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SYNTHESIS, PROPERTIES, AND CRYSTAL STRUCTURE OF DDQ-ADDUCTS OF ETHYNYLATED 2*H*-CYCLOHEPTA[*b*]FURAN-2-ONES†

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Abstract – Ethynylated 2*H*-cyclohepta[*b*]furan-2-ones reacted with 2,3-dichrolo-5,6-dicyano-1,4-benzoquinone (DDQ) in a formal [2+2] cycloaddition reaction to afford the corresponding DDQ-adducts in good yields. The electronic properties of the DDQ-adducts were investigated by UV/Vis spectroscopy. One of the DDQ-adducts was revealed the molecular structure by X-ray crystallographic analysis. The redox behavior of the new compounds was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

INTRODUCTION

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is well known as an oxidizing reagent for the formal dehydrogenation reaction in organic synthesis.[1] Recently, Diederich[2] and Trofimov[3] have reported that DDQ is reacted with various alkyne derivatives in a formal [2+2] cycloaddition reaction to give the corresponding cycloaddition products. They have also reported the unusual reactivities and properties of

† Dedicated to Professor Victor Snieckus on the occasion of his 77th birthday.

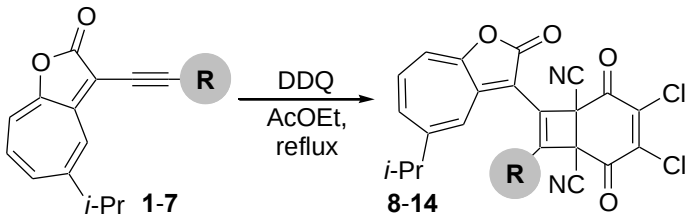
the adducts, such as carbon-skeleton rearrangement,[2,4] intramolecular charge-transfer absorption, third-order optical nonlinearities,[2] and so on. These results show the DQQ-adducts have a potential as a new series of advanced organic materials.

2*H*-Cyclohepta[*b*]furan-2-one is known as a heteroazulene, a versatile precursor for azulene derivatives.[5] Although its unusual reactivity has already been revealed by many research groups,[6] there are few 2*H*-cyclohepta[*b*]furan-2-one derivatives for the application to the advanced materials with potentially useful electronic properties. For the extension of this chemistry, we have focused our studies on the synthesis of tetracyanobutadiene (TCBD)[7] and dicyanoquinodimethane (DCNQ)[8] derivatives of 2*H*-cyclohepta[*b*]furan-2-one by the formal [2+2] cycloaddition–cycloreversion reaction of the corresponding alkyne derivatives with tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ), respectively. The study revealed the TCBD and DCNQ derivatives are featured by a strong ICT absorption in their UV/Vis spectra. Ethynyl-2*H*-cyclohepta[*b*]furan-2-one derivatives are also expected to show high reactivity with DDQ toward the [2+2] cycloaddition reaction to afford the novel DDQ-adducts owing to the electron-donating nature of the 2*H*-cyclohepta[*b*]furan-2-one functions.

Herein, we describe the synthesis of the DDQ-adducts **8**–**14** with 2*H*-cyclohepta[*b*]furan-2-one substituents by the [2+2] cycloaddition reaction of ethynyl-2*H*-cyclohepta[*b*]furan-2-ones **1**–**7** with DDQ. The electronic properties of the new compounds obtained by this reaction were characterized by CV, DPV, and absorption spectroscopy. In addition one of the DDQ-adducts was revealed the molecular structure by X-ray crystallographic analysis.[9]

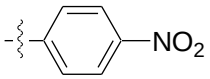
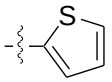
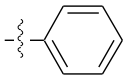
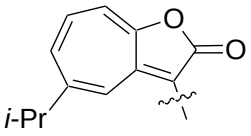
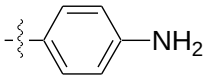
RESULT AND DISCUSSION

SYNTHESIS: Ethynyl-2*H*-cyclohepta[*b*]furan-2-ones **1**–**7** were prepared by Sonogashira–Hagihara reaction, according to the procedure reported by us, recently. For the synthesis of the novel DDQ-adducts, we have examined the [2+2] cycloaddition reaction of the ethynyl-2*H*-cyclohepta[*b*]furan-2-ones **1**–**7** with DDQ, according to the procedure described in the literature. The yield of the products is summarized in Table 1.



Scheme 1

Table 1. Reaction of Ethynyl-2*H*-cyclohepta[*b*]furan-2-ones **1**−**7** with DDQ

Substrate	R	Product, Yield [%]	Substrate	R	Product, Yield [%]
1	H	**8**, 83	**5**		**12**, 74
2	$SiMe_3$	**9**, 70	**6**		**13**, 76
3		**10**, 84	**7**		**14**, 59
4		**11**, 15			

The reaction of **1** with DDQ in refluxing ethyl acetate yielded **8** in 83% yield. In the reaction of acetylene derivatives with TCNE, the [2+2] cycloaddition reaction with an alkyne moiety afford the cyclobutene intermediate, following to the ring-opening reaction of the cyclobutene derivative gives the thermodynamically stable TCBDs. Formation of the DDQ-adducts with a cyclobutene substructure in this reaction might be attributable to the structural effect of the fused cyclohexene ring.

To investigate the substituent effect on the alkyne terminal, the reaction of **2**−**7** with DDQ were examined under the similar reaction conditions. Acetylene derivatives **2** and **3** also reacted readily with DDQ to afford the corresponding DDQ-adducts **9** and **10** in 70% and 84% yields, respectively, as similar to the reaction of **1** with DDQ. The cycloaddition reaction of **4** gave the presumed DDQ-adduct **11** in 15% yield along with a certain amount of an inseparable complex mixture, although the cycloaddition reaction of **5** with an electron-withdrawing function with DDQ afforded the presumed **12** in 74% yield as a sole product. These results indicate the aryl group with highly electron-donating function on the acetylene terminal should be prevented the [2+2] cycloaddition reaction with DDQ in the acetylene moiety. The [2+2] cycloaddition reaction of thiophene-substituted alkyne **6** with DDQ also afforded the corresponding DDQ-adduct **13** in 76% yield, under the similar reaction conditions. The reaction of symmetrically substituted alkyne **7** with DDQ yielded the corresponding cycloadduct **14** in 59% yield.

PROPERTIES: These new compounds **8**–**14** were fully characterized by the spectral data. Mass spectra of **8**–**14** ionized by ESI showed the correct molecular ion peaks observed as $[M + Na]^+$ ion peaks. The characteristic stretching vibration band of the C≡N moieties of **8**–**14** was observed at ν_{max} = 2219–2239 cm^{-1} on their IR spectra, instead of the characteristic stretching band for C≡C triple bond of the starting acetylene derivatives. Assignment of peaks in the ^1H NMR spectra of the compounds was accomplished

by decoupling and 2D COSY experiments. These results are consistent with the structure of these products.

Single crystals of **9** suitable for X-ray crystallographic analysis were obtained by recrystallization from CH_2Cl_2. The DDQ-adduct **9** was crystallized in an orthorhombic cell. The molecular structure of **9** was revealed as shown in Figure 1. The cycloheptafuranone ring in **9** has an approximately orthogonal conformation with the substituted cyclobutene ring. Recently, Diederich *et al*. have reported the planarity between the dimethylanilino group and the cyclobutene ring of compound **15** by X-ray crystallographic analysis (Figure 2). The structural deformation of **9** might be ascribed to the steric bulkiness of both trimethylsilyl group and isopropyl moiety substituted on the cycloheptafuranone ring. The effect may become much more serious than that of simpler dimethylanilino group in **15**.

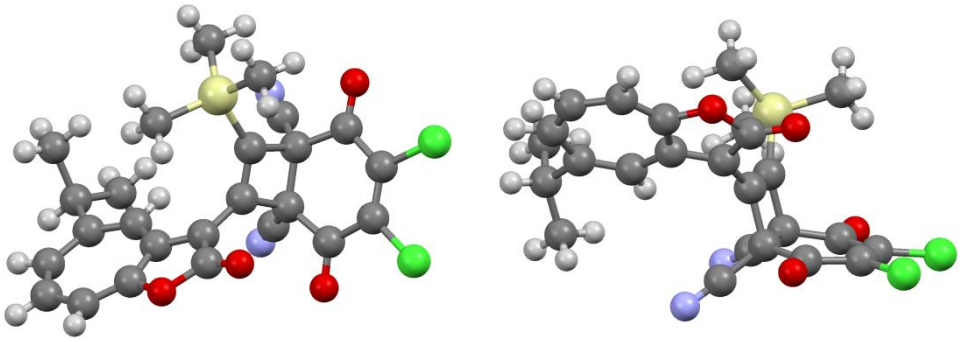
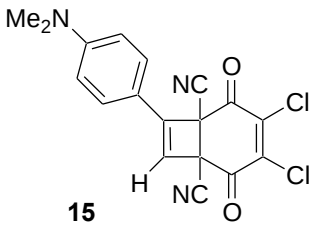


Figure 1. X-Ray structures of **9** (left: top view, right: side view)[10]



15

Figure 2. Structure of **15**

The UV/Vis spectra of compounds **10**–**14** showed characteristic absorptions arising from the cycloheptafuranone system in the visible region. The absorption maxima (λ_{max}) and the coefficients (log ε) of the DDQ-adducts **10**–**14** and the corresponding acetylene derivatives **3**−**7** are summarized in Table 2. The absorption maxima of the DDQ-adduct **10** showed broad absorption bands at λ_{max} = 418 nm and 451 (sh) nm, respectively. The UV/Vis spectrum of **11**, with a *p*-anilino substituent, exhibited absorption bands at λ_{max} = 376 nm and 439 nm, respectively. The absorption maximum of **12** (λ_{max} = 463 nm) exhibited a bathochromic shift relative to those of **10** and **11**. These results reflect to the *p*-nitrobenzene moiety results in a decrease of the HOMO-LUMO gap of **12**, compared to those of **10** and **11**. The DDQ-adduct **13** substituted by 2-thienyl group showed a broad absorption at around λ_{max} = 400–600 nm in CH_2Cl_2. Compound **14** exhibited two absorption bands at λ_{max} = 400 nm and λ_{max} = 507 (sh) nm. Intensity of the absorption band was twice as large as that of **10**−**13**. It should be ascribed to the overlapping of the transition from the two cycloheptafuranone rings in the molecule. The absorption coefficient of the DDQ-adducts **10**–**14** was decreased compared with that of acetylene derivatives **3**−**7**. These results suggest the less effective conjugation between the cycloheptafuranone and aryl moieties, due to the low planarity as observed by X-ray crystallographic analysis of DDQ-adduct **9**.

Table 2. Absorption maxima [nm] and their coefficients (log ε) of DDQ-adducts **10**−**14** in CH_2Cl_2 and acetylenes **3**−**7** as references[7]

Sample	λ_{max} (log ε) in CH_2Cl_2	Sample	λ_{max} (log ε) in CH_2Cl_2
3	426 (4.40)	**10**	418 (4.15), 451 sh (4.11)
4	435 (4.39)	**11**	376 (4.01), 439 (4.10)
5	380 sh (3.94), 446 (4.43)	**12**	463 (4.21)
6	431 (4.38)	**13**	405 (3.54), 486 sh (3.18)
7	394 sh (4.09), 421 sh (4.26), 485 (4.51)	**14**	400 (4.40), 507 sh (3.97)

To clarify the electrochemical properties, the redox behavior of **10**–**14** was examined by CV and DPV. Measurements were carried out with a standard three-electrode configuration. Tetraethylammonium perchlorate (0.1 M) in benzonitrile was used as the supporting electrolyte with a platinum wire and disk as the auxiliary and working electrodes, respectively. All measurements were carried out under an argon atmosphere, and potentials were related to an Ag/Ag^+ reference electrode and Fc/Fc^+ as an internal reference, which discharged at +0.15 V. The redox potentials (in V vs. $Ag/AgNO_3$) of DDQ-adducts **10**–**14** obtained by the DPV analysis are summarized in Table 3.

Table 3. Redox potentials of DDQ-adducts **10**−**14**[11]

Sample	Method	E_1^{ox} [V]	E_2^{ox} [V]	E_1^{red} [V]	E_2^{red} [V]	E_3^{red} [V]
10	DPV	+1.19	−	−0.59	−1.15	−
11	DPV	+0.65	−	−0.92	−1.13	−1.67
12	DPV	+1.27	−	−0.54	−1.10	−1.43[12]
13	DPV	+1.11	−	−0.58	−1.16	−1.89
14	DPV	+0.88	+1.30	−0.62	−1.86	−

All DDQ-adducts **10**–**14** showed irreversible oxidation and reduction waves by CV. Differential pulse voltammograms for the oxidation and reduction of **14** are shown in Figure 3. DDQ-adducts with aryl substituents **10**, **11**, and **12** displayed an irreversible two- or three-stage reduction wave, depending on the *p*-substituent on the substituted-benzene ring. The first reduction potential of **12** (−0.54 V) was less negative than that of **10** (−0.59 V) and **11** (−0.92 V). These results reflect that the electron-withdrawing NO_2 substituent on the benzene ring directly results in a decrease of the LUMO level of the molecule. The lowest oxidation potential among these series of **11** (+0.65 V) should be attributed to the redox reaction of the substituted highly electron-donating *p*-anilino group. The electrochemical oxidation and reduction of

13 showed irreversible waves on DPV (E_1^{ox} = +1.11 V and E_1^{red} = −0.58 V) by the formation of a radical cationic and anionic species, respectively. Compound **14** also exhibited irreversible oxidation and reduction waves. The first redox potentials of **14** were identified as +0.88 V and −0.62 V by DPV. Recently, Diederich *et al*. have reported the compound **15** and its derivatives exhibit reversible multi-stage oxidation and reduction waves by CV.[2] The irreversibility for the redox wave of DDQ-adducts **10**–**14** should be attributed to the instability of the 2*H*-cyclohepta[*b*]furan-2-one ring, compared to *N*,*N*-dimethylanilino group, in the electrochemical reaction.

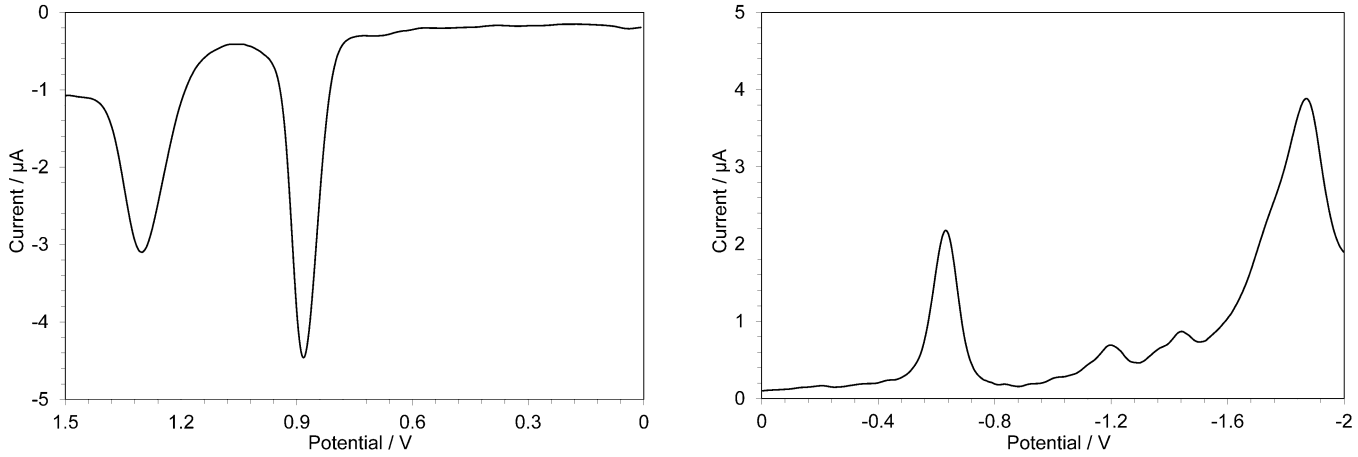


Figure 3. Differential pulse voltammograms of the oxidation (left) and reduction (right) of **14** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate=100 mVs^{-1}

In conclusion, the novel DDQ-adducts with 2*H*-cyclohepta[*b*]furan-2-one substituents **8**–**14** were synthesized by the [2+2] cycloaddition reaction of the ethynyl-2*H*-cyclohepta[*b*]furan-2-ones **1**–**7** with DDQ in good yields, except for the DDQ-adduct with electron-donating *p*-anilino substituent. The electronic and structural properties of the DDQ-adducts **8**–**14** were clarified by UV/Vis spectroscopy and X-ray crystallographic analysis. Electrochemical analyses by CV and DPV showed that these compounds **10**–**14** exhibited irreversible oxidation and reduction waves, whose potentials were depended considerably on the substituted aryl groups.

Azulene derivatives also have attracted much interest due to their characteristic electronic properties.[13] As described above, 2*H*-cyclohepta[*b*]furan-2-one derivatives are one of versatile precursors for azulene derivatives. Thus, DDQ-adducts **8**–**14** may become a possible precursor for the DDQ-adducts with azulene functions. To evaluate the reactivity of the novel DDQ-adducts with cycloheptafuranone functions, conversion of the compounds **8**–**14** into azulene derivatives is currently progress in our laboratory.

EXPERIMENTAL

Melting points were determined with a Yanagimoto MPS3 micro melting apparatus and are uncorrected. Mass spectra were obtained with a Bruker APEX II instrument. IR and UV/Vis spectra were measured with JASCO FT/IR-4100 and Shimadzu UV-2550 spectrophotometers, respectively. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCE400 spectrometer (at 400 MHz and 100 MHz, respectively), or a JEOL ECA500 spectrometer (at 500 MHz and 125 MHz, respectively). Voltammetry measurements were carried out with a BAS 100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes and a reference electrode formed from $Ag/AgNO_3$ (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.1 M). Elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Compound 8

DDQ (28 mg, 0.12 mmol) was added to a solution of **1** (21 mg, 0.10 mmol) in EtOAc (5 mL). The resulting mixture was refluxed for 12 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc as an eluent to give **8** (36 mg, 83%) as reddish brown crystals. Mp 105.0−107.0 °C (decomp.); IR (KBr disk): ν_{max} = 2971 (w), 2220 (w), 1733 (s), 1712 (s), 1701 (s), 1611 (m), 1583 (m), 1564 (m), 1511 (s), 1490 (s), 1346 (w), 1324 (w), 1279 (m), 1251 (w), 1215 (m), 1197 (m), 1143 (m), 1052 (w), 1042 (w), 926 (w), 890 (w), 879 (w), 820 (m), 804 (m), 780 (w), 762 (w), 726 (w), 698 (w), 647 (w) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 7.89 (d, 1H, *J* = 1.2 Hz, H-4), 7.65–7.59 (m, 2H, H-7,8), 7.52–7.46 (m, 1H, H-6), 7.20 (s, 1H, H-8'), 3.19 (sept, 1H, *J* = 6.8 Hz, *i*-Pr), 1.38 (d, 3H, *J* = 6.8 Hz, *i*-Pr), 1.37 (d, 2H, *J* = 6.8 Hz, *i*-Pr) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 178.29, 178.01, 166.12, 162.98, 158.38, 147.93, 141.77, 141.61, 140.93, 137.69, 136.40, 129.90, 127.00, 119.89, 115.16, 114.83, 96.90, 57.64, 56.00, 39.98, 24.10, 24.02 ppm; HRMS (ESI) Calcd for $C_{22}H_{12}Cl_2N_2O_4 + Na^+$ $[M + Na]^+$ 461.0066. Found: 461.0065; Anal. Calcd for $C_{22}H_{12}Cl_2N_2O_4 \cdot 1/2H_2O$: C, 58.95; H, 2.92; N, 6.25. Found: C, 58.68; H, 3.07; N, 6.16.

Compound 9

The procedure used for the preparation of **8** was adopted here. The reaction of **2** (28 mg, 0.10 mmol) with DDQ (28 mg, 0.12 mmol) in EtOAc (5 mL) at refluxing temperature for 10 h afforded **9** (36 mg, 70%) as reddish brown crystals. Mp 95.0−98.0 °C (decomp.); IR (KBr disk): ν_{max} = 2958 (w), 2219 (w), 1735 (s), 1711 (m), 1698 (m), 1645 (w), 1631 (w), 1595 (m), 1560 (w), 1512 (m), 1497 (m), 1464 (m), 1336 (w), 1314 (w), 1282 (m), 1252 (m), 1202 (w), 1141 (m), 1057 (w), 921 (w), 880 (w), 849 (m), 801 (m), 762 (w), 743 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.94 (d, 1H, *J* = 1.2 Hz, H-4), 7.36 (dd, 1H, *J* = 11.2, 9.2 Hz, H-7), 7.27 (dd, 1H, *J* = 9.2, 1.2 Hz, H-8), 7.21 (ddd, 1H, *J* = 11.2, 1.2, 1.2 Hz, H-6), 3.09

(sept, 1H, *J* = 6.8 Hz, *i*-Pr), 1.40 (d, 6H, *J* = 6.8 Hz, *i*-Pr), 0.27 (s, 9H, $SiMe_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 177.46, 176.59, 165.95, 162.02, 158.45, 157.69, 150.09, 149.22, 143.04, 142.50, 135.11, 134.80, 126.42, 117.79, 113.38, 113.09, 97.80, 57.27, 53.26, 39.97, 23.47, 23.25, −1.59 ppm; HRMS (ESI) Calcd for $C_{25}H_{20}Cl_2N_2O_4Si + Na^+$ $[M + Na]^+$ 533.0462. Found: 533.0461; Anal. Calcd for $C_{25}H_{20}Cl_2N_2O_4Si$: C, 58.71; H, 3.94; N, 5.48. Found: C, 58.53; H, 4.18; N, 5.43.

Compound 10

The procedure used for the preparation of **8** was adopted here. The reaction of **3** (30 mg, 0.10 mmol) with DDQ (28 mg, 0.12 mmol) in EtOAc (5 mL) at refluxing temperature for 14 h afforded **10** (45 mg, 84%) as reddish brown crystals. Mp 111.5−113.0 °C (decomp.); IR (KBr disk): ν_{max} = 2965 (w), 2934 (w), 2872 (w), 2239 (w), 1736 (s), 1713 (m), 1701 (m), 1622 (w), 1588 (m), 1570 (m), 1514 (m), 1489 (s), 1464 (m), 1447 (w), 1404 (w), 1348 (w), 1320 (w), 1281 (m), 1269 (m), 1242 (m), 1204 (w), 1136 (w), 1046 (w), 1017 (w), 916 (w), 895 (w), 814 (w), 791 (w), 770 (w), 762 (w), 750 (w), 718 (w), 698 (w), 689 (w), 652 (w), 639 (w), 419 (w) cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 260 (4.62), 280 sh (4.39), 306 sh (4.01), 418 (4.15), 451 sh (4.11) nm; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 7.60 (dd, 1H, *J* = 11.2, 9.2 Hz, H-7), 7.55–7.46 (m, 5H, H-Ph), 7.47 (dd, 1H, *J* = 9.2, 0.8 Hz, H-8), 7.35 (ddd, 1H, *J* = 11.2, 1.2, 0.8 Hz, H-6), 6.90 (d, 1H, *J* = 1.2 Hz, H-4), 2.72 (sept, 1H, *J* = 6.8 Hz, *i*-Pr), 0.97 (d, 3H, *J* = 6.8 Hz, *i*-Pr), 0.96 (d, 3H, *J* = 6.8 Hz, *i*-Pr); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 178.84, 177.47, 166.08, 162.21, 159.48, 149.33, 143.37, 142.54, 140.14, 136.66, 135.48, 133.66, 132.12, 130.18, 130.16, 128.66, 126.28, 118.23, 114.17, 113.70, 97.62, 56.99, 55.96, 39.57, 22.84, 22.74 ppm; HRMS (ESI): Calcd for $C_{28}H_{16}Cl_2N_2O_4 + Na^+$ $[M + Na]^+$ 537.0379. Found: 537.0377; Anal. Calcd for $C_{28}H_{16}Cl_2N_2O_4 \cdot 2/5H_2O$: C, 64.36; H, 3.24; N, 5.36. Found: C, 64.37; H, 3.28; N 5.38.

Compound 11

The procedure used for the preparation of **8** was adopted here. The reaction of **4** (303 mg, 1.00 mmol) with DDQ (272 mg, 1.20 mmol) in EtOAc (30 mL) at refluxing temperature for 5 min afforded **11** (80 mg, 15%) as reddish brown crystals. Mp 224.0−227.0 °C (decomp.); IR (KBr disk): ν_{max} = 3413 (w), 2968 (w), 2239 (w), 1768 (s), 1737 (s), 1621 (s), 1603 (m), 1525 (m), 1510 (m), 1492 (m), 1432 (w), 1401 (w), 1345 (w), 1316 (w), 1348 (m), 1284 (m), 1267 (m), 1239 (w), 1209 (m), 1175 (m), 1092 (w), 1059 (w), 1033 (w), 971 (w), 897 (m), 835 (m), 815 (m), 792 (m), 765 (m), 732 (w), 711 (w), 667 (w) cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 242 sh (4.47), 265 (4.51), 310 sh (4.20), 324 (4.25), 376 (4.01), 439 (4.10) nm; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 7.28 (d, 2H, *J* = 8.0 Hz, H-3',5'), 7.20 (d, 2H, *J* = 11.2 Hz, H-7), 7.14 (d, 2H, *J* = 11.2 Hz, H-8), 6.97 (d, 2H, *J* = 11.2 Hz, H-6), 6.92 (s, 1H, H-4), 6.61 (d, 2H, *J* = 8.0 Hz, H-2',6'), 4.07 (s, 2H, NH_2), 2.64 (sept, 2H, *J* = 6.5 Hz, *i*-Pr), 1.07 (d, 3H, *J* = 6.5 Hz, *i*-Pr), 1.05 (d, 3H, *J*

= 6.5 Hz, *i*-Pr) ppm; HRMS (ESI): Calcd for $C_{28}H_{17}Cl_2N_3O_4$ + Na $[M + Na]^+$ 552.0494. Found: 552.0490; Anal. Calcd for $C_{28}H_{17}Cl_2N_3O_4$: C, 63.41; H, 3.23; N, 7.92. Found: C, 63.20; H, 3.44; N 7.80. Low solubility hampered the measurement of ^{13}C NMR.

Compound 12

The procedure used for the preparation of **8** was adopted here. The reaction of **5** (160 mg, 0.48 mmol) with DDQ (172 mg, 0.76 mmol) in EtOAc (10 mL) at refluxing temperature for 18 h afforded **12** (199 mg, 74%) as reddish brown crystals. Mp 268.0−270.0 °C (decomp.); IR (KBr disk): ν_{max} = 2960 (w), 2931 (w), 2219 (w), 1729 (s), 1700 (s), 1617 (w), 1588 (m), 1565 (w), 1560 (w), 1522 (m), 1515 (m), 1501 (w), 1487 (s), 1459 (w), 1340 (s), 1324 (m), 1286 (m), 1273 (w), 1247 (w), 1140 (w), 853 (w), 813 (w), 764 (w), 713 (w) cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 257 (4.58), 274 sh (4.45), 322 sh (3.94), 352 sh (3.94), 368 (4.00), 463 (4.21) nm; ^1H NMR (400 MHz, DMSO-d_6): δ_H = 8.39 (ddd, 2H, *J* = 9.2, 2.4, 2.0 Hz, Ph-3,5), 7.76 (ddd, 2H, *J* = 9.2, 2.4, 2.0 Hz, Ph-2,6), 7.71 (dd, 1H, *J* = 11.2, 9.2 Hz, H-7), 7.58 (dd, 1H, *J* = 9.2, 0.8 Hz, H-8), 7.46 (ddd, 1H, *J* = 11.2, 1.2, 0.8 Hz, H-6), 7.04 (d, 1H, *J* = 1.2 Hz, H-4), 2.75 (sept, 1H, *J* = 6.8 Hz, *i*-Pr), 1.03 (d, 3H, *J* = 6.8 Hz, *i*-Pr), 1.01 (d, 3H, *J* = 6.8 Hz, *i*-Pr) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 177.06, 165.76, 163.14, 159.21, 149.04, 148.81, 141.58, 140.41, 138.75, 138.21, 136.88, 136.63, 135.91, 129.87, 127.10, 125.30, 120.12, 114.35, 102.30, 96.66, 57.14, 56.36, 39.27, 23.50, 23.39 ppm; HRMS (ESI): Calcd for $C_{28}H_{15}Cl_2N_3O_6$ + Na^+ $[M + Na]^+$ 582.0230. Found: 582.0228; Anal. Calcd for $C_{28}H_{15}Cl_2N_3O_6 \cdot 3/5H_2O$: C, 58.88; H, 2.86; N, 7.36. Found: C, 58.96; H, 3.00; N 7.48.

Compound 13

The procedure used for the preparation of **8** was adopted here. The reaction of **6** (178 mg, 0.60 mmol) with DDQ (169 mg, 0.77 mmol) in EtOAc (10 mL) at refluxing temperature for 7 h afforded **13** (239 mg, 76%) as reddish brown crystals. Mp 228.0−230 °C (decomp.); IR (KBr disk): ν_{max} = 2967 (w), 2873 (w), 2253 (w), 2233 (w), 1735 (w), 1697 (m), 1685 (s), 1676 (s), 1636 (w), 1589 (m), 1555 (s), 1526 (m), 1517 (w), 1491 (m), 1453 (s), 1420 (m), 1356 (w), 1340 (w), 1269 (s), 1196 (m), 1175 (s), 1075 (m), 1053 (w), 1010 (w), 998 (m), 897 (m), 887 (m), 801 (m), 775 (w), 765 (w), 745 (w), 723 (m), 606 (w) cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 271 (4.36), 284 sh (4.31), 347 (3.83), 406 (3.54), 486 sh (3.18) nm; ^1H NMR (400 MHz, DMSO-d_6): δ_H = 8.03 (dd, 1H, *J* = 4.8, 0.8 Hz, H-5'), 7.64−7.58 (m, 2H, H-8,7), 7.44–7.41(m, 1H, H-6), 7.32 (dd, 1H, *J* = 4.8, 4.0 Hz, H-4'), 7.28 (dd, 1H, *J* = 4.0, 0.8 Hz, H-3'), 7.19–7.16 (m, 1H, H-6), 7.12 (d, 1H, *J* = 0.8 Hz, H-4), 2.84 (sept, 1H, *J* = 6.8 Hz, *i*-Pr), 0.98 (d, 6H, *J* = 6.8 Hz, *i*-Pr) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 177.93, 177.07, 165.83, 162.07, 158.63, 149.00, 141.50, 139.82, 138.18, 137.22, 136.45, 134.46, 132.27, 130.68, 129.76, 128.56, 125.68, 119.23, 114.36, 96.25, 57.43, 56.31, 55.87, 38.92, 23.33, 23.30 ppm; HRMS (ESI): Calcd for $C_{26}H_{14}Cl_2N_2O_4S$ + Na^+ [M

+ Na]$^+$ 542.9944. Found: 542.9940; Anal. Calcd for $C_{26}H_{14}Cl_2N_2O_4S$: C, 59.90; H, 2.71; N, 5.37. Found: C, 59.61; H, 2.91; N, 5.22.

Compound 14

The procedure used for the preparation of **8** was adopted here. The reaction of **6** (107 mg, 0.27 mmol) with DDQ (96 mg, 0.42 mmol) in EtOAc (10 mL) at refluxing temperaturre for 1 h afforded **13** (99 mg, 59%) as reddish brown crystals. Mp 250.0−253.0 °C (decomp.); IR (KBr disk): ν_{max} = 2963 (w), 2928 (w), 2909 (w), 2869 (w), 2222 (w), 1756 (s), 1741 (s), 1724 (s), 1712 (s), 1624 (w), 1588 (s), 1561 (w), 1519 (s), 1498 (s), 1484 (s), 1435 (w), 1427 (m), 1411 (w), 1384 (w), 1378 (w), 1365 (w), 1347 (w), 1304 (m), 1274 (s), 1258 (m), 1245 (m), 1213 (m), 1194 (w), 1151 (m), 1077 (w), 1061 (w), 1046 (w), 1014 (w), 924 (w), 911 (w), 899 (w), 803 (m), 797 (w), 795 (w), 784 (w), 764 (w), 757 (w), 717 (w), 707 (w), 648 (w), 626 (w) cm^{-1}; UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 266 (4.64), 400 (4.40), 507 sh (3.97) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.31 (dd, 2H, *J* = 10.8, 9.2 Hz, H-7), 7.29 (br. s, 2H, H-4), 7.23 (d, 2H, *J* = 9.2 Hz, H-8), 7.06 (d, 2H, *J* = 10.8 Hz, H-6), 2.77 (sept, 2H, *J* = 6.8 Hz, *i*-Pr), 1.11 (d, 6H, *J* = 6.8 Hz, *i*-Pr), 1.09 (d, 6H, *J* = 6.8 Hz, *i*-Pr) ppm; HRMS (ESI): Calcd for $C_{34}H_{22}Cl_2N_2O_6$ + Na^+ [M + Na]$^+$ 647.0747. Found: 647.0745; Anal. Calcd for $C_{34}H_{22}Cl_2N_2O_6 \cdot 1/2H_2O$: C, 64.36; H, 3.65; N, 4.42. Found: C, 64.33; H, 3.69; N 4.37; Low solubility hampered the measurement of ^{13}C NMR.

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9. A synthetic part of this study was reported previously as a preliminary form: T. Shoji, J. Higashi, S. Ito, M. Yasunami, and N. Morita, *Heterocycles*, 2011, **83**, 2271.
10. Crystallographic data for the X-ray structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 891965 for compound **13a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Selectee crystal data for **8**: *P*bca, orthorhombic, a = 20.0005(7) Å, b = 20.9837(5) Å, c = 12.0204(3) Å, α = 90º, β = 90º, γ = 90º, V = 5044.8(2) $Å^3$, Z = 8, D_{calc} = 1.347 g cm^3, μ (MoKa) = 3.38 cm^{-1}, R = 0.134, Rw = 0.123, R1 = 0.048.
11. Redox potentials were measured by CV and DPV [V vs. $Ag/AgNO_3$, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mVs^{-1}, and Fc/Fc^+ = +0.15 V].
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