

Supporting Information

Bipolar Electrochemical Fluorination of Triphenylmethane and Bis(phenylthio)diphenylmethane Derivatives in a U-shaped Cell

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Materials

All chemicals and anhydrous solvents were purchased from commercial sources and used without further purification unless otherwise stated. Cesium fluoride (CsF) was dried under vacuum prior to use. Poly(ethylene glycol) (PEG, average molecular weight: 600) was dried under reduced pressure prior to use. **1b-1e**,¹ **3**,² **4a-4d**³ were prepared according to the reported procedures. Indium-tin-oxide (ITO) glass plates (10 Ω/\square) were obtained from GEOMATEC Co., Ltd.

Instruments

Direct current (DC) power was supplied to the feeder electrodes using an EC1000SA AC/DC power source (NF Corporation). Cyclic voltammetry (CV) measurements were carried out using an ALS 6005C Electrochemical Analyzer using a platinum (Pt) disk electrode as a working electrode ($\phi = 1.6$ mm), a platinum plate as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode at a scan rate of 100 mV/s. ^{19}F NMR spectra were recorded on a JEOL ECP-300 (282.00 MHz) spectrometer in CDCl_3 . The chemical shifts for ^{19}F NMR spectra were given in δ (ppm) from monofluorobenzene (-113.15 ppm) as an internal standard. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-700 spectrometer. COMSOL Multiphysics 5.4 software was used to evaluate the electric field distribution.

General Procedure for Electrochemical Fluorination

Electrochemical fluorination of triphenylmethane in the U-shaped cell equipped with a split BPE (s-BPE) was carried out in an acetonitrile solution containing 5 mM of CsF, 30 mM of PEG ($M_n \sim 600$) and in the presence of the substrates. 25–100 V of cell voltage was applied between Pt driving electrodes with the s-BPE composed of Pt, in which the current through the s-BPE was monitored with an ammeter at 25°C for 4 F/mol. After the electrolysis, the reaction mixture was extracted with hexane, then the solvent was evaporated under a reduced pressure. Product yields were estimated by ^{19}F NMR using monofluorobenzene as an internal standard. The attempt to isolate fluorinated compounds by silica gel column chromatography was failed due to the very close elution time of starting materials and the corresponding fluorinated products under any solvent conditions attempted. ^{19}F NMR data for **2a**,⁴ **2d**,⁵ **5a-5c**,⁶ **6d**⁷ were corresponded to the previous reports. **2b**, **2c**, **2e** were characterized by ^{19}F NMR and high-resolution mass spectroscopy.

Diphenyl(*p*-bromophenyl)methyl fluoride (**2b**)

^{19}F NMR (254 MHz, CDCl_3): δ -50.5 (s, 1F), HRMS (EI): calcd for $\text{C}_{19}\text{H}_{14}^{79}\text{BrF}$ ($[\text{M}]^+$) m/z 340.0263, found 340.0260.

Diphenyl(*p*-chlorophenyl)methyl fluoride (**2c**)

^{19}F NMR (254 MHz, CDCl_3): δ -50.8 (s, 1F), HRMS (EI): calcd for $\text{C}_{19}\text{H}_{14}^{35}\text{ClF}$ ($[\text{M}]^+$) m/z 296.0768, found 296.0766.

Diphenyl(*p*-trifluoromethylphenyl)methyl fluoride (**2e**)

^{19}F NMR (254 MHz, CDCl_3): δ -52.0 (s, 1F) δ 12.4 (s, 3F); HRMS (EI): calcd for $\text{C}_{20}\text{H}_{14}\text{F}_4$ ($[\text{M}]^+$) m/z 330.1032, found 330.1030.

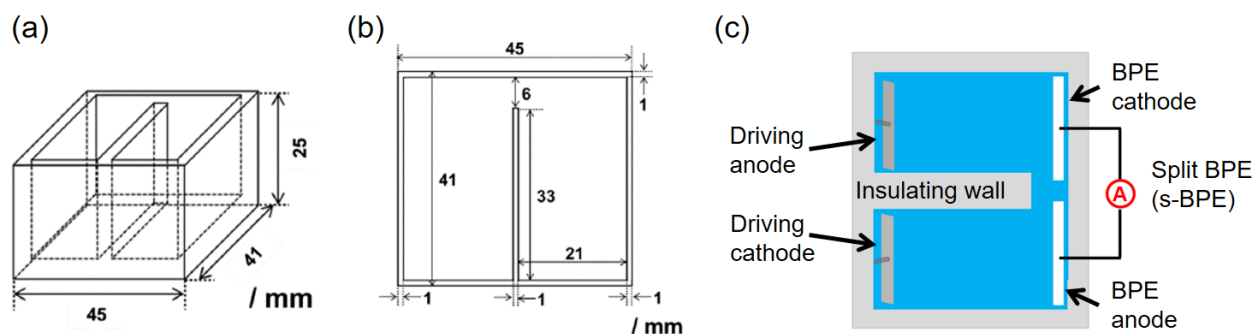


Figure S1. Scale of the U-shaped cell (a) oblique view and (b) top view. (c) Illustration of the cell configuration with driving electrodes and s-BPE for the bipolar electrochemical reaction.

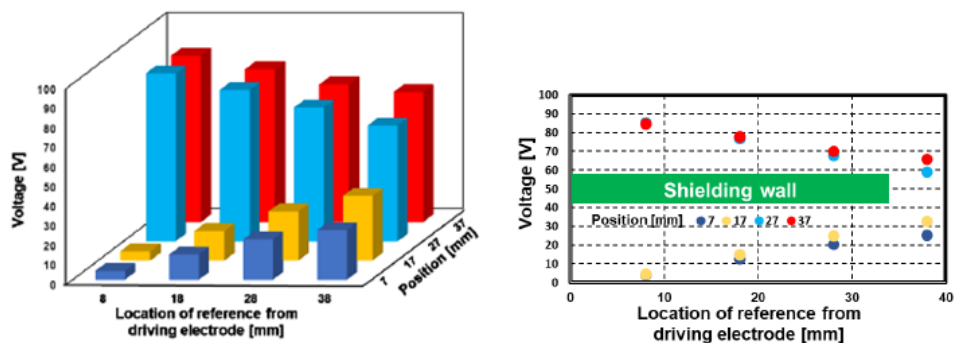


Figure S2. Experimentally measured IR-drop in the U-shaped cell.⁸

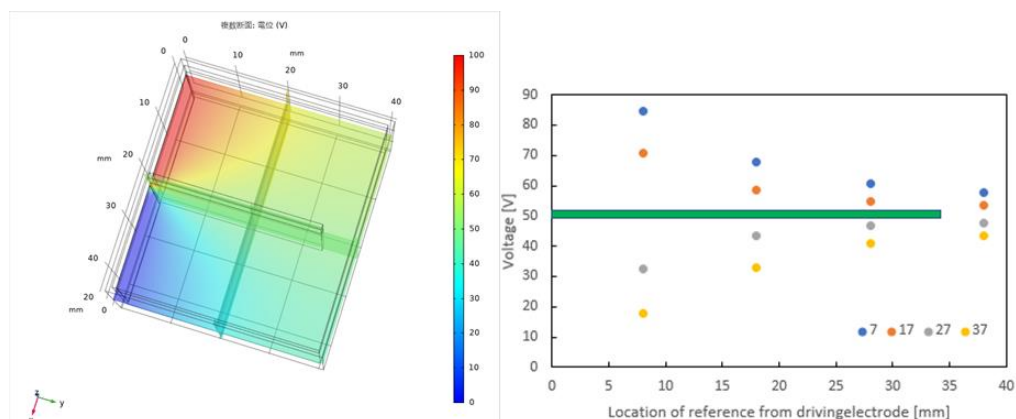
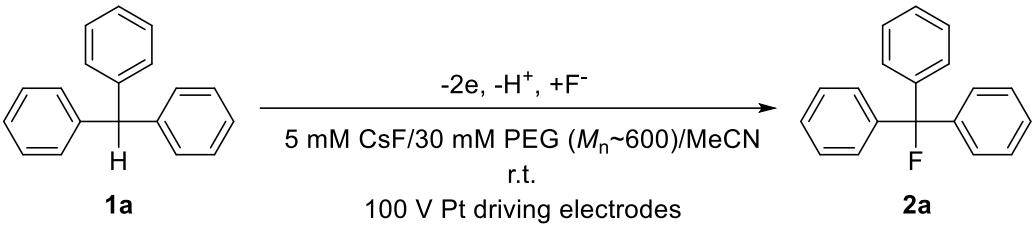


Figure S3. Computationally simulated electric field in the U-shaped cell.

Table S1. Electrochemical fluorination of **1a** in the U-shaped cell without the s-BPE. Each entry corresponds to that of **Table 1**.

 <p style="text-align: center;"> $-2e, -H^+, +F^-$ 5 mM CsF/30 mM PEG ($M_n \sim 600$)/MeCN r.t. 100 V Pt driving electrodes </p>			
Entry	Concentration of 1a [mM]	Reaction time [min]	Yield of 2a [%] ^a
1 ^b	5	230	8
2	5	200	18
3	2	60	43
4	1	30	18

a) ¹⁹F NMR yield. b) Without stirring.

Table S2. Potential differences and currents through the s-BPE (reproduced from **Table S1** of the previous paper, reference 8).^a

Cell voltage (V)	5	10	20	25	50	75	100
Potential difference s-BPE (V)	1.9	3.6	6.0	7.5	14.6	21.8	29.1
Current s-BPE (mA) ^b	0.03	0.16	0.46	0.76	1.9	3.1	4.3

a) 5 mM CsF and 0.6 M PEG (200) in MeCN. b) Presence of 5 mM triphenylmethane.

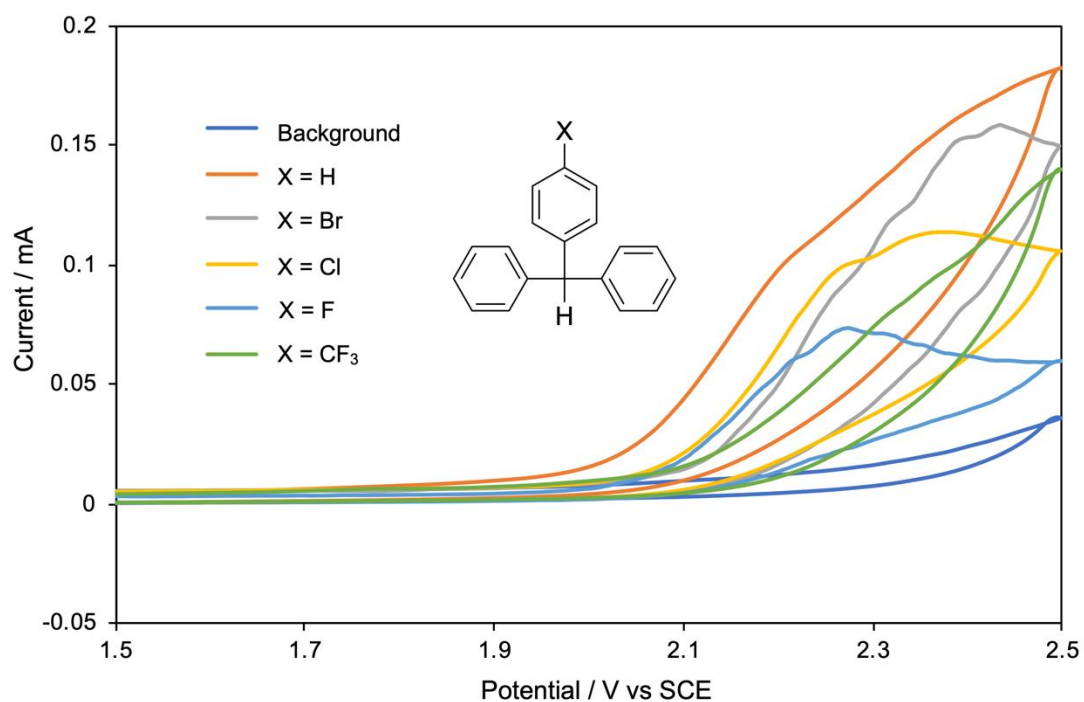


Figure S4. Cyclic voltammograms of 10 mM **1a-1e** in 0.1 M $n\text{Bu}_4\text{NPF}_6/\text{MeCN}$ using a Pt disk working electrode at a scan rate of 0.1 V/s. CV recorded in the background solution is also shown.

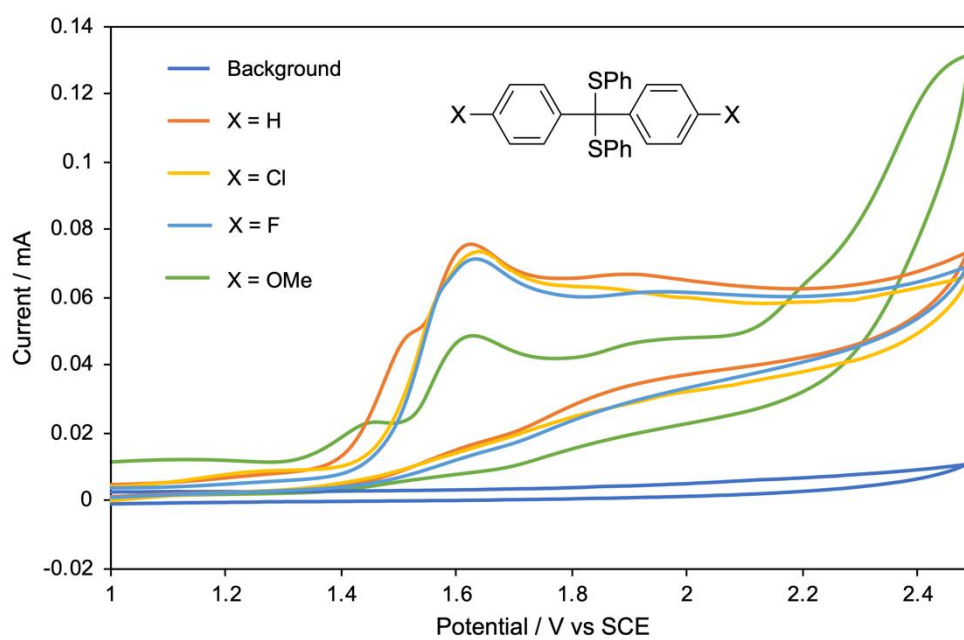


Figure S5. Cyclic voltammograms of 10 mM **4a-4d** in 0.1 M $n\text{Bu}_4\text{NPF}_6/\text{MeCN}$ using a Pt disk working electrode at a scan rate of 0.1 V/s.

References

1. H. S. P. Rao and A. V. B. Rao, *Beilstein J. Org. Chem.*, **12**, 496 (2016).
2. M. Micha-Screttas and C. G. Screttas, *J. Org. Chem.*, **42**, 1462 (1977).
3. T. Yoshiyama and T. Fuchigami, *Chem. Lett.*, **21**, 1995 (1992).
4. C. M. Wang and T. E. Mallouk, *J. Am. Chem. Soc.*, **112**, 2016 (1990).
5. S. Yolles and J. H. R. Woodland, *J. Organomet. Chem.*, **54**, 95 (1973).
6. T. Fuchigami and M. Sano, *J. Electroanal. Chem.*, **414**, 81 (1996).
7. G. K. S. Prakash, V. P. Reddy, X-Y. Li, and G. A. Olah, *Synlett*, **10**, 594 (1990).
8. K. Miyamoto, H. Nishiyama, I. Tomita, and S. Inagi, *ChemElectroChem*, **6**, 97 (2019).