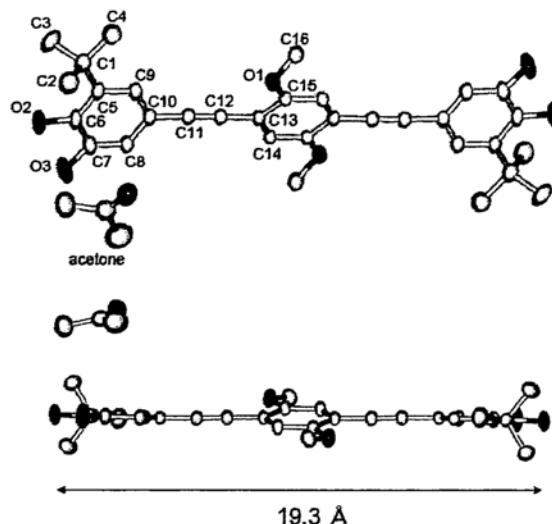
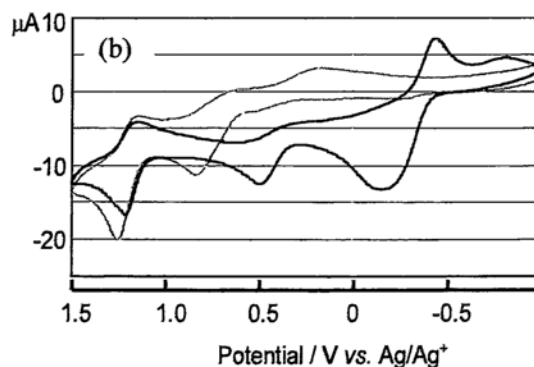
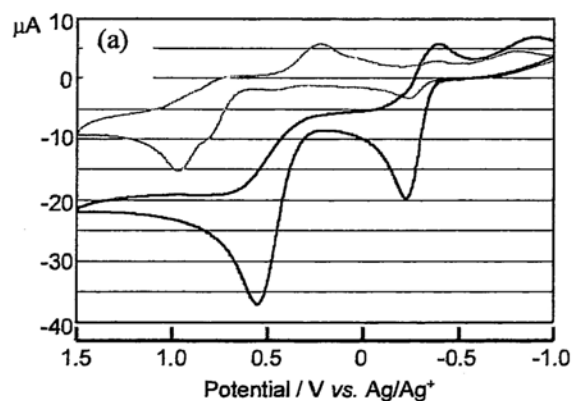


Figure 2. Molecular structure of **Biscat 2**

Electrochemical property of Biscat

Cyclic voltammograms of all Biscat have been recorded in acetonitrile solution containing 0.1 M (*n*Bu₄N)PF₆ as the supporting electrolyte with a Pt working electrode and a Ag/AgNO₃ reference electrode. Ferrocene was used as an internal standard, and potentials are referenced versus the ferrocenium/ferrocene couple (Fc⁺/Fc). Table 3 summarizes the results. CVs of **Biscat 1**, **Biscat 2** and **Biscat 3** showed irreversible oxidation wave at a potential around 1 V under neutral conditions because the activation energy for deprotonation from the OH group is large. This oxidation wave undergoes a 4-electrons oxidative transformation to give benzoquinone. However, the electrochemical



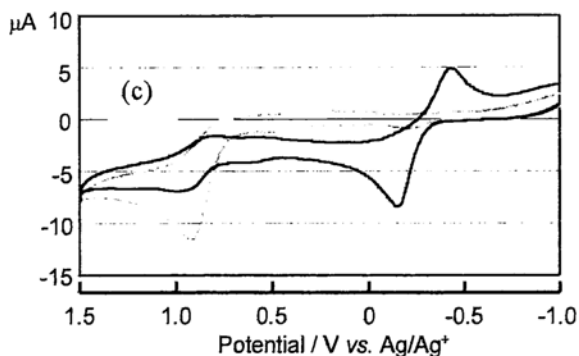


Figure 3. Cyclic voltammogram of (a) Biscat 1, (b) Biscat 2 and (c) Biscat 3.

— Alkali - - - Neutral

oxidation of three Biscats under alkaline conditions was partly quasi-reversible at a scan rate of 50-500 mV/s. **Biscat 1** shows one set reduction waves and other oxidation wave at potentials of -0.228 and +0.55 V (vs Fc^+/Fc), respectively (Figure 3(a)). The first one set reduction waves are separated by approximately 0.17 V, suggesting that they correspond to Sq-Sq/Bq-Bq, but not Cat-Cat/Sq-Sq. The second one may correspond to Bq-Bq hydrolysis steps ($\text{Bq-Bq} + 4\text{H}_3\text{O}^+ + 4\text{e}^- \rightarrow \text{Cat-Cat} + 4\text{H}_2\text{O}$). After repeating at a scan rate of 100 mV/s, these waves are disappeared and black precipitates were obtained from the solution [17]. This indicates a polymerization or oligomerization reaction through the Bq-Bq structures. In **Biscat 2**, the CV shows one set reduction waves, an

oxidation wave and also one set of oxidation waves. The first is a closely-spaced irreversible reduction wave and second is irreversible oxidation, and the third is reversible oxidation (Figure 3(b)). The first oxidations are separated by approximately 0.28 V, suggesting that they correspond to Sq-Sq/Bq-Bq as with **Biscat 1**. The second wave corresponds to Bq-Bq hydrolysis steps. The third is a reversible oxidation wave and is identified as the one-electron redox in the dimethoxyphenyl ring of **Biscat 2**. After repeating at a scan rate of 100 mV/s the first oxidation waves disappeared. In **Biscat 3**, the CV is different from those of **Biscat 1** and **2** as shown in Figure 3(c). The first reduction waves are separated by approximately 0.28 V, suggesting that they correspond to Sq-Sq/Bq-Bq. The second wave is the irreversible oxidation wave and is identified as the one-electron redox in the benzene ring of **Biscat 3**. After repeating at a scan rate of 100 mV/s there is no change in the cyclic voltammogram. This means that **Biscat 3** forms the bent structure shown and the π -conjugated resonance structure through triple bonds. Bq-Bq formation is stabilized in this solution compared with the other two compounds.

Table 3. Electrochemical property of Biscat.

| Biscat | 2-/0 | | | E_p^{anode} | 0/+1 | | |
|----------|------------------------|----------------------|-------------------------------|----------------------|------------------------|----------------------|-------------------------------|
| | E_p^{cathode} | E_p^{anode} | ΔE (mV) ^{*)} | | E_p^{cathode} | E_p^{anode} | ΔE (mV) ^{*)} |
| Biscat 1 | -0.398 | -0.228 | 170 | 0.550 | — | — | — |
| Biscat 2 | -0.436 | -0.152 | 284 | 0.495 | 1.142 | 1.213 | 71 |
| Biscat 3 | -0.434 | -0.152 | 282 | — | 0.797 | 0.990 | 193 |

All potentials are referenced to the ferrocenium/ferrocene couple ($E_{1/2} = 0.083$ V)

*) $\Delta E = E_p^{\text{anode}} - E_p^{\text{cathode}}$

4. Summary

Cyclic voltammograms of these Biscat compounds show an irreversible oxidation wave at around 1 V under neutral conditions. However, in alkaline conditions new reduction waves appear at around -300 mV that correspond to Sq-Sq/Bq-Bq. Moreover, only **Biscat 3** showed stable redox

waves after repeat CVs at a scan rate of 100 mV/s. These results indicate the observed redox behavior is based on the π -conjugated resonance structure and that **Biscat 3** has a stable Bq-Bq structure in solution.

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