

**Dicarboxylate-containing and fully substituted ferrocene with rapid dissolvability, high solubility, good stability, and moderate formal potential for mediated electrochemical detection**

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## Experimental Section

NMR spectra were recorded in CDCl<sub>3</sub> and DMSO-d<sub>6</sub> at 300 K on a 400 MHz Fourier-transform NMR spectrometer. Infrared (IR) spectra are reported as absorption wavenumbers (cm<sup>-1</sup>). High-resolution mass spectra (HRMS) were acquired on high-resolution mass spectrometers: Q-TOF (ionization mode: ESI).

**Synthesis of Fc8m2c.** Bis(tetramethylcyclopentadienyl)iron(II) was prepared according to the reported procedure.<sup>1</sup> A 250 mL-round bottom flask was dried using a heat gun in vacuum and purged with nitrogen through a septum. Succinic anhydride (1.0 g, 10 mmol) and AlCl<sub>3</sub> (2.7 g, 20 mmol) were added to a 250 mL-round bottom flask containing dichloromethane (5 mL) and a magnetic stir bar. After cooling to 0 °C using an ice bath, bis(tetramethylcyclopentadienyl)iron(II) (1.5 g, 5.0 mmol) in dichloromethane (10 mL) was added dropwise to the flask over 30 min. Next, the ice bath was removed, and the reaction mixture was stirred at 25 °C for 16 h. Then, the reaction mixture was slowly quenched with water (30 mL), which allowed the desired product to precipitate. Purification via filtration afforded **A-(CO<sub>2</sub>H)<sub>2</sub>** as a pale red solid. (338 mg, 13% yield): mp 220-222 °C; IR (film) 2963, 2902, 1702, 1649, 1387, 1259 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO) δ 2.74 (t, *J* = 6.3 Hz, 4H), 2.45 (t, *J* = 6.3 Hz, 4H), 1.89 (s, 12H), 1.66 (s, 12H); <sup>13</sup>C NMR (100 MHz, DMSO) δ 204.4, 174.0, 84.9, 82.2, 75.6, 38.1, 27.9, 11.2, 8.7; HRMS (ESI) calcd for C<sub>26</sub>H<sub>35</sub>FeO<sub>6</sub> [M+H]<sup>+</sup> 499.1778, found 499.1773.

**A-(CO<sub>2</sub>H)<sub>2</sub>** (100 mg, 0.20 mmol) and NaOH (15.2 mg, 0.38 mmol) were added to water (5 mL) in a 20 mL-glass vial equipped with a magnetic stir bar. After stirring in a preheated reaction block at 80 °C for 16 h, the reaction mixture was cooled to 25 °C and transferred to a 125 mL-separatory funnel and treated with water (10 mL) and DCM (10 mL). The organic layer was extracted with water (10 mL × 3). The combined aqueous layers were concentrated to afford **Fc8m2c** as a pale red solid (89 mg, 81% yield).

**Synthesis of Fc8m1c.** A 250 mL-round bottom flask was dried using a heat gun in vacuum and purged with nitrogen through a septum. Methyl 4-chloro-4-oxobutyrates (736 μL, 6.0 mmol) and AlCl<sub>3</sub> (800 mg, 6.0 mmol) were added to a 250 mL-round bottom flask containing dichloromethane (16 mL) and a magnetic stir bar. After cooling to 0 °C using an ice bath, bis(tetramethylcyclopentadienyl)iron(II) (1.8 g, 6.0 mmol) in dichloromethane (32 mL) was added dropwise to the flask over 30 min. Next, the ice bath was removed, and the reaction mixture was stirred at 25 °C for 16 h. Then, the reaction mixture was slowly quenched with water (30 mL) and transferred to a separatory funnel. The aqueous layer was washed with dichloromethane (30 mL), and the combined organic layers were concentrated under vacuum. Purification by flash column chromatography (hexanes/EtOAc = 9:1) provided **B-CO<sub>2</sub>Me** as a red solid (847 mg, 34% yield). Subsequently, **B-CO<sub>2</sub>Me** (815 mg, 2.0 mmol) and NaOH (1.6 g, 40 mmol) were added to water (5 mL) and DMSO (5 mL) in a 40 mL-glass vial equipped

with a magnetic stir bar. After stirring in a preheated reaction block at 80 °C for 16 h, the reaction mixture was cooled to 25 °C and transferred to a 125 mL-separatory funnel and treated with an aqueous solution of HCl (2 N, 20 mL) and DCM (10 mL). The aqueous layer was extracted with DCM (10 mL × 3), and the combined organic layers were concentrated. The residue was purified by flash column chromatography (hexanes/EtOAc = 1:1) to provide **B-CO<sub>2</sub>H** as a pale red solid (681 mg, 85% yield): mp 169-171 °C; IR (film) 2950, 2905, 1701, 1643, 1377, 1255 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.03 (t, *J* = 6.3 Hz, 2H), 2.71 (t, *J* = 6.3 Hz, 2H), 2.07 (s, 6H), 1.81 (s, 6H), 1.66 (s, 6H), 1.59 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 205.2, 179.5, 85.4, 82.4, 81.5, 81.2, 75.2, 71.6, 37.9, 28.6, 12.5, 10.7, 9.9, 8.9; HRMS (ESI) calcd for C<sub>22</sub>H<sub>31</sub>FeO<sub>3</sub> [M+H]<sup>+</sup> 399.1617, found 399.1610.

**B-CO<sub>2</sub>H** (100 mg, 0.25 mmol) and NaOH (9.2 mg, 0.23 mmol) were added to water (5 mL) in a 20 mL-glass vial equipped with a magnetic stir bar. After stirring in a preheated reaction block at 80 °C for 16 h, the reaction mixture was cooled to 25 °C and transferred to a 125 mL-separatory funnel and treated with water (10 mL) and DCM (10 mL). The organic layer was extracted with water (10 mL × 3). The combined aqueous layers were concentrated to afford **Fc8m1c** as a pale red solid (62 mg, 64%).

**Synthesis of Fc9m1c.** Nonamethylferrocene was prepared according to the reported procedure.<sup>2, 3</sup> A 250 mL-round bottom flask was dried using a heat gun in vacuum and purged with nitrogen through a septum. Methyl 4-chloro-4-oxobutyrates (1.1 mL, 8.0 mmol) and AlCl<sub>3</sub> (1.3 g, 8.0 mmol) were added to a 250 mL-round bottom flask containing dichloroethane (8 mL) and a magnetic stir bar. After cooling to 0 °C using an ice bath, nonamethylferrocene (2.5 g, 8.0 mmol) in dichloroethane (17 mL) was added dropwise to the flask for 30 min. Next, the ice bath was removed, and the reaction mixture was stirred at 25 °C for 16 h. Then, the reaction mixture was slowly quenched with water (10 mL) and transferred to a separatory funnel. The aqueous layer was washed with dichloromethane (30 mL), and the combined organic layers were concentrated under vacuum. Purification by flash column chromatography (hexanes/EtOAc = 9:1) provided **C-CO<sub>2</sub>Me** as a red solid (960 mg, 29% yield). Subsequently, **C-CO<sub>2</sub>Me** (958 mg, 2.3 mmol) and NaOH (1.8 g, 45 mmol) were added to water (5 mL) and DMSO (5 mL) in a 40 mL-glass vial equipped with a magnetic stir bar. After stirring in a preheated reaction block at 80 °C for 16 h, the reaction mixture was cooled to 25 °C and transferred to a 125 mL-separatory funnel and treated with aqueous solution of HCl (2 N, 20 mL) and DCM (10 mL). The organic layer was extracted with DCM (10 mL × 3), and the combined organic layers were concentrated. Purification by flash column chromatography (hexanes/EtOAc = 1:1) provided **C-CO<sub>2</sub>H** as a pale red solid (619 mg, 67% yield): mp 197-199 °C; IR (film) 2953, 2902, 1700, 1641, 1377, 1259 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.94 (t, *J* = 6.3 Hz, 2H), 2.70 (t, *J* = 6.3 Hz, 2H), 2.02 (s, 6H), 1.77 (s, 6H), 1.61 (s, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 205.5, 178.7, 85.5, 82.3, 80.1, 75.2, 38.2, 28.8, 12.2, 9.6, 9.2;

HRMS (ESI) calcd for  $C_{23}H_{32}FeO_3$   $[M]^+$  412.1701, found 412.1702.

**C-CO<sub>2</sub>H** (207 mg, 0.5 mmol) and NaOH (40 mg, 0.5 mmol) were added to water (5 mL) in a 20 mL-glass vial equipped with a magnetic stir bar. After stirring in a preheated reaction block at 80 °C for 16 h, the reaction mixture was cooled to 25 °C and transferred to a 125 mL-separatory funnel and treated with water (10 mL) and DCM (10 mL). The organic layer was extracted with water (10 mL × 3). The combined aqueous layers were concentrated to afford **Fc9m1c** as a pale red solid (123 mg, 56%).

**Synthesis of Fc2c.** **Fc2c** was prepared according to the reported procedure.<sup>4</sup> A 250 mL-round bottom flask was dried using a heat gun in vacuum and purged with nitrogen through a septum. Succinic anhydride (3.2 g, 32 mmol) and AlCl<sub>3</sub> (6.4 g, 48 mmol) were added to a 250 mL-round bottom flask containing dichloromethane (25 mL) and a magnetic stir bar. After cooling to 0 °C using an ice bath, ferrocene (3.0 g, 16 mmol) in dichloromethane (25 mL) was added dropwise to the flask over 30 min. Next, the ice bath was removed, and the reaction mixture was stirred at 25 °C for 2 h. Then, the reaction mixture was slowly quenched with water (30 mL), which allowed the desired product to precipitate. Purification via filtration afforded **D-(CO<sub>2</sub>H)<sub>2</sub>** (1,1'-bis(3-carboxy-propionyl)-ferrocene) as a pale yellow solid. (2.9 g, 46% yield). <sup>1</sup>H NMR (400 MHz, DMSO) δ 12.12 (s, 2H), 4.93-4.86 (m, 4H), 4.69-4.62 (m, 4H), 3.36-3.33 (m, 4H), 2.96 (t, *J* = 5.5 Hz, 4H), 1.66 (s, 12H). The obtained spectral data are equivalent to the ones reported in the literature.<sup>4</sup>

**D-(CO<sub>2</sub>H)<sub>2</sub>** (772 mg, 2.0 mmol) and NaOH (160 mg, 4.0 mmol) were added to water (20 mL) in a 40 mL-glass vial equipped with a magnetic stir bar. After stirring in a preheated reaction block at 80 °C for 16 h, the reaction mixture was cooled to 25 °C and transferred to a 125 mL-separatory funnel and treated with water (10 mL) and DCM (10 mL). The organic layer was extracted with water (10 mL × 3). The combined aqueous layers were concentrated to afford **Fc2c** as a pale red solid (714 mg, 83% yield).

**Synthesis of Fc1c.** **Fc1c** was prepared according to the reported procedure.<sup>5</sup> A 250 mL-round bottom flask was dried using a heat gun in vacuum and purged with nitrogen through a septum. Succinic anhydride (0.8 g, 8.0 mmol) and AlCl<sub>3</sub> (3.2 g, 24 mmol) were added to a 250 mL-round bottom flask containing dichloromethane (25 mL) and a magnetic stir bar. After cooling to 0 °C using an ice bath, ferrocene (3.0 g, 16 mmol) in dichloromethane (25 mL) was added dropwise to the flask over 30 min. Next, the ice bath was removed, and the reaction mixture was stirred at 25 °C for 2 h. Then, the reaction mixture was slowly quenched with water (30 mL), which allowed the desired product to precipitate. Purification via filtration afforded **E-CO<sub>2</sub>H** (4-(ferrocenyl)-4-oxobutanoic acid) as a red solid. (1.7 g, 72% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.82 (t, *J* = 1.9 Hz, 2H), 4.53 (t, *J* = 1.9 Hz, 2H), 4.24 (s, 5H), 3.09 (t, *J* = 6.7 Hz, 2H), 2.75 (t, *J* = 6.2 Hz, 2H). The obtained spectral data are equivalent to the ones reported

in the literature.<sup>5</sup>

**E-CO<sub>2</sub>H** (572 mg, 2.0 mmol) and NaOH (80 mg, 2.0 mmol) were added to water (20 mL) in a 40 mL-glass vial equipped with a magnetic stir bar. After stirring in a preheated reaction block at 80 °C for 16 h, the reaction mixture was cooled to 25 °C and transferred to a 125 mL-separatory funnel and treated with water (10 mL) and DCM (10 mL). The organic layer was extracted with water (10 mL × 3). The combined aqueous layers were concentrated to afford **Fc1c** as a pale red solid (459 mg, 74% yield).

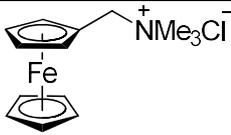
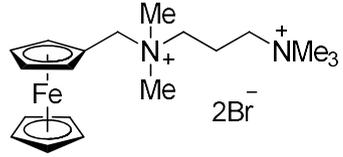
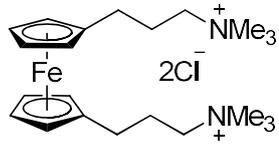
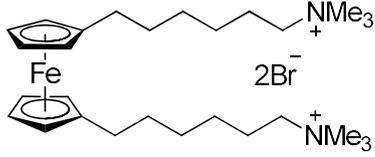
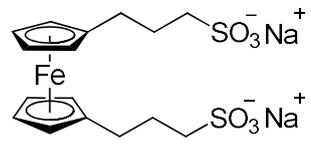
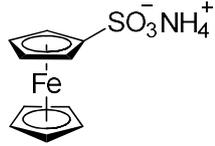
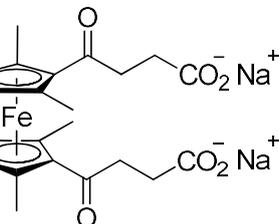
**Solubility Measurement.** Solubility tests were performed using the reported procedure.<sup>6</sup> Each ferrocene compound was dissolved in 0.3 mL of deionized water at room temperature until undissolved solids appeared. The saturated solution was filtered through a small amount of cotton in a 1 mL-syringe, and the filtrate was transferred to a pre-weighed 8-mL vial, which contained 2 mL of acetonitrile. The mixture was evaporated using a rotary evaporator and then further dried under vacuum. Finally, the vial was weighed.

**Preparation of Electrodes.** PBS containing BSA (PBSB) contained all the ingredients in PBS along with 1% (w/v) BSA, and 0.5 M NaCl. Prior to modification, the ITO electrodes (1cm × 2 cm) were pretreated by dipping them in a mixed solution of H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> (30%), and NH<sub>4</sub>OH (30%) at a volume ratio of 5:1:1 for 1 h at 70 °C. The electrodes were then washed with distilled water and dried under a flow of nitrogen gas. To obtain the avidin- and BSA-modified ITO electrodes, 70 μL of a carbonate buffer solution (50 mM, pH 9.6) containing 10 μg/mL avidin was dropped onto the pretreated ITO electrodes and incubated for 2 h at 20 °C. Next, 70 μL of PBSB solution was dropped onto the avidin-modified ITO electrodes and incubated for 30 min.

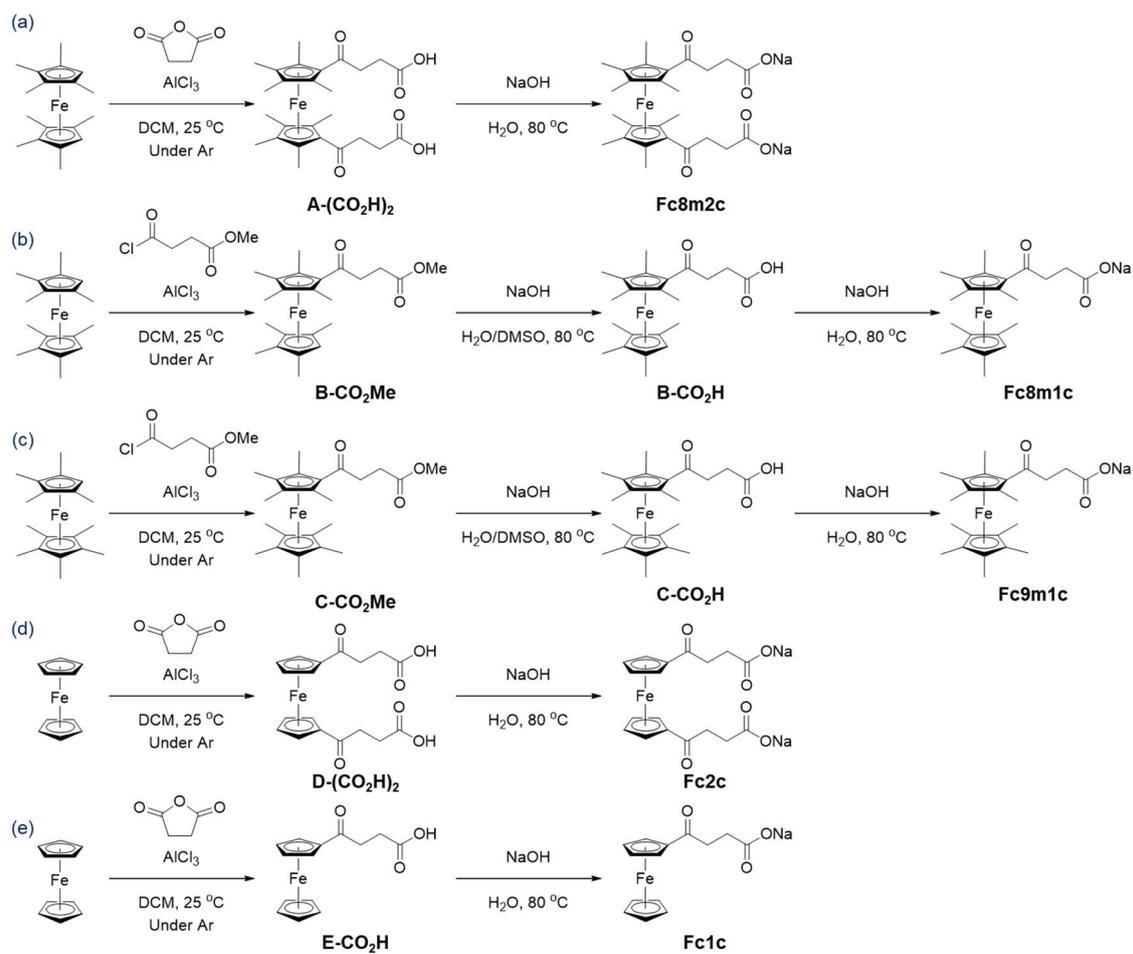
**Diffusion Coefficient Measurement.** The diffusion coefficient (*D*) of three ferrocene compounds was measured from linear sweep voltammetry at carbon ultramicroelectrode (Fig. S7), and the limiting currents (*I*<sub>lim</sub>) from the voltammograms was used to calculate it.

$$I_{\text{lim}} = 4nFDcr$$

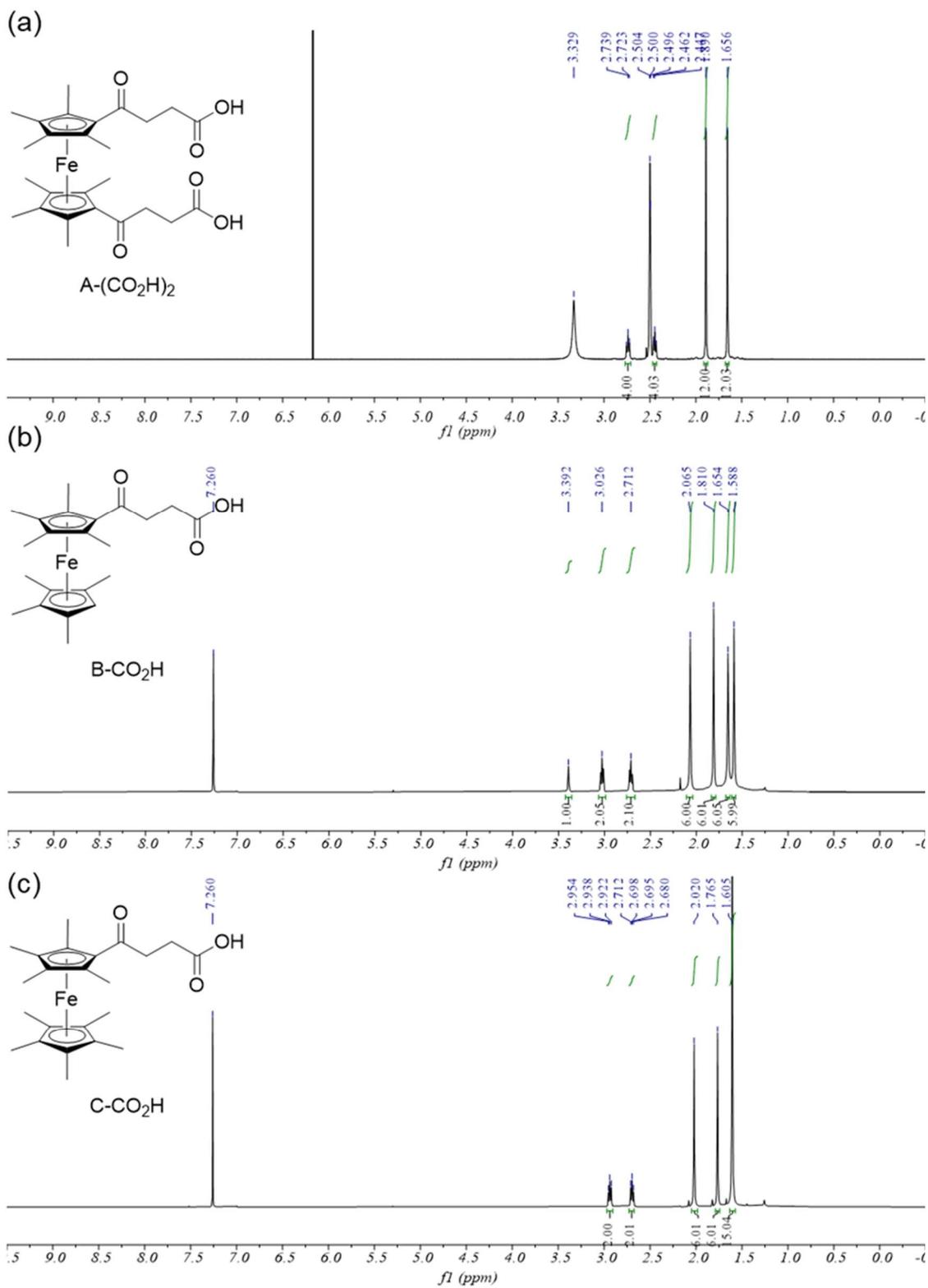
where *n*, *F*, *C*, and *r* represent the number of electrons involved in the redox reaction of a ferrocene compound, Faradaic constant, the concentration of a ferrocene compound (1 mM), and the radius of carbon ultramicroelectrode (5 μm). The calculated *D* values are shown in Table 1.

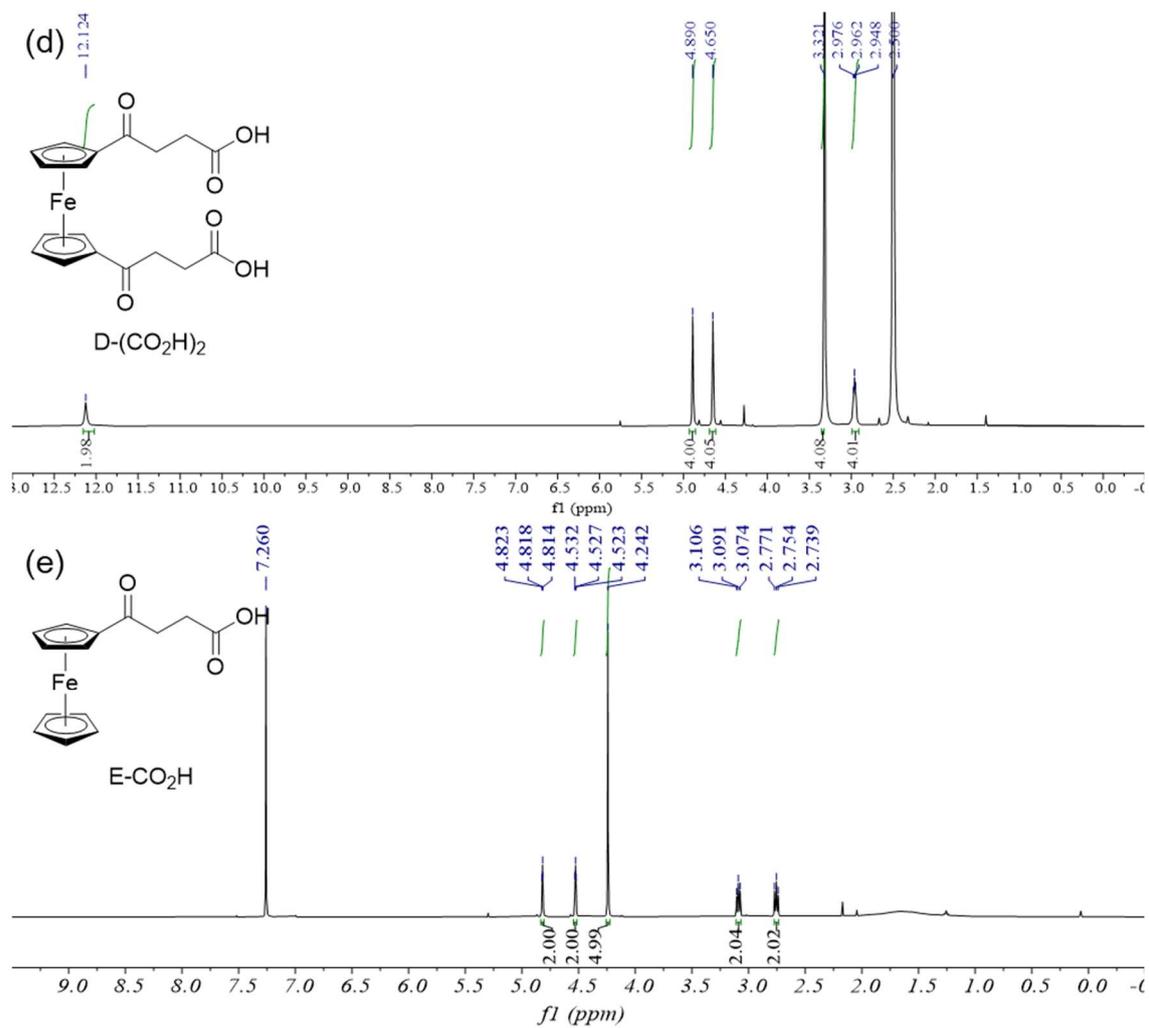
Fc Mediators	Redox potential	Aqueous solubility	ref
 <p><b>FcNCl</b></p>	0.61 V vs NHE	4 M in H <sub>2</sub> O 3 M in 2 M NaCl	7
 <p><b>FcN<sub>2</sub>Br<sub>2</sub></b></p>	0.61 V vs NHE	3.1 M in H <sub>2</sub> O 2 M in 2 M NaCl	7
 <p><b>FcN<sub>2</sub>Br<sub>2</sub></b></p>	0.39 V vs SHE	1.9 M in H <sub>2</sub> O	8
 <p><b>BTMAP-Fc</b></p>	0.28 V vs SHE	3.1 M in H <sub>2</sub> O	9
 <p><b>BQH-Fc</b></p>	0.35 V vs Ag/AgCl	2.5 M in H <sub>2</sub> O	10
 <p><b>Fc-SO<sub>3</sub>Na</b></p>	0.4 V vs Ag/AgCl	0.41 M in H <sub>2</sub> O 0.18 M in 2 M NaCl	11
 <p><b>Fc-SO<sub>3</sub>NH<sub>4</sub></b></p>	0.17 V vs Ag/AgCl	0.63 M in H <sub>2</sub> O	-

**Table S1.** Development of aqueous ferrocene mediators

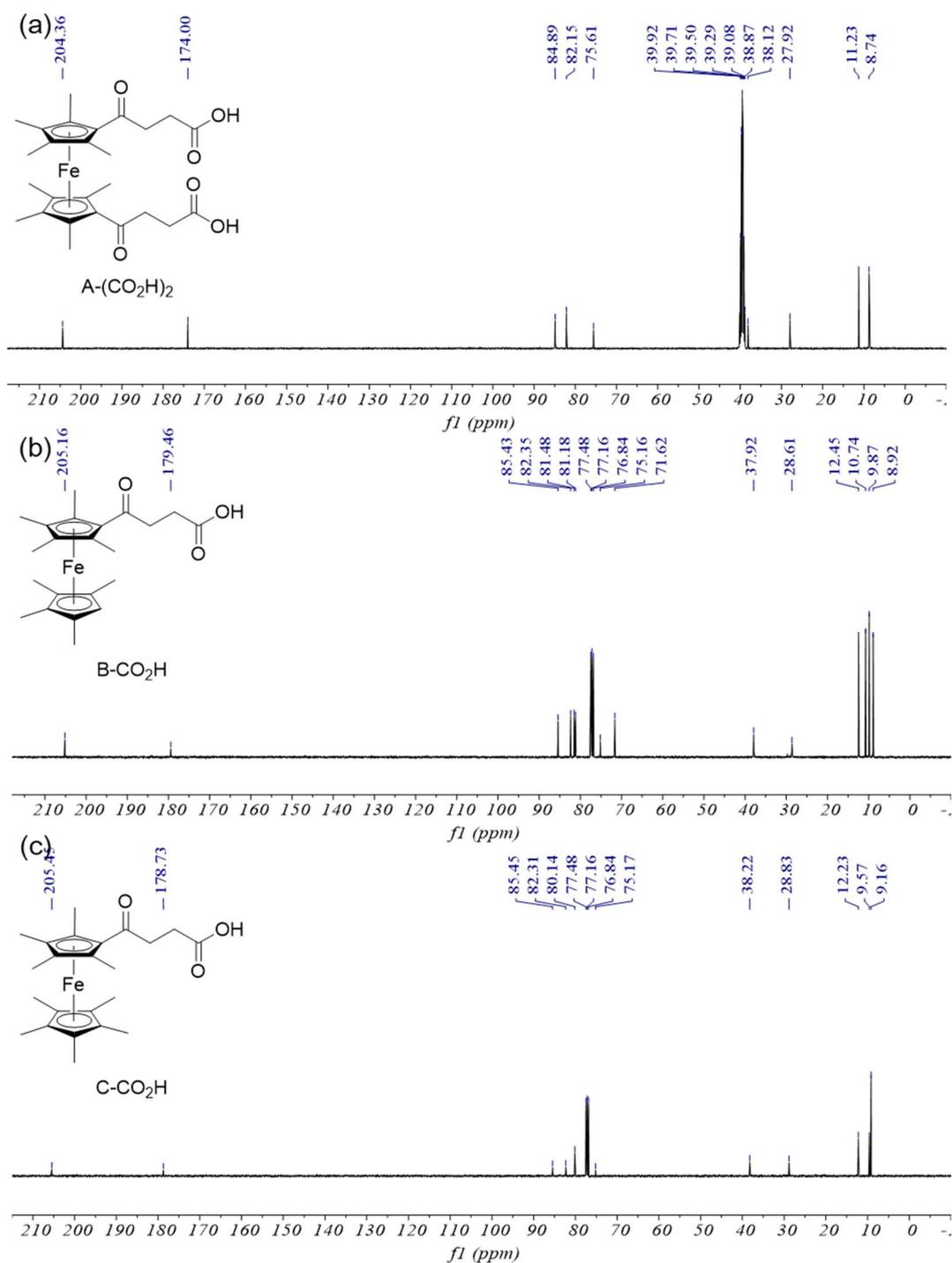


**Fig. S1.** Synthetic routes for (a) **Fc8m2c**, (b) **Fc8m1c**, (c) **Fc9m1c**, (d) **Fc2c**, and (e) **Fc1c**.

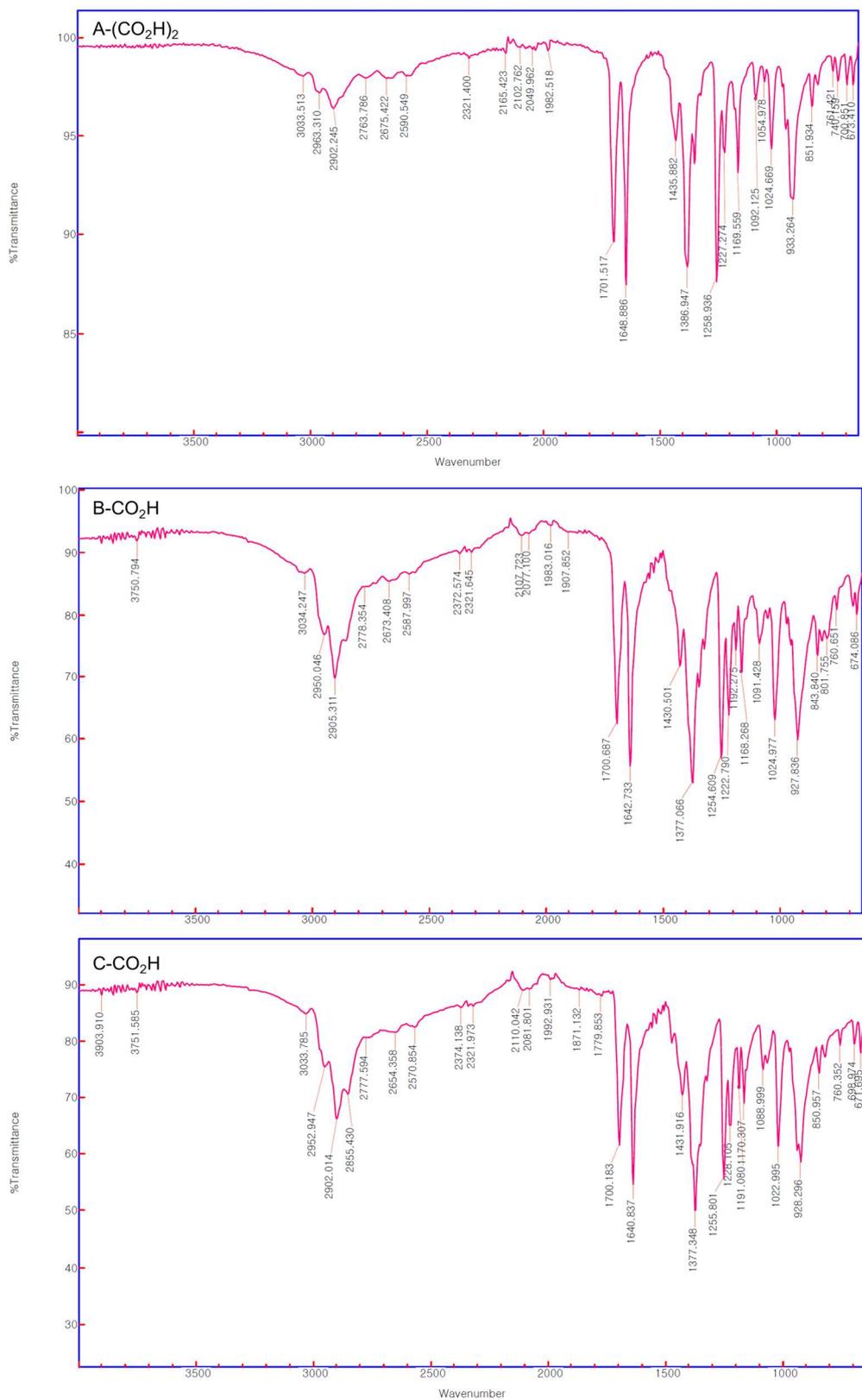




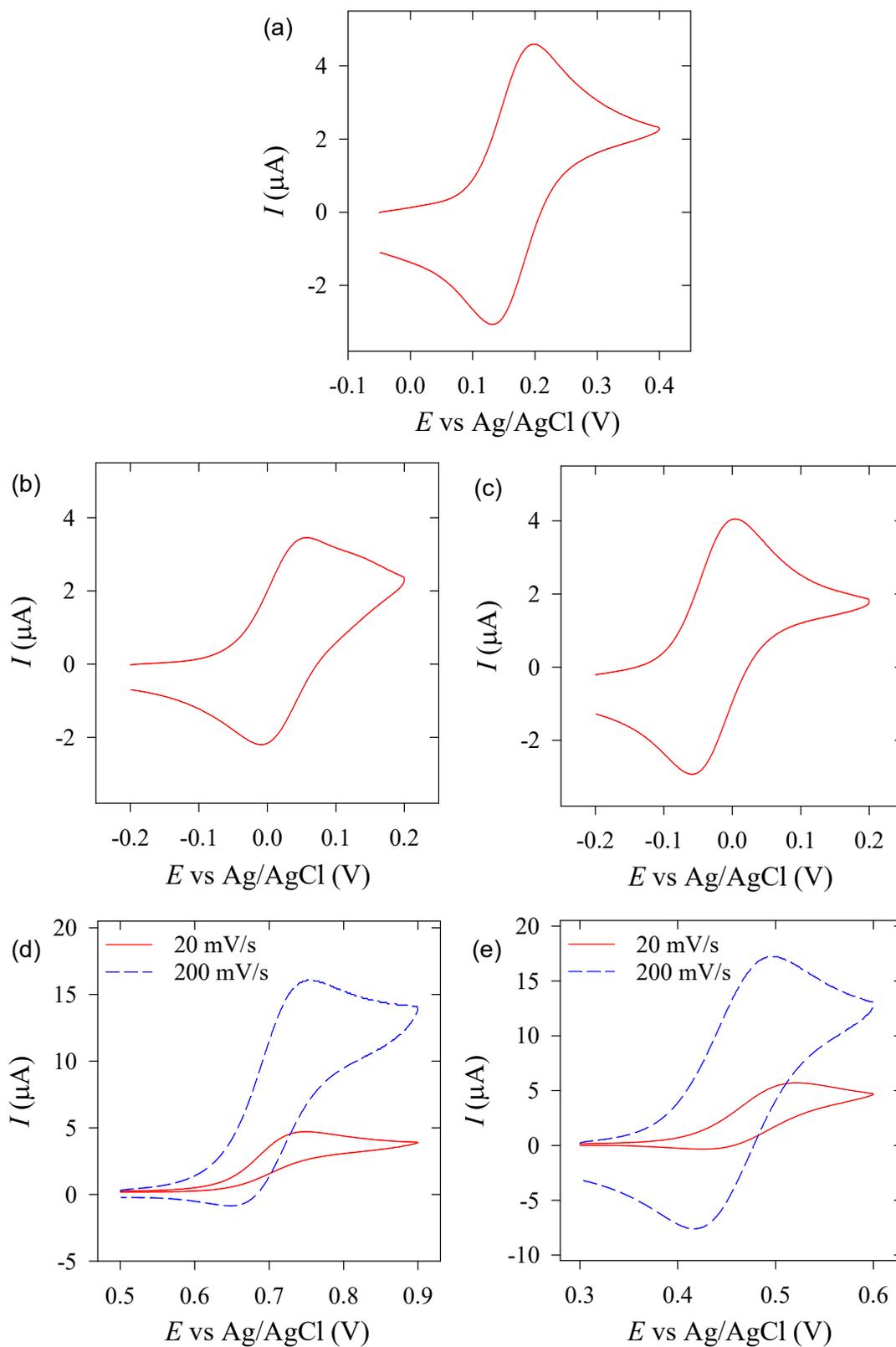
**Fig. S2.**  $^1H$  NMR spectra of the acidic forms of (a) **Fc8m2c** (DMSO- $d_6$ , 400 MHz), (b) **Fc8m1c** (CDCl $_3$ , 400 MHz), (c) **Fc9m1c** (CDCl $_3$ , 400 MHz), (d) **Fc2c** (DMSO- $d_6$ , 400 MHz), and (e) **Fc1c** (CDCl $_3$ , 400 MHz).



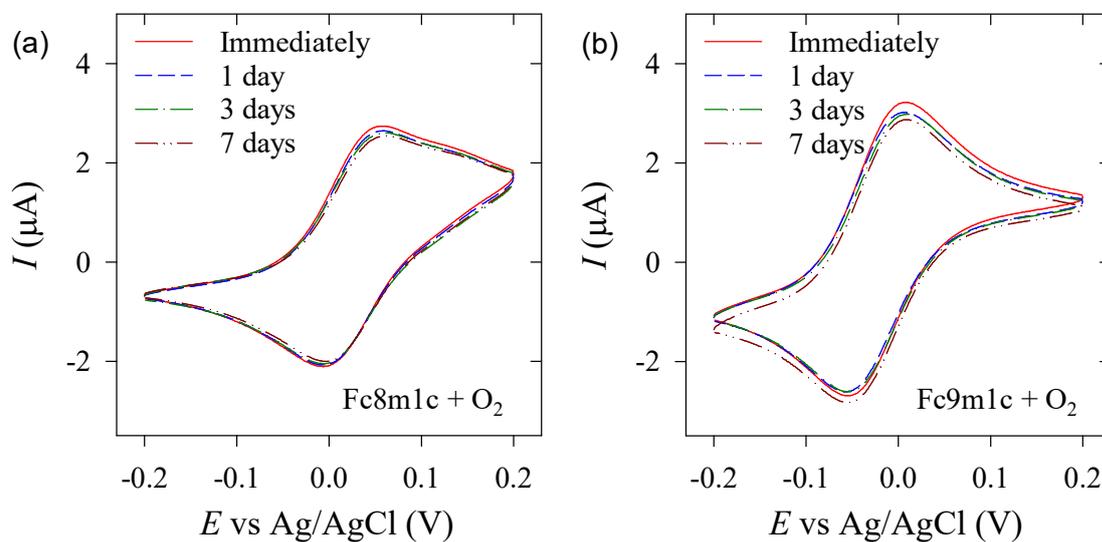
**Fig. S3.** <sup>13</sup>C NMR spectra (DMSO, 100 MHz) of the acidic forms of (a) **Fe8m2c** (DMSO-d<sub>6</sub>, 100 MHz), (b) **Fe8m1c** (CDCl<sub>3</sub>, 100 MHz), and (c) **Fe9m1c** (CDCl<sub>3</sub>, 100 MHz).



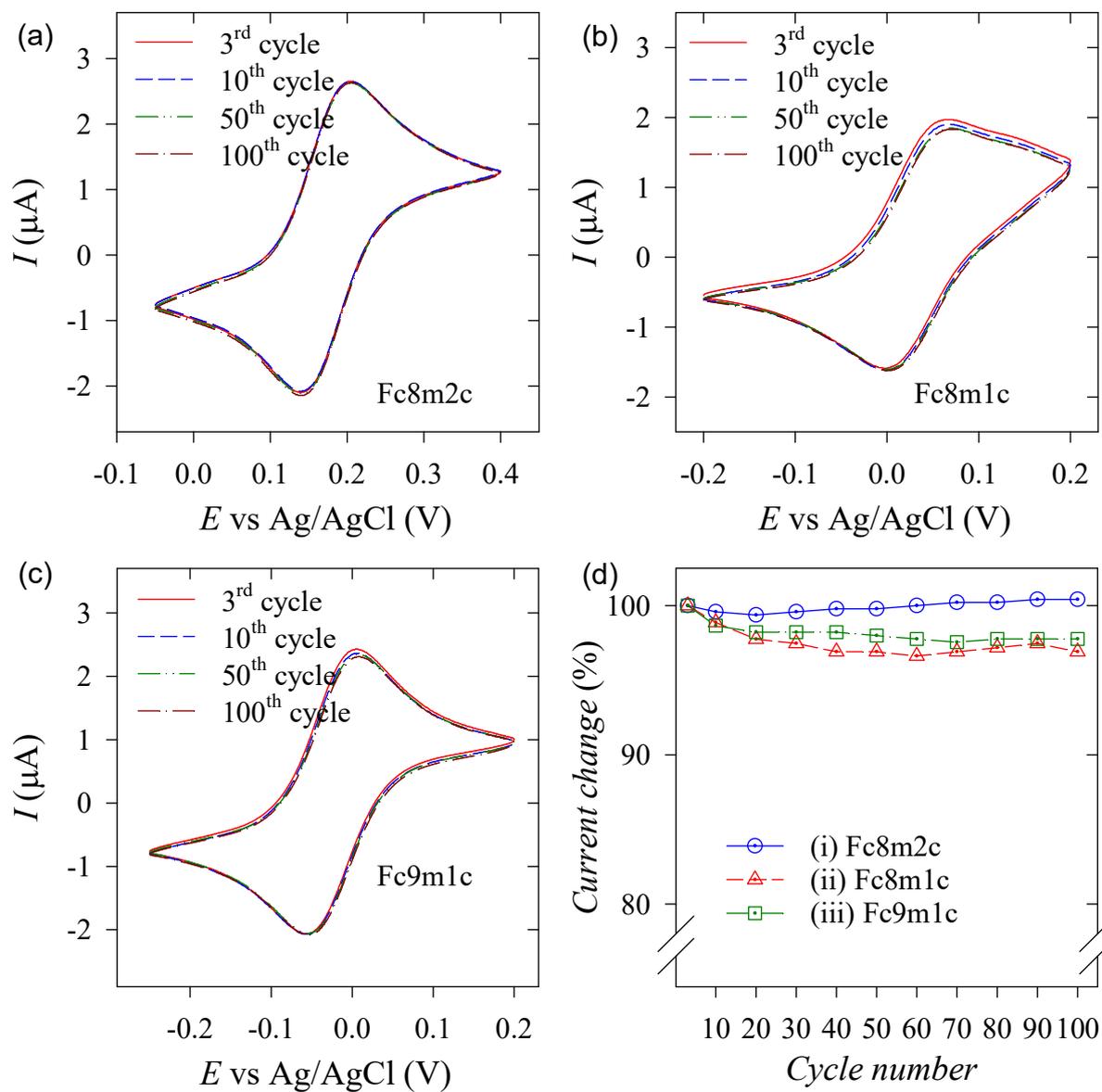
**Fig. S4.** IR spectra of the acidic forms of (a) **Fc8m2c**, (b) **Fc8m1c**, and (c) **Fc9m1c**.



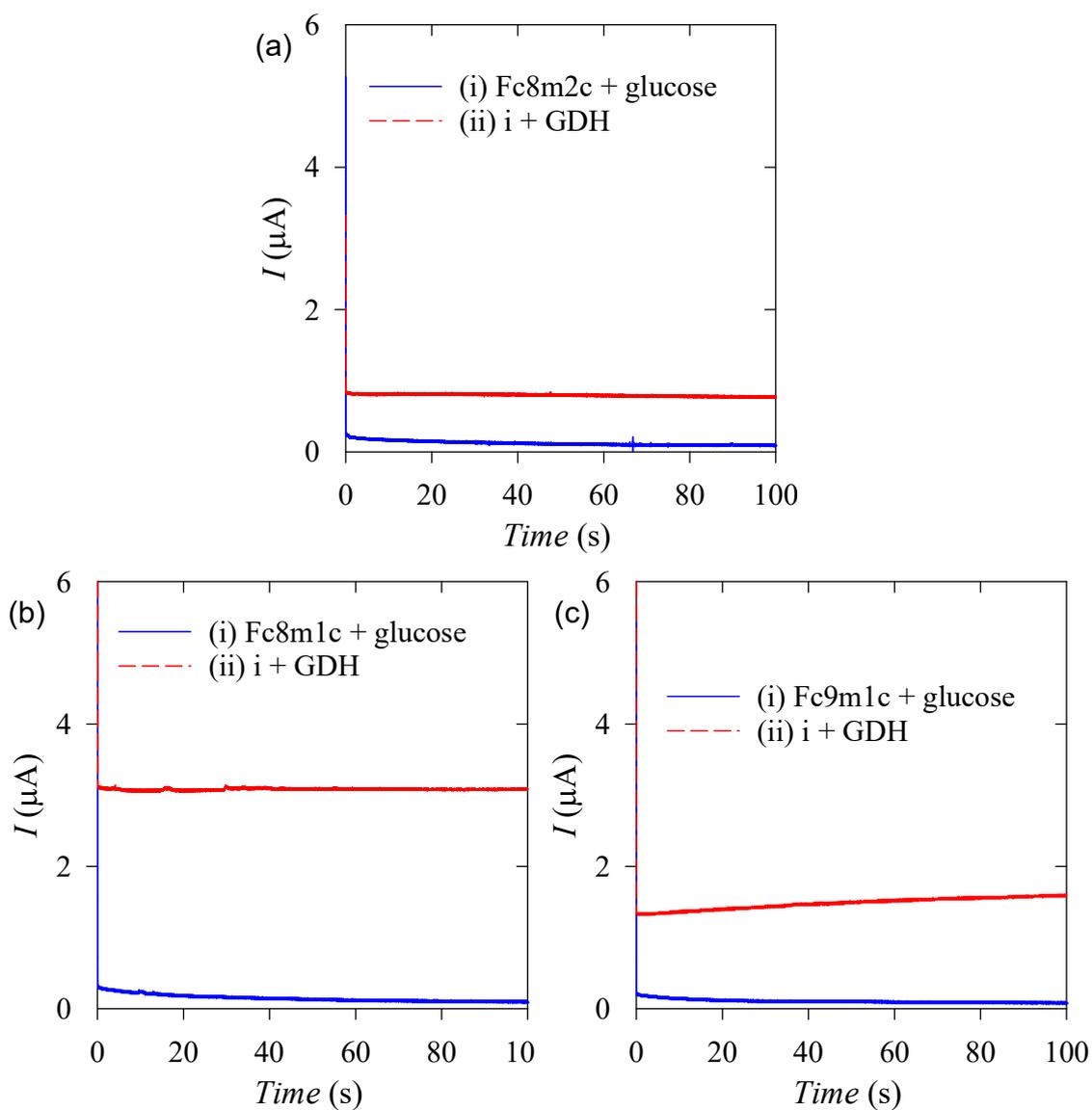
**Fig. S5.** Cyclic voltammograms (1st scan) obtained (at scan rates of 20 and 200 mV/s) using glassy carbon electrodes in air-saturated PBS (pH 7.4) containing 1.0 mM of (a) **Fc8m2c**, (b) **Fc8m1c**, (c) **Fc9m1c**, (d) **Fc2c**, and (e) **Fc1c**.



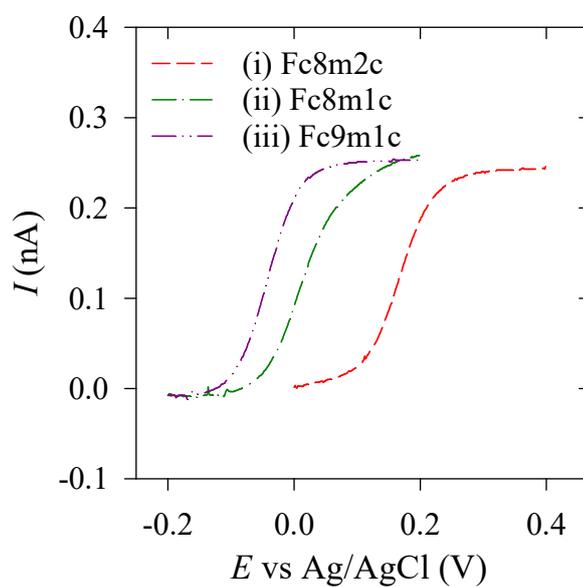
**Fig. S6.** Time dependence of cyclic voltammograms (3rd scan) obtained (at a scan rate of 20 mV/s) using glassy carbon electrodes in air-saturated PBS (pH 7.4) containing 1.0 mM of (a) **Fc8m1c** and (b) **Fc9m1c** in the absence of ambient light in a room.



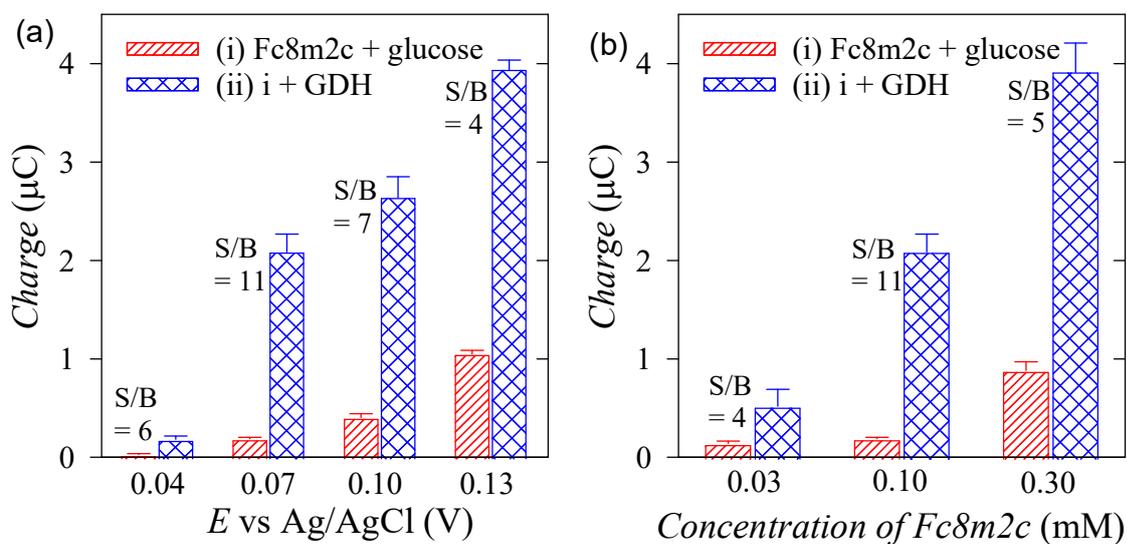
**Fig. S7.** Cyclic voltammograms (for the 3<sup>rd</sup>, 10<sup>th</sup>, 50<sup>th</sup>, and 100<sup>th</sup> cyclic scans) obtained (at a scan rate of 10 mV/s) using glassy carbon electrodes in air-saturated PBS (pH 7.4) containing 1.0 mM (a) **Fc8m2c** and in air-saturated mixed solution of PBS and DMSO (4:1) containing 1.0 mM (b) **Fc8m1c** and (c) **Fc9m1c** in the presence of ambient light in a room. (d) Dependence of the difference between the anodic and cathodic peak currents on the cycle number.



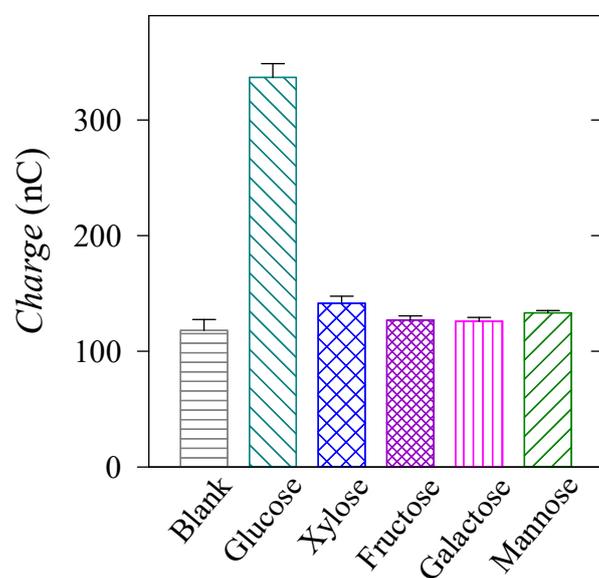
**Fig. S8.** Chronoamperograms obtained using avidin- and BSA-modified ITO electrodes at an applied potential of 0.4 V in air-saturated PBS (pH 7.4) containing (a) (i) 50  $\mu\text{M}$  **Fc8m2c** and 5.0 mM glucose, (ii) 50  $\mu\text{M}$  **Fc8m2c**, 0.5  $\mu\text{M}$  PQQ-GDH, and 5.0 mM glucose, (b) (i) 50  $\mu\text{M}$  **Fc8m1c** and 5.0 mM glucose, (ii) 50  $\mu\text{M}$  **Fc8m1c**, 0.5  $\mu\text{M}$  PQQ-GDH, and 5.0 mM glucose, (c) (i) 50  $\mu\text{M}$  **Fc9m1c** and 5.0 mM glucose, and (ii) 50  $\mu\text{M}$  **Fc9m1c**, 0.5  $\mu\text{M}$  PQQ-GDH, and 5.0 mM glucose.  $I_{\text{lim}}$  was obtained by subtracting the current value of the line i measured at 100 s from the current value of the line ii measured at 100 s.



**Fig. S9.** Linear sweep voltammograms obtained using a carbon ultramicroelectrode (diameter = 10  $\mu\text{m}$ ) at a scan rate of 5 mV/s in PBS (pH 7.4) containing 1.0 mM of (i) **Fc8m2c**, (ii) **Fc8m1c**, and (iv) **Fc9m1c** in  $\text{N}_2$ -saturated glove box.



**Fig. S10.** Histograms of the signal-to-background ratios calculated from the charge values measured at 5 s from the chronocoulograms obtained at avidin- and BSA-modified ITO electrodes after an incubation period of 5 min at 25 °C (a) in artificial serum containing (i) 0.10 mM **Fc8m2c** and 5.0 mM glucose and (ii) 0.10 mM **Fc8m2c**, 0.5  $\mu\text{M}$  GDH, and 5.0 mM glucose at four different applied potentials (0.04, 0.07, 0.10, and 0.13 V) and (b) in artificial serum containing (i) three different concentrations (0.03, 0.10, or 0.30 mM) of **Fc8m2c** and 5.0 mM glucose and (ii) three different concentrations (0.03, 0.10, or 0.30 mM) of **Fc8m2c**, 0.5  $\mu\text{M}$  GDH, and 5.0 mM glucose



**Fig. S11.** Comparison of the charge values at 5 s in the chronocoulograms obtained at an applied potential of 0.07 V using ITO electrodes for artificial serum spiked with PBS containing 0.1 mM **Fc8m2c**, 0.5  $\mu$ M GDH, 1 U/mL AOx, and blank or 10 mM of glucose, xylose, fructose, galactose, or mannose.

## References

1. A. Paul, R. Borrelli, H. Bouyanfif, S. Gottis and F. Sauvage, *ACS Omega*, 2019, **4**, 14780-14789.
2. J. C. Lansing, J. M. Camara, D. E. Gray and T. B. Rauchfuss, *Organometallics*, 2014, **33**, 5897-5906.
3. C. Zou and M. S. Wrighton, *J. Am. Chem. Soc.*, 1990, **112**, 7578-7584.
4. D. Apreutesei, G. Lisa, N. Hurduc and D. Scutaru, *Open chem.*, 2004, **2**, 553-562.
5. Y. Bernhard, J. Gilbert, T. Bousquet, A. Favrelle-Huret, P. Zinck, S. Pellegrini and L. Pelinski, *Eur. J. Org. Chem.*, 2019, **2019**, 7870-7873.
6. J. B. Gerken, A. Stamoulis, S. E. Suh, N. D. Fischer, Y. J. Kim, I. A. Guzei and S. S. Stahl, *Chem. Commun.*, 2020, **56**, 1199-1202.
7. B. Hu, C. DeBruler, Z. Rhodes and T. L. Liu, *J. Am. Chem. Soc.*, 2017, **139**, 1207-1214.
8. E. S. Beh, D. De Porcellinis, R. L. Gracia, K. T. Xia, R. G. Gordon and M. J. Aziz, *ACS Energy Lett.*, 2017, **2**, 639-644.
9. Q. Chen, Y. Li, Y. Liu, P. Sun, Z. Yang and T. Xu, *ChemSusChem*, 2021, **14**, 1295-1301.
10. J. Yu, M. Salla, H. Zhang, Y. Ji, F. Zhang, M. Zhou and Q. Wang, *Energy Storage Mater.*, 2020, **29**, 216-222.
11. Y. Yao, H. Xu, Z. Tian, J. Zhang, F. Zhan, M. Yan and C. Jia, *ACS Appl. Energy Mater.*, 2021, **4**, 8052-8058.