Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Dual role of novel highly efficient radical generators for UV/LED-activated polymerization processes

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Contents

General procedure of synthesis of diphenyliodonium tosylates

Unsymmetrical diphenyliodonium tosylates (IODs) were obtained according to the procedure described below. The general pathway for synthesis of novel compounds (IOD-1 – IOD-4) is presented in Fig. S1 and Fig. S2.

The first step included the formation of [hydroxy(tosyloxy)iodo]nitrobenzene (HTINB) as the main substrate for preparation of novel diphenyliodonium salts (IOD-1 – IOD-4).

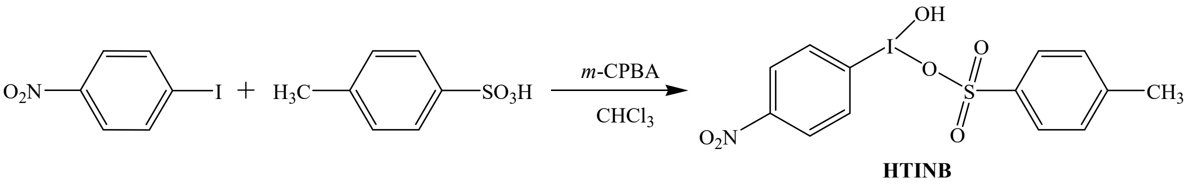


Fig. S1 General route for the synthesis of HTINB substrate.

Step 1

The procedure was combined of 1-iodo-4-nitrobenzene (1.0 g, 4.0 mmol), *p*-toluenesulfonic acid monohydrate - TsOH (0.84 g, 4.4 mmol) and *m*-chloroperbenzoic acid - *m*-CPBA (0.76 g, 4.4 mmol). The substrates were dissolved in chloroform (20 mL) and the solution was stirred at room temperature for 12 hours. After that, 10 mL of diethyl ether (Et_2O) was added to the mixture, which caused immediate precipitation. The obtained product was filtered under reduced pressure, washed with Et_2O and dried.

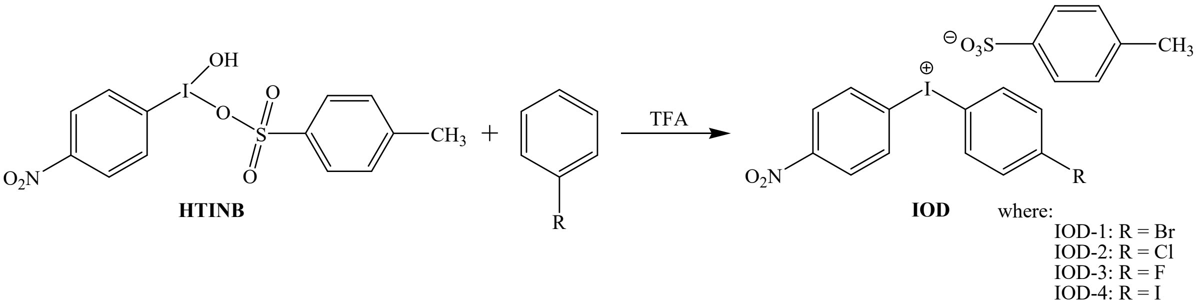


Fig. S2 General route for the synthesis of IOD derivatives.

Step 2

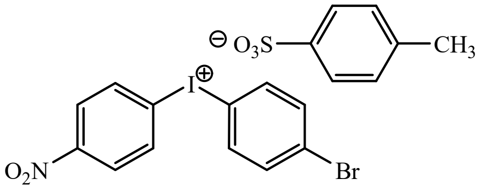
Synthesized in the first step HTINB (1.0 g, 2.3 mmol) was dissolved in 2.0 ml trifluoroacetic acid (TFA). Next, the appropriate substituted benzene (4.6 mmol) was added. The mixture was stirred at room temperature for 12 hours. After that, trifluoroacetic acid was evaporated and a few drops of methanol (MeOH) and Et_2O (10 mL) were added. The precipitate (yellow pale to white solid) of diphenyliodonium tosylate was filtrated under reduced pressure, washed with diethyl ether and dried without exposure to light.

Structural characterization of synthesized compounds

The chemical structure of synthesized compounds was confirmed by NMR spectroscopy. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using an Ascend III spectrometer (Bruker, USA), operating at 400 MHz. Deuterated dimethylsulfoxide (DMSO-d_6) was used as solvent ant tetramethylsilane (TMS) or trichlorofluoromethane ($CFCl_3$ for ^{19}F) as internal standard. Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hz.

Melting point values (uncorrected) were measured on the Mel-Temp apparatus (Electrothermal, Poland).

Obtained diphenyliodonium salts:



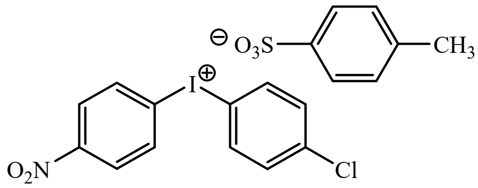
(4-Bromophenyl)-(4-nitrophenyl)iodonium tosylate (**IOD-1**)

^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 2.29 (s, 3H, CH_3), 7.10-7.12 (d, 2H, Ar, J = 8 Hz), 7.45-7.47 (d, 2H, Ar, J = 8 Hz), 7.77-7.79 (d, 2H, Ar), 8.24-8.31 (dd, 4H, Ar), 8.47-8.50 (d, 2H, Ar, J = 12 Hz)

^{13}C NMR (400 MHz, DMSO-d_6), δ (ppm): 15.63, 19.80, 21.24, 65.38, 115.98, 123.41, 124.67, 125.96, 126.72, 127.07, 128.52, 131.09, 135.27, 136.93, 137.86, 138.10, 146.14, 149.89

M.p.: 195-197^{0}C

Yield: 53%



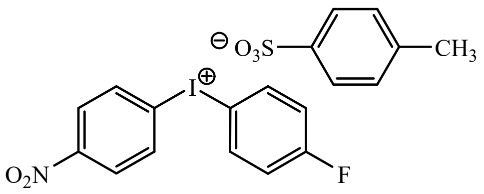
(4-Chlorophenyl)-(4-nitrophenyl)iodonium tosylate (**IOD-2**)

^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 2.29 (s, 3H, CH_3), 7.10-7.12 (d, 2H, Ar, J = 8 Hz), 7.46-7.48 (d, 2H, Ar, J = 8 Hz), 7.64-7.66 (m, 2H, Ar), 8.30-8.34 (m, 4H, Ar), 8.48-8.50 (m, 2H, Ar)

^{13}C NMR (400 MHz, DMSO-d_6), δ (ppm): 15.63, 19.79, 21.24, 65.38, 115.27, 123.45, 124.67, 125.96, 126.30, 126.73, 128.51, 131.09, 132.39, 136.92, 137.79, 138.07, 138.18, 146.17, 149.89

M.p.: 185-187^{0}C

Yield: 59%



(4-Fluorophenyl)-(4-nitrophenyl)iodonium tosylate (**IOD-3**)

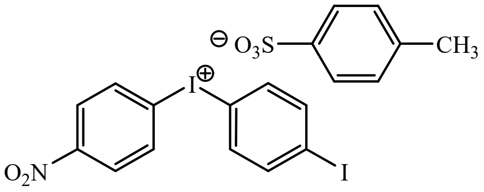
^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 2.29 (s, 3H, CH_3), 7.10-7.12 (d, 2H, Ar, J = 8 Hz), 7.43-7.48 (t, 4H, Ar), 8.31-8.33 (d, 2H, Ar, J = 8 Hz), 8.39-8.42 (m, 2H, Ar), 8.47-8.49 (m, 2H)

^{13}C NMR (400 MHz, DMSO-d_6), δ (ppm): 21.24, 111.59, 119.77, 120.00, 123.47, 125.96, 126.72, 128.49, 136.81, 138.01, 138.06, 138.87, 138.96, 146.26, 149.88, 163.35, 165.85

^{19}F NMR (400 MHz, DMSO-d_6), δ (ppm): -106.06 (s, 1F)

M.p.: 214-215^{0}C

Yield: 51%



(4-Iodophenyl)-(4-nitrophenyl)iodonium tosylate (**IOD-4**)

^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 2.30 (s, 3H, CH_3), 7.11-7.13 (d, 2H, Ar, J = 8 Hz), 7.47-7.49 (d, 2H, Ar, J = 8 Hz), 7.55-7.57 (d, 2H, Ar, J = 8 Hz), 7.90-7.92 (d, 2H, Ar, J = 8 Hz), 8.00-8.02 (d, 2H, Ar, J = 8 Hz), 8.25-8.27 (d, 2H, Ar, J = 8 Hz)

^{13}C NMR (400 MHz, DMSO-d_6), δ (ppm): 15.63, 19.80, 21.25, 65.38, 100.72, 116.33, 117.16, 124.67, 125.96, 128.49, 131.08, 132.27, 132.60, 135.65, 137.25, 138.00, 140.85, 146.30

M.p.: 175-177 ^{0}C

Yield: 41%

NMR spectra of synthesized IODs

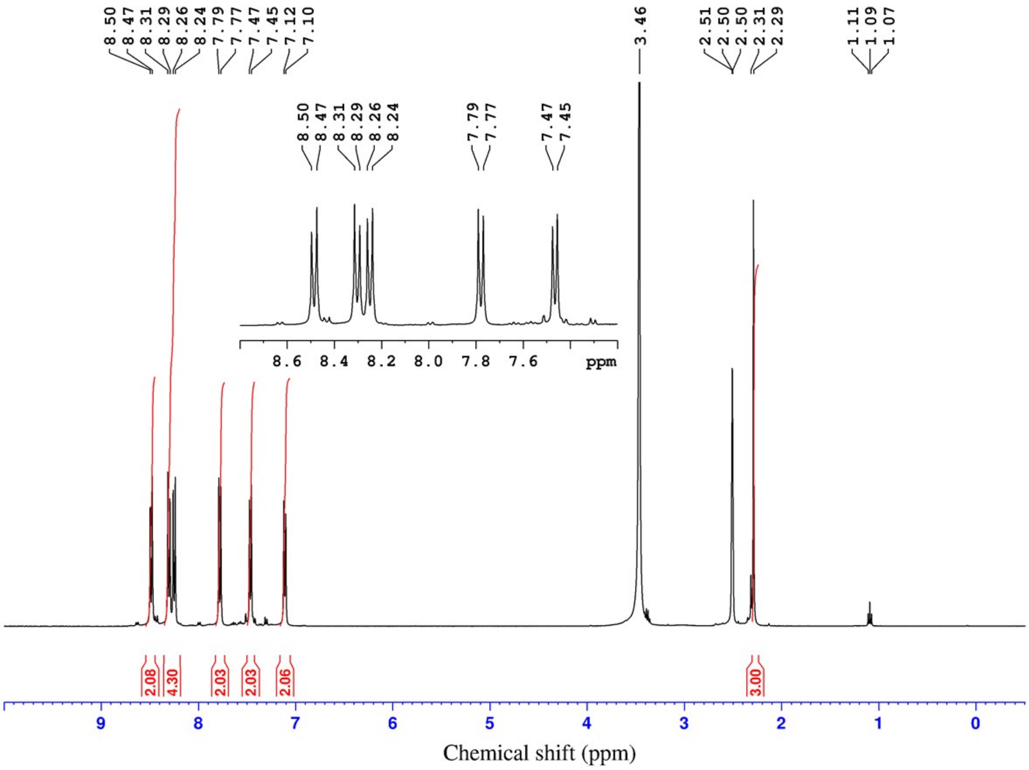


Fig. S3 ^{1}H NMR spectrum of **IOD-1**.

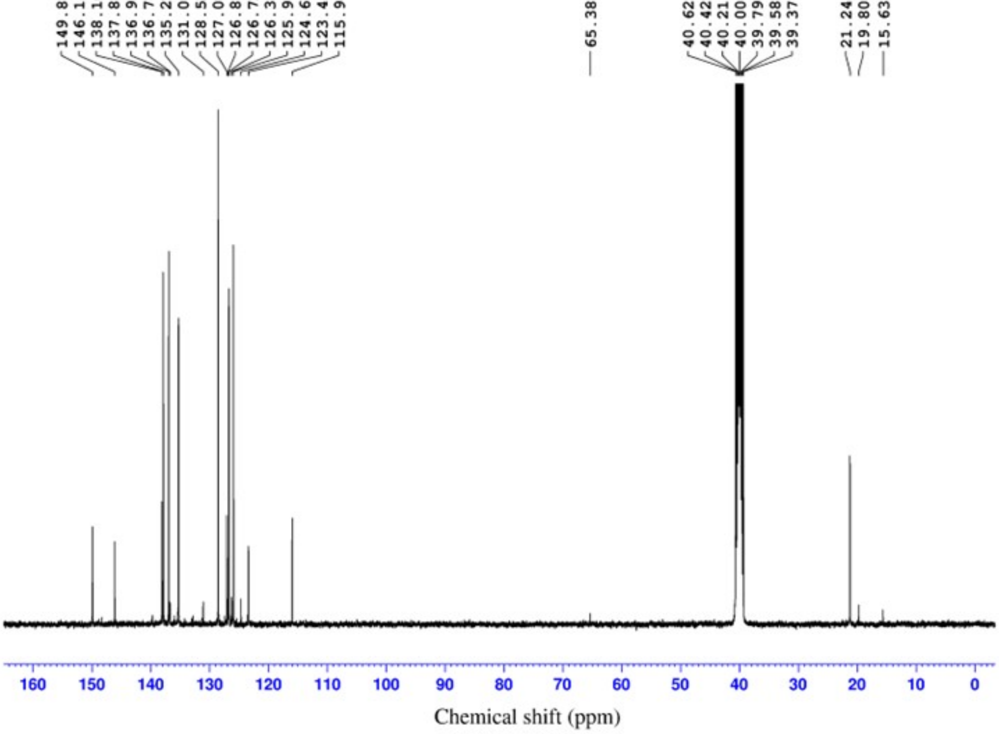


Fig. S4 ^{13}C NMR spectrum of **IOD-1**.

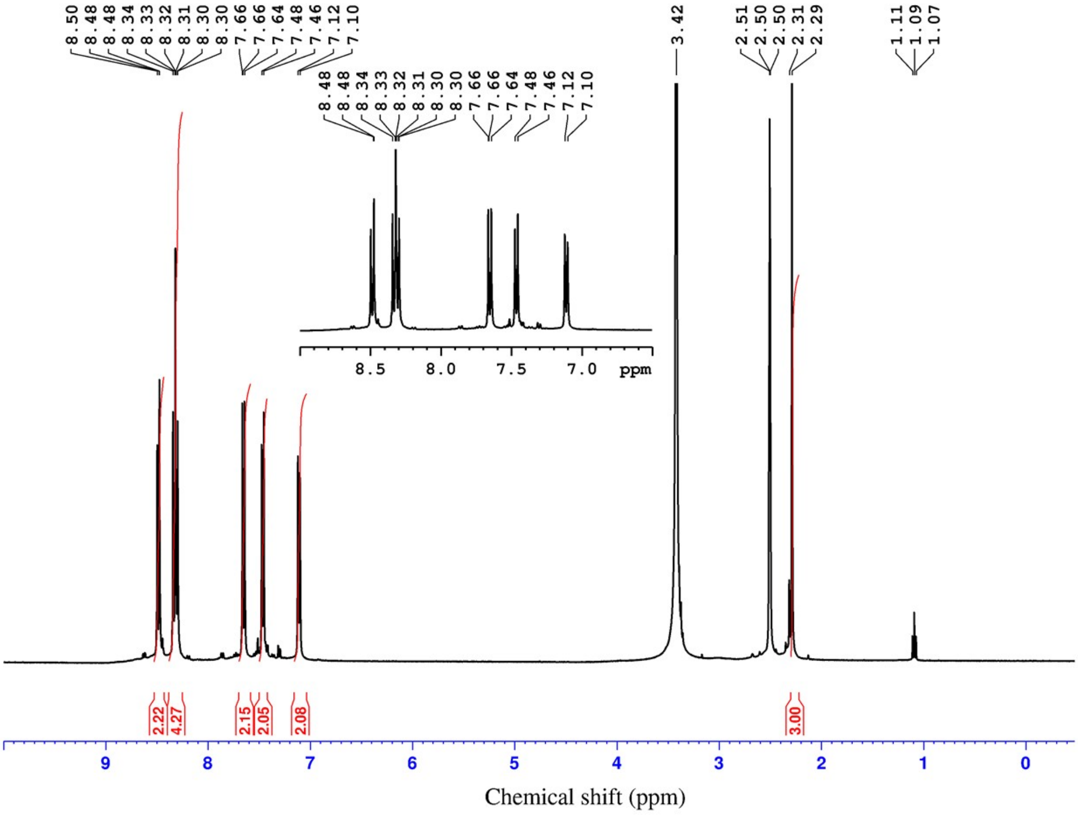


Fig. S5 ^{1}H NMR spectrum of **IOD-2**.

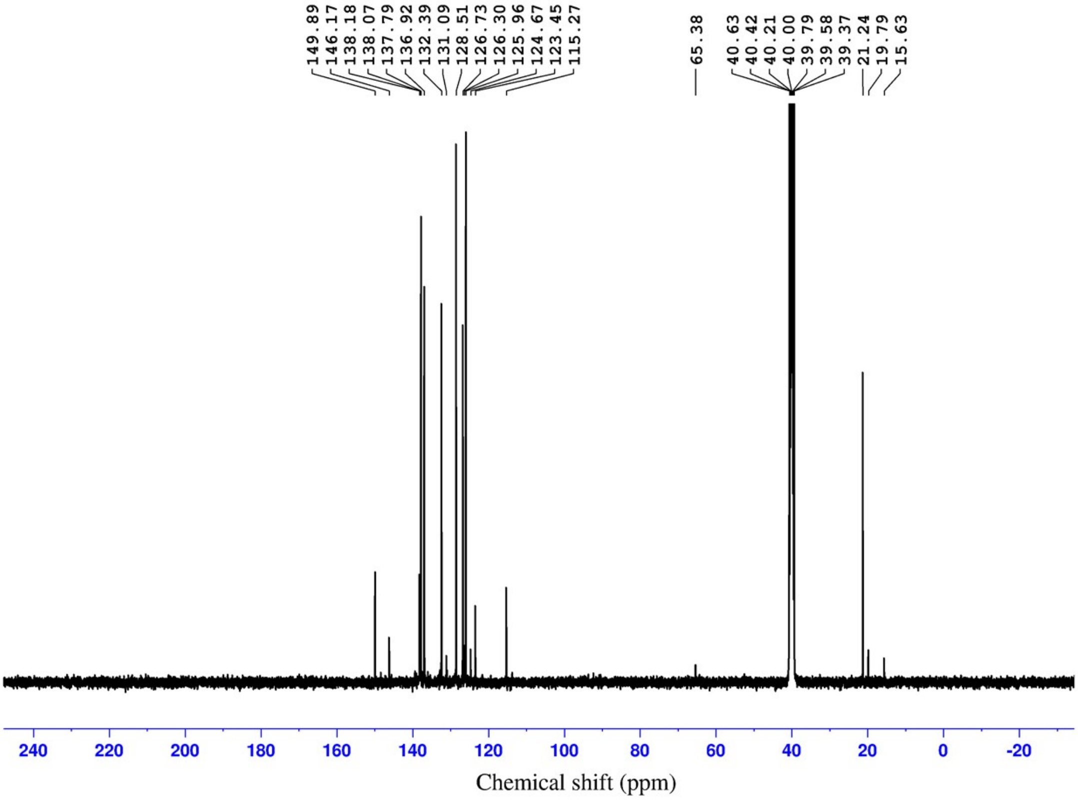


Fig. S6 ^{13}C NMR spectrum of **IOD-2**.

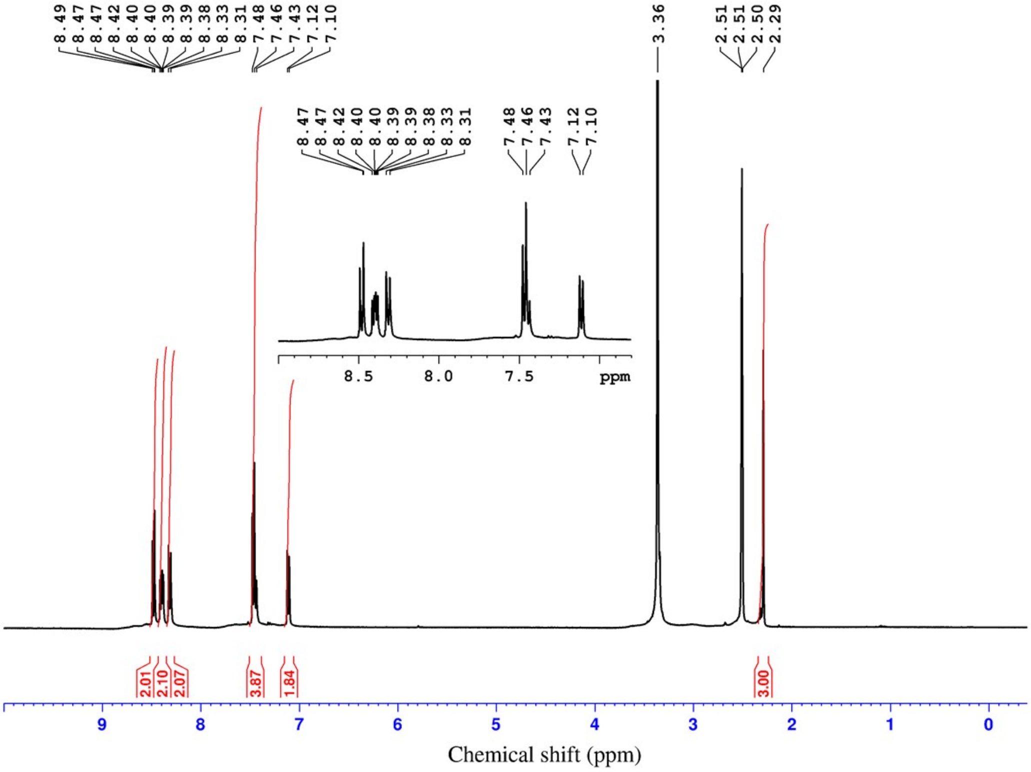


Fig. S7 ^{1}H NMR spectrum of **IOD-3**.

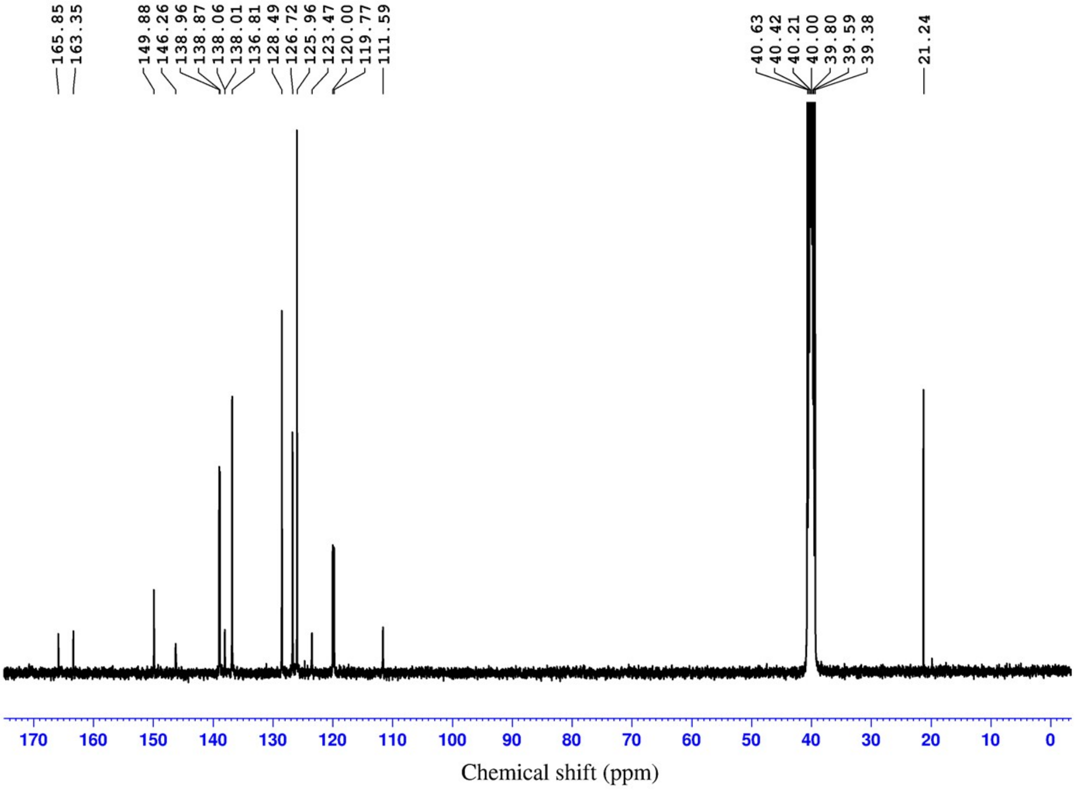


Fig. S8 ^{13}C NMR spectrum of **IOD-3**.

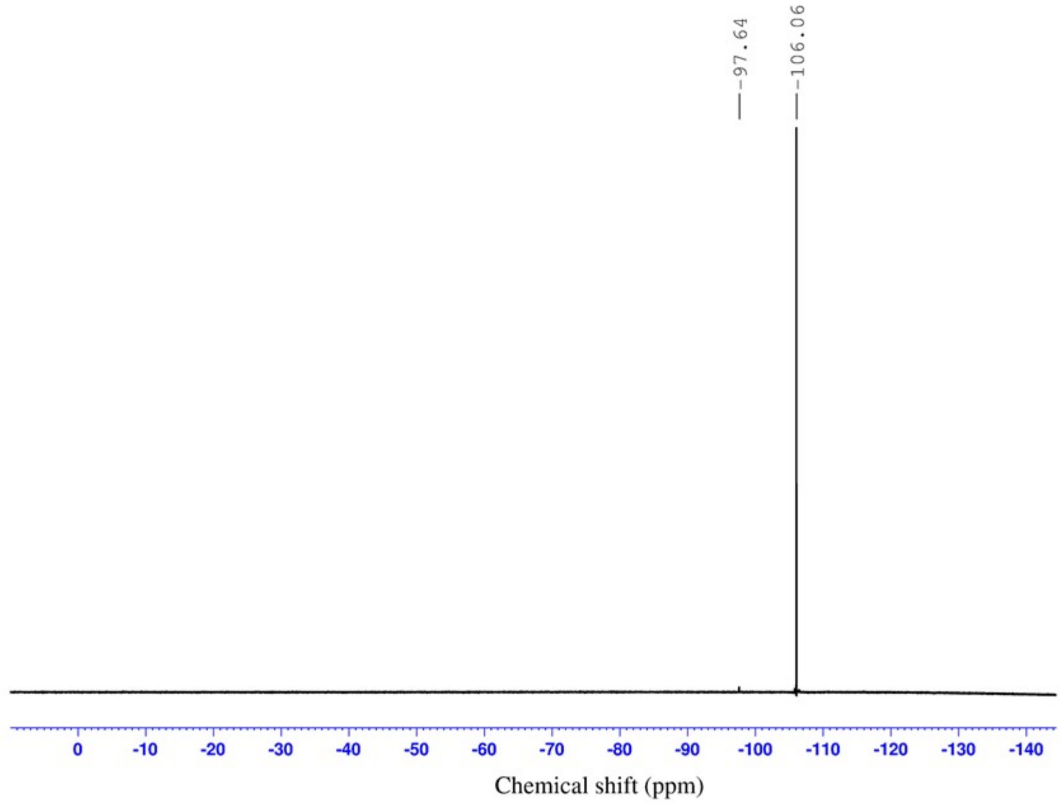


Fig. S9 ^{19}F NMR spectrum of **IOD-3**.

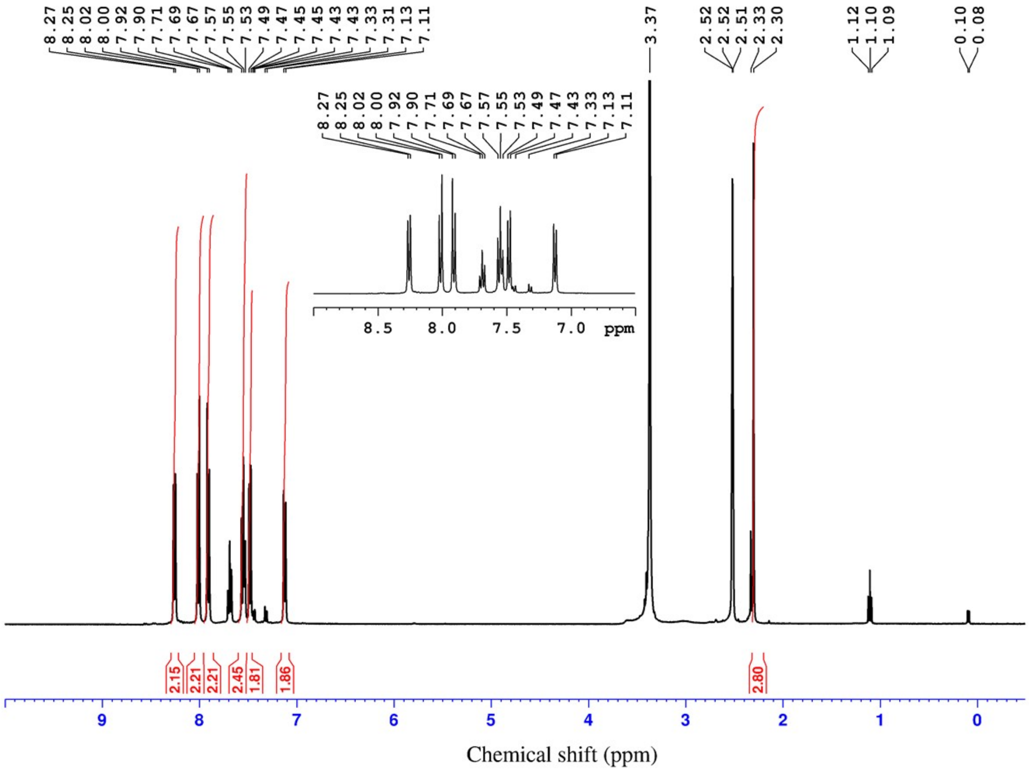


Fig. S10 ^{1}H NMR spectrum of **IOD-4**.

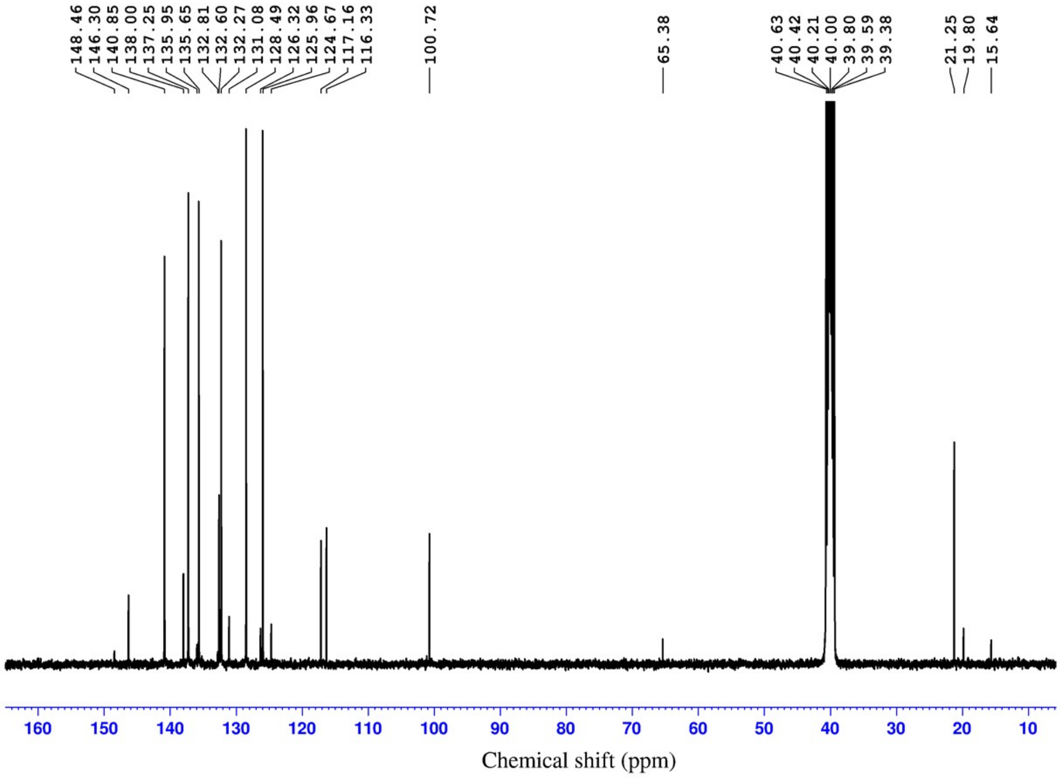


Fig. S11 ^{13}C NMR spectrum of **IOD-4**.

Steady state photolysis

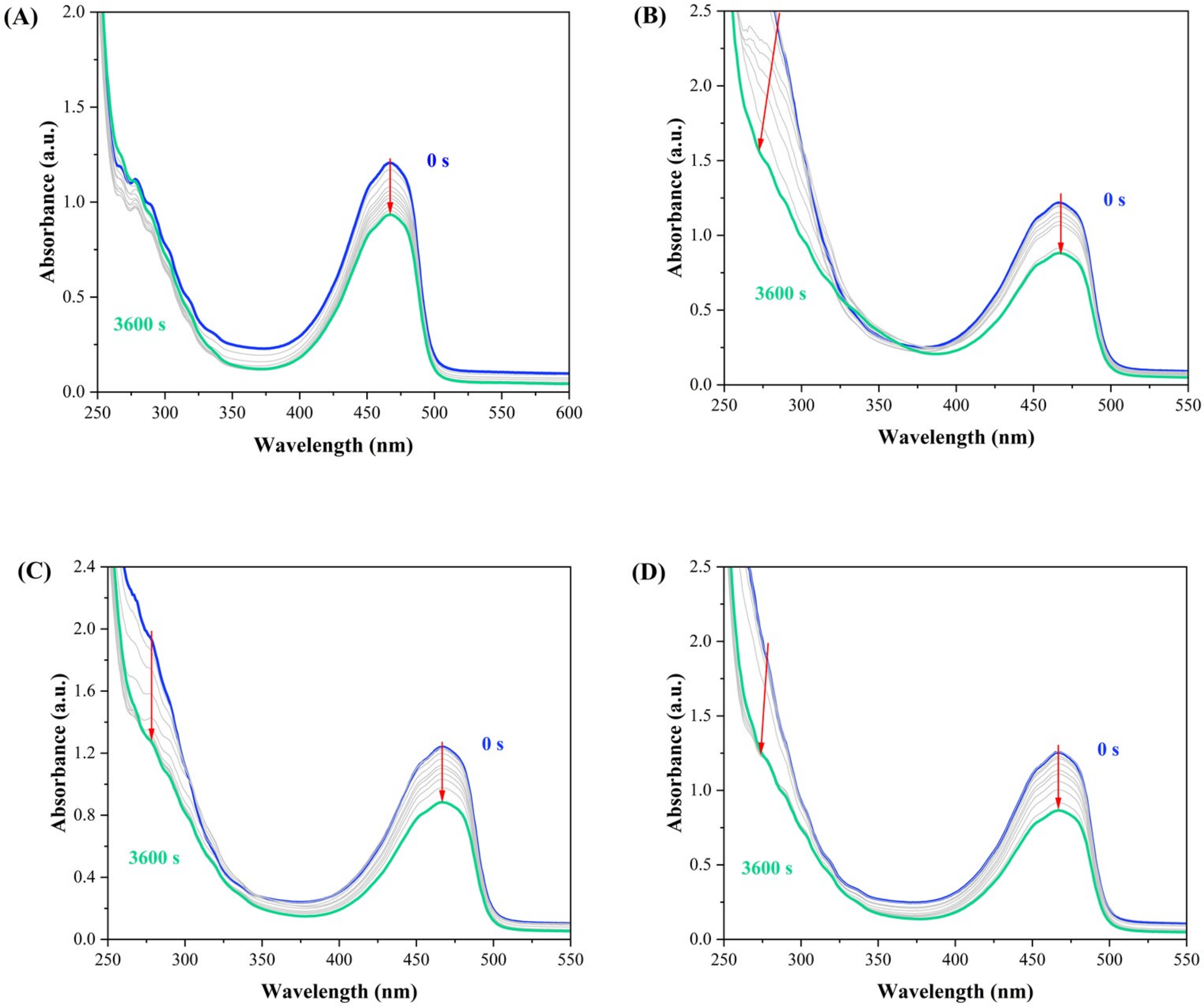
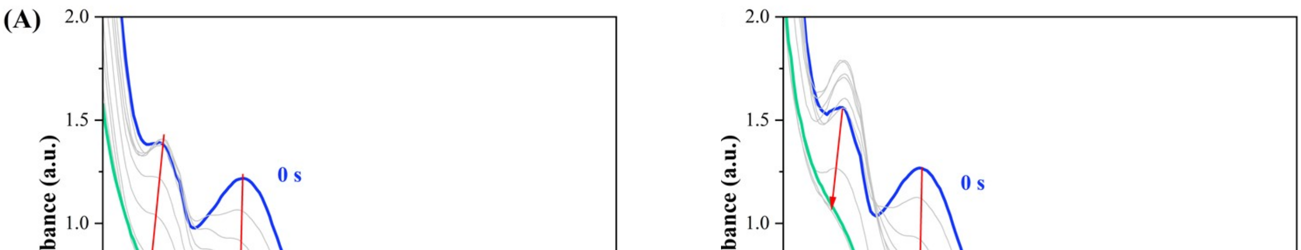


Fig. S12 Steady-state photolysis of (A) **CQ**, (B) **CQ/IOD-1**, (C) **CQ/IOD-2** and (D) **CQ/IOD-4** systems measured in acetonitrile upon exposure to LED@455 nm, I_0 = 78.03 mW cm^{-2}.



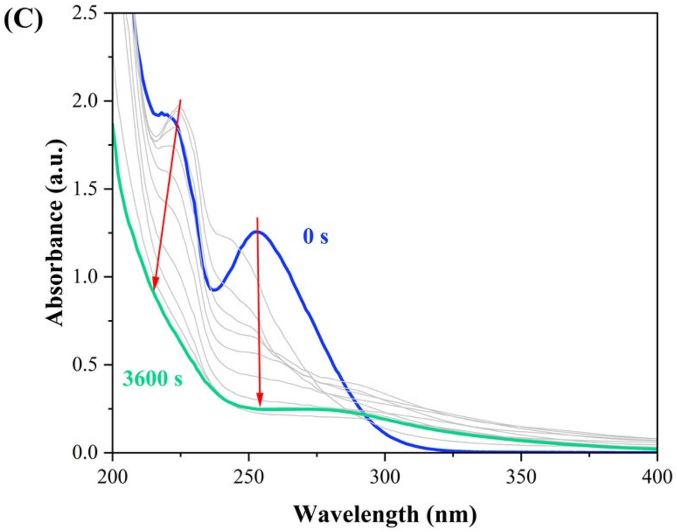
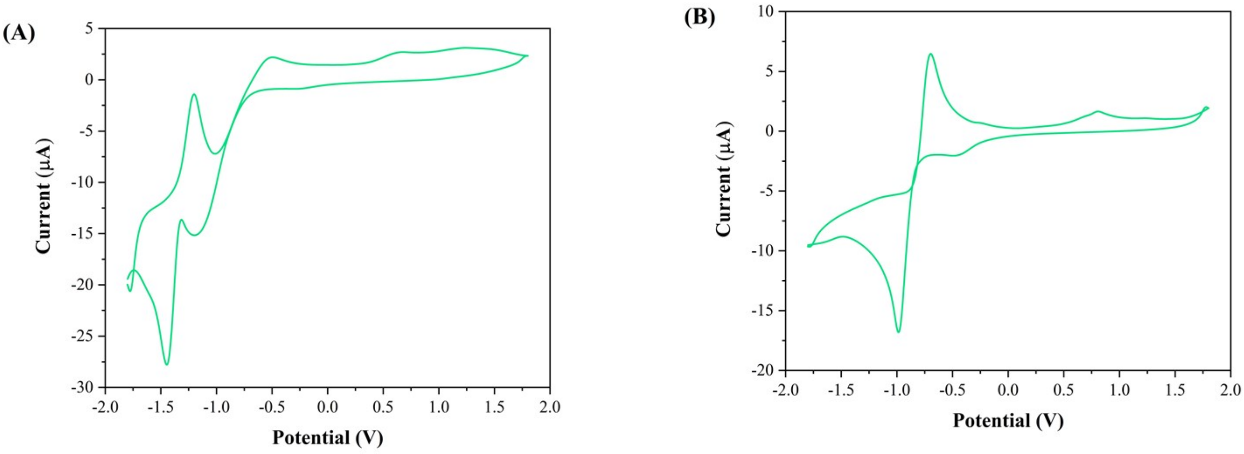


Fig. S13 Steady-state photolysis of (A) **IOD-1**, (B) **IOD-2** and (C) **IOD-4** iodonium salts measured in acetonitrile upon exposure to UV irradiation system, λ_{max} = 254 nm, I_0 = 50 mW cm^{-2}.

Cyclic voltammograms



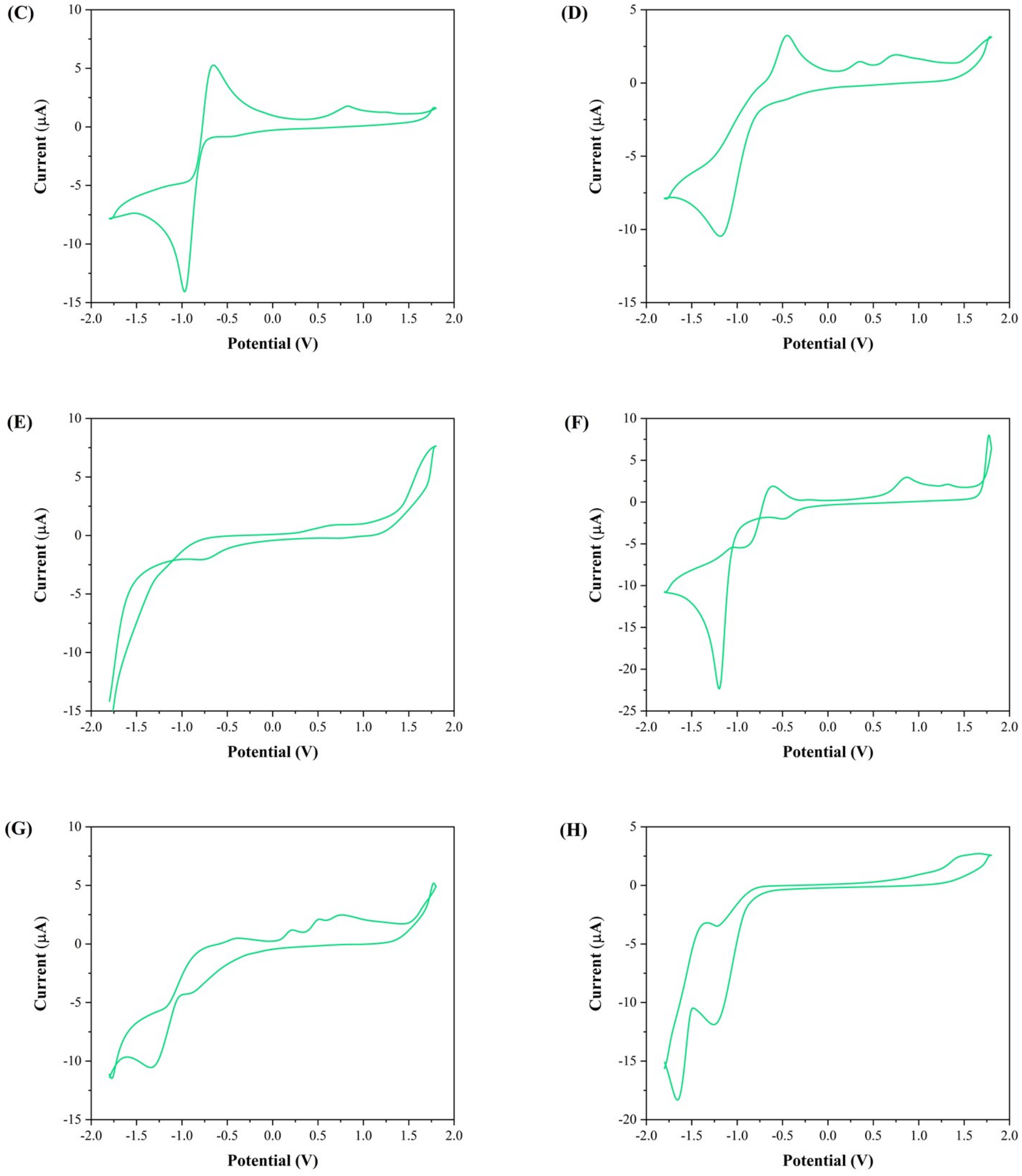


Fig. S14 Cyclic voltammogram of (A) **CQ**, (B) **IOD-2**, (C) **IOD-3**, (D) **IOD-4**, (E) **I1**, (F) **I2**, (G) **I3** and (H) **BAPO** recorded in anhydrous acetonitrile at 25^{0}C.