Electronic Supplementary Information

Non-corrosive, Low-Toxicity Gel-based Microbattery from Organic and Organometallic Molecules

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Experimental Methods

Synthesis of BTMAP-Vi: BTMAP-Vi was synthetized as previously described by Beh *et al*.[1] The scheme of its synthesis is shown in Figure S1a. Initially, 9.91 g (62.9 mmol) of 1-bromo-3-chloropropane was stirred with 6.6 mL (210.0 mmol) of a 25% solution of trimethylamine in methanol. After stirring at room temperature for 15 hours, the reaction mixture was diluted with ~50 mL of methyl tert-butyl ether (MTBE) and the suspended solid collected by vacuum filtration. The solid was rinsed with MTBE and dried in vacuo to give trimethyl(3-chloropropyl)ammonium bromide (**1**). Yield: 4.38 g (85.7%) of a fine white powder. This material was used without purification in the following step.

Then, 3.98 g (18.4 mmol) of **1** and 1.41g (9.0 mmol) of 4,4'-dipyridyl were suspended in ~10 mL of anhydrous DMF and heated to reflux under argon. Upon heating, all solids dissolved, followed shortly after by the formation of a large amount of pale yellow precipitate. After heating for 1 hour, the reaction mixture had partially solidified and had turned greenish. The reaction was cooled to room temperature and solid was collected by vacuum filtration, and then finally dried in vacuo to give (3-trimethylammonio)propyl viologen dibromide dichloride. The product was recrystallized by the addition of DMF to an aqueous solution. (**2**). Yield: 1.71 g (32.1%) of a pale-yellow powder.

A solution of 11.48 g (19.48 mmol) of **2** in ~100 mL of deionized H_2O was passed through ~0.5 kg of wet Amberlite IRA-900 resin (chloride form). The resin was washed with ~1 L of deionized H_2O. The eluted solution was evaporated in vacuo to give pure (3-trimethylammonio)propyl viologen tetrachloride (BTMAP-Vi). Yield: 9.76 g (99.9%) of an off-white deliquescent solid. ^{1}H NMR spectrum of the final product BTMAP-Vi is shown in Figure S1b.

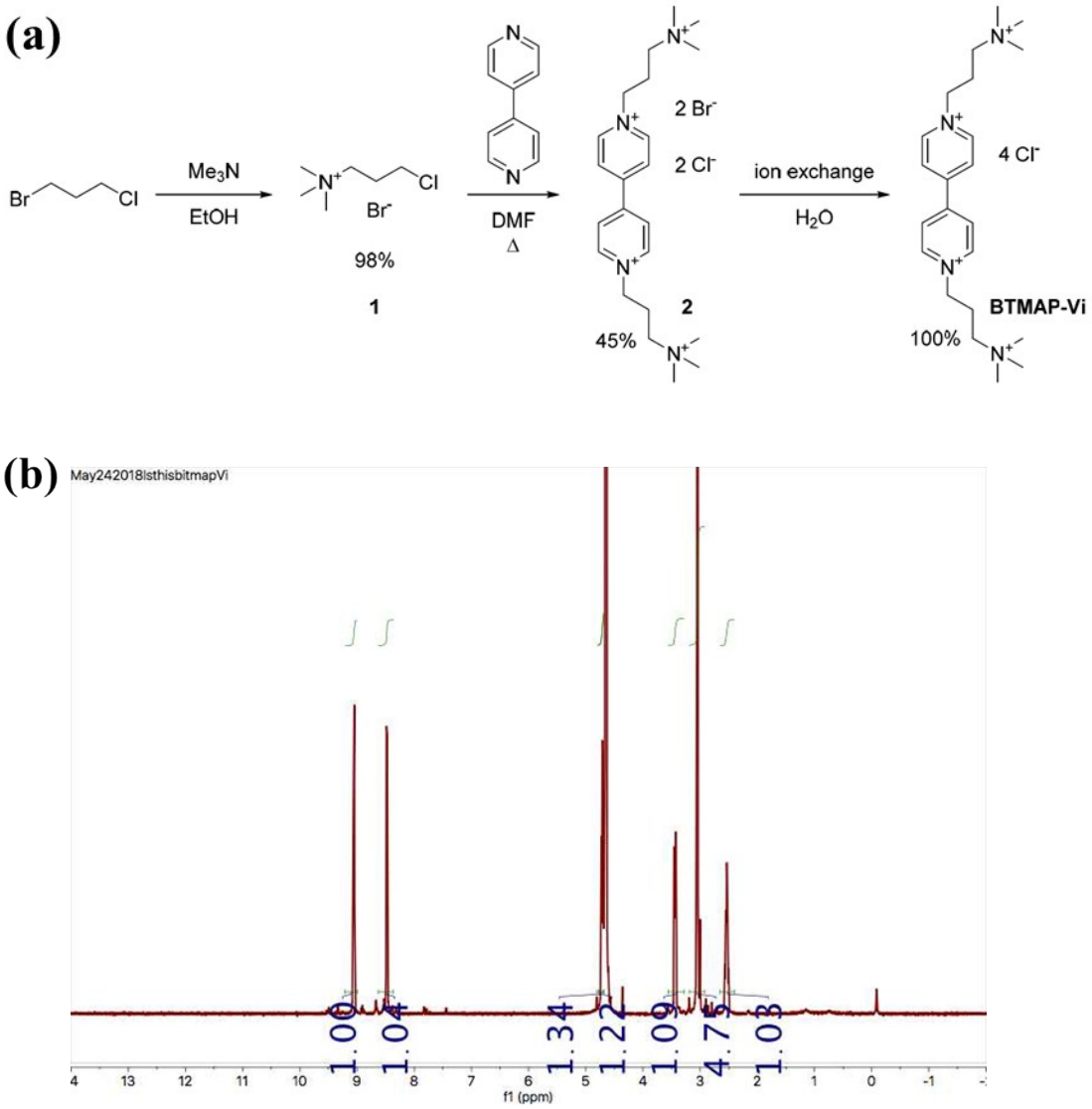


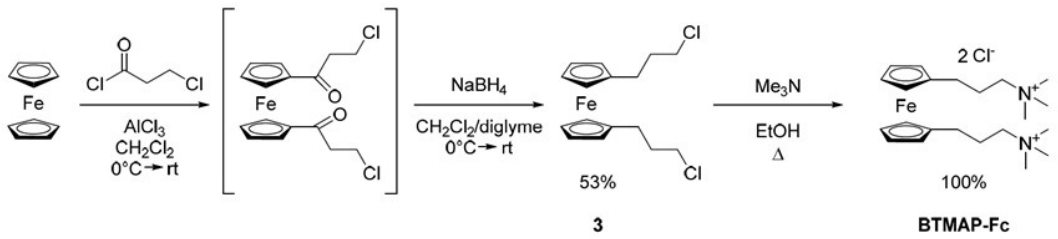
Figure S1. (a) Scheme of synthesis of BTMAP-Vi and (b) ^{1}H NMR spectrum of BTMAP-Vi recorded at 500 MHz, in D_2O. δ 9.12 (d, 4H), 8.63 (d, 4H), 4.87 (t, 4H), 3.61 (m, 4H), 3.22 (s, 18H), 2.72 (m, 4H).

Synthesis of BTMAP-Fc: BTMAP-Fc was synthetized as previously described by Beh *et al.*[1] The scheme of its synthesis is shown in Figure S2a. Initially, 14.67 g (110.0 mmol) of $AlCl_3$ was suspended in ~100 mL of anhydrous CH_2Cl_2. A solution of 12.70 g (100.0 mmol) of 3-chloropropionyl chloride in ~50 mL of anhydrous CH_2Cl_2 was added by syringe and the mixture stirred at room temperature for 2 hours. Once this was complete, the resulting slightly turbid golden-yellow solution was transferred *via* cannula into another flask, which had been

cooled to 0 °C, containing a solution of 9.30 g (50.0 mmol) of ferrocene in ~100 mL of anhydrous CH_2Cl_2. After stirring overnight, the reaction mixture was again cooled to 0 °C and a solution of 200 mL of 0.5 M $NaBH_4$ (100.0 mmol) in anhydrous diglyme was added *via* cannula and stirring was continued for a further 4 hours. Following that, the reaction was carefully quenched by the addition of ~500 mL of 1 M aqueous HCl. The organic phase was isolated and the aqueous phase extracted with CH_2Cl_2 (3 × 100 mL). The extracts were combined, dried over anhydrous Na_2SO_4, filtered and evaporated to give the crude product of 1,1'-bis(3-chloropropyl)ferrocene (**3**). Yield: 16.02 g (94.5%) of a red-brown oil.

16.02 g (47.3 mmol) of column purified **3** was dissolved in ~100 mL of a 4.2 M solution of trimethylamine in ethanol. The solution was sealed in a heavy-walled glass tube and heated to 60 °C for 5 days. Following that, all volatiles were removed *in vacuo* to give a dark brown oil. The oil was stirred in H_2O (~400 mL) and filtered to remove unreacted ferrocene and other water-insoluble impurities. The filtrate was evaporated *in vacuo* to give pure BTMAP-Fc. Yield: 20.76 g (96.1 %) of a dark brown glassy solid. ^{1}H NMR spectrum of the final product BTMAP-Fc is shown in Figure S2b.

(a)



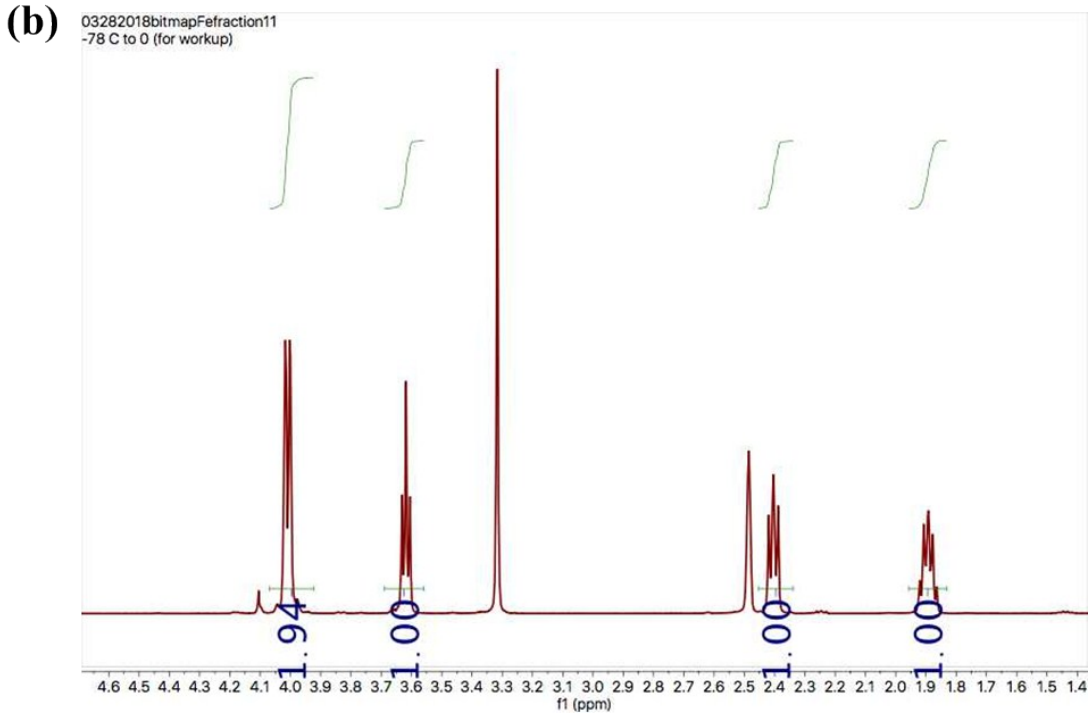


Figure S2. (a) Scheme of synthesis of BTMAP-Fc and ^{1}H NMR spectrum of BTMAP-Fc recorded at 500 MHz, in D_2O. δ 4.15 (m, 8H), 3.27 (m, 4H), 3.05 (s, 18H), 2.55 (t, 4H), 1.94 (m,4H).

Cyclic voltammetry: Cyclic voltammograms (CVs) were recorded in a Gamry Reference 3000 potentiostat (Gamry Instruments, United States) using an array of flexible carbon fibers (FCFs), Pt wire and Ag/AgCl electrode (3 M KCl filling solution) as working, counter and reference electrodes, respectively. Pt wire and Ag/AgCl electrode were obtained from BASi® (United States). Before the measurements, an array of FCFs was extracted from a carbon cloth (from Biolinker, Brazil) and chemically treated with $KMnO_4$ in H_2SO_4 solution.[2]

Hydrogel preparation: The hydrogels with BTMAP-Vi and BTMAP-Fc were prepared suspending 1.5 % (w/w) agarose in 1.0 M KCl containing 0.50 M of BTMAP-Vi and BTMAP-Fc. After, the suspensions were heated until 90 ^{o}C, because agarose dissolves in near-boiling water. Then, 100 μL of each mixture was dropped on the top of FCF electrodes.

The system was cooled to room temperature to form the gels. The composition of the hydrogels is shown in table S1. At pH 7.0 both BTMAP-Fc and BTMAP-Vi are positively charged and highly soluble in water, almost up to 2.0 M for both reactants. However, BTMAP-Vi and BTMAP-Fc concentrations higher than 0.5 M were not used in the microbattery because they affect the agarose gelling. In addition, the agarose forms a water-swollen polymer network at room temperature, the crosslink density, and thus the diffusion of species absorbed within the hydrogel, can be controlled by tuning the agarose concentration.

Table S1. Composition of the BTMAP-Vi and BTMAP-Fc hydrogels.

Component	% (w/w) in the BTMAP-Fc hydrogel	% (w/w) in the BTMAP-Vi hydrogel
Agarose	1.1 %	1.1 %
KCl	5.6 %	5.4 %
BTMAP-Fc	17.4 %	-
BTMAP-Vi	-	21.0 %
Water	75.8 %	72.5 %

PFGE-^{1}H-NMR measurements: The diffusion coefficients of both BMAP-Vi and BTMAP-Fc were measured in 1M KCl solution in D_2O and in a hydrogel with the same composition as table S1 using D_2O instead of water. The measurements were made using a Varian INOVA, 600 MHz NMR spectrometer using a 5mm TRX/PFG triple resonance probe with a 70 gauss/cm maximum Z-gradient. Experiments were done using a 2 ms diffusion gradient length and a 150 ms diffusion delay time. The NMR data was processed using the built-in VNMR-J software from Varian.

Microbattery assembly: A microbattery with a Selemion DSV anion exchange separator was built with two polyacrylate pieces (1.50 cm × 1.50 cm × 1.50 mm) with a pool (0.72 cm × 0.72 cm × 1.50 mm) in the center to give a compartment for each gel. The dimensions of the entire microbattery are mainly attributed to the polyacrylate package. The separator was placed between the two compartments. The cell was gasketed by Viton sheets of 270 μm in thickness. 100 μL of heated mixture containing 0.50 M BTMAP-Fc (positive side) and 0.50 M BTMAP-Vi (positive side) in 1.0 M KCl and 1.5 % agarose were dropped in each compartment and cooled to room temperature to form the gel. One array of FCF was used as the electrode in each side of the battery, the geometric area exposed to the hydrogel was 0.025 cm^2. The microbattery was sealed with silicone resin.

Microbattery measurements: Full cell tests were performed with a BioLogic BCS-815 battery cycling system. All measurements were carried out at room temperature and inside a glove bag in a N_2 atmosphere. The charge and discharge current densities were calculated based on the anode area, which is 0.025 cm^2. The measurements were carried out immediately after assembly of the microbattery. The microbattery was charged at 1.10 V for 30 min. If we define 100% SOC as the theoretical capacity (4.8 C), then charging the battery at constant potential for 30 min, achieves 20% SOC (0.89 C). The polarization curve was obtained at ~20% SOC by cyclic voltammetry where the potential is swept from 0.30 V to 1.10 V with a scan rate of 100 mV s^{-1}. During the sweep in potential, the cell discharged less than 0.05 C.

Hydrogel cost

Agarose is a natural and low-cost polysaccharide used for preparation of hydrogels.[3] The price of laboratory grade agarose powder is around $6.50 per 15 g. With 15 g it is possible to

prepare 1.0 L of 1.5% agarose gel. Considering one microbattery is composed of 200 µL of agarose gel (100 µL of negolyte + 100 µL of posolyte), with 1.0 L of gel it is possible to fabricate 5,000 microbatteries. This means that with $1 it is possible to prepare hydrogel for 770 microbatteries at laboratory-scale prices.

Capability of the microbattery to hold its charge

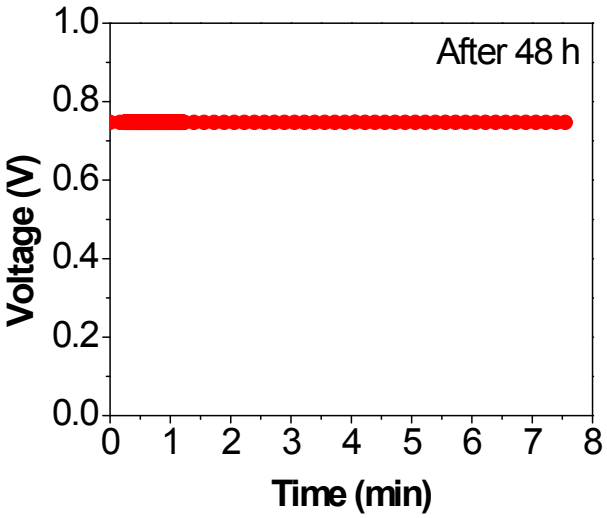


Figure S3. Measurement of cell voltage after 48 h of storage (no current drained).

References

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2. M. V. Martins, A. R. Pereira, R. S. Luz, R. M. Iost, F. N. Crespilho. *Phys. Chem. Chem. Phys.*, 2014, **16**, 17426-17436.
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