Supplementary Information

Acridinium salts as photoredox organocatalysts for photomediated cationic RAFT and DT polymerizations of vinyl ethers

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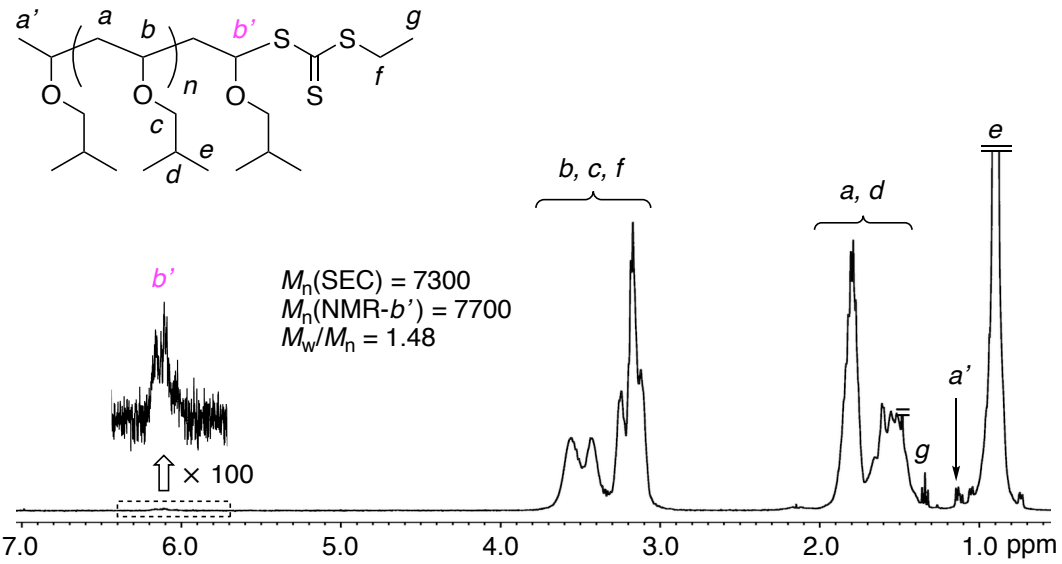

Fig. S1 ^{1}H NMR spectrum ($CDCl_3$, 55 °C) of poly(IBVE) obtained in photo-mediated cationic RAFT polymerization of IBVE with **C1**/**A2** in CH_2Cl_2 at –40 °C under irradiation of blue LED: $[M]_0/[\mathbf{C1}]_0/[\mathbf{A2}]_0$ = 500/5.0/0.50 mM.

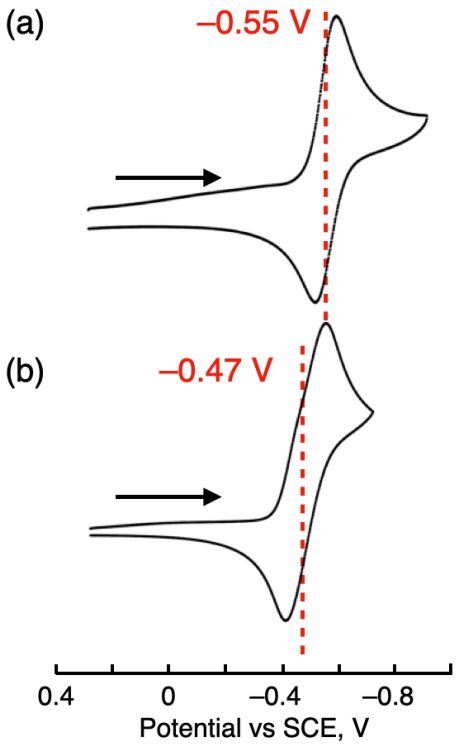

Fig. S2 Cyclic voltammograms of (a) **A5** and (b) **A4** (1 mM) in deaerated CH_2Cl_2 containing $TBA^+ClO_4^-$ (0.1 M) at 298 K.

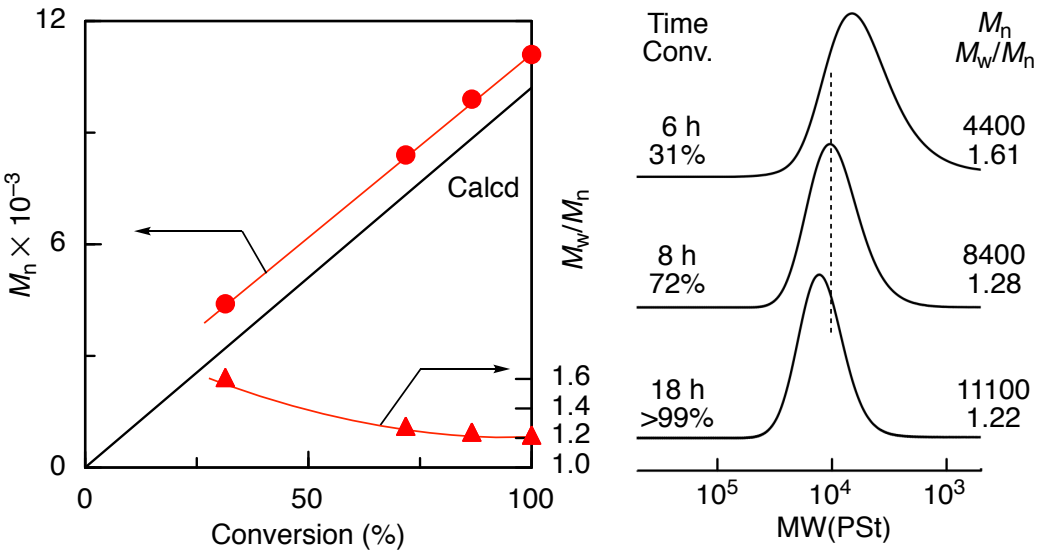

Fig. S3 Photo-mediated cationic DT polymerization of IBVE with **C5**/**A2** in *n*-hexane/CH_2Cl_2 (3/1) at –40 °C under irradiation of blue LED: $[M]_0/[\mathbf{C5}]_0/[\mathbf{A2}]_0$ = 1000/10/0.20 mM.

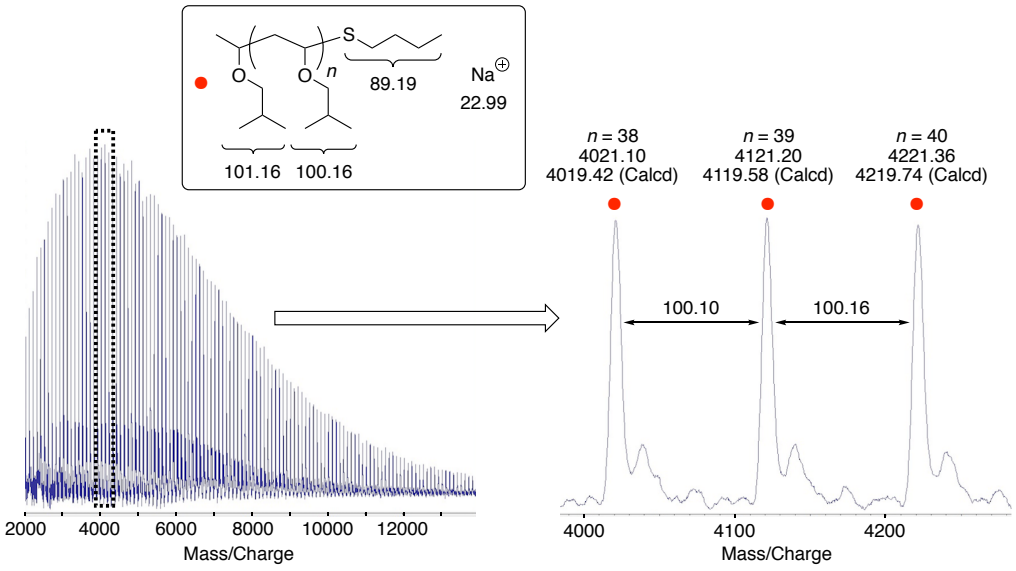

Fig. S4 MALDI-TOF-MS spectrum of poly(IBVE) (M_n(SEC) = 8500, M_w/M_n = 1.28) obtained in photo-mediated cationic DT polymerization of IBVE with **C5**/**A2** in *n*-hexane/CH_2Cl_2 (3/1) at –40 °C under irradiation of blue LED: $[M]_0/[\mathbf{C5}]_0/[\mathbf{A2}]_0$ = 1000/10/0.20 mM.

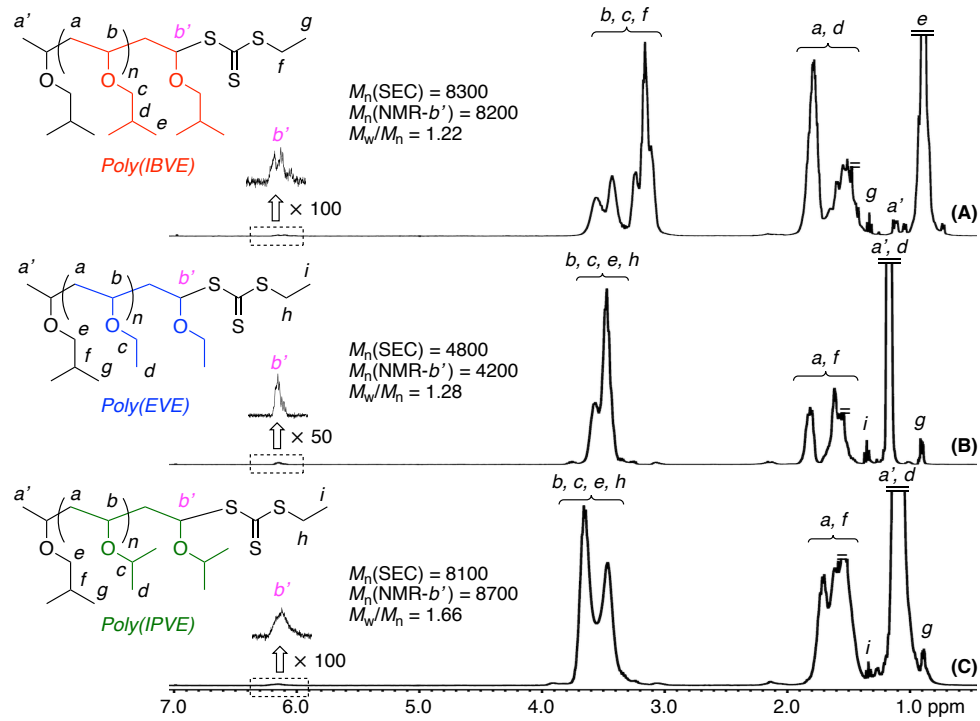

Fig. S5 ^{1}H NMR spectra ($CDCl_3$, 55 °C) of poly(IBVE) (A), poly(EVE) (B), and poly(IPVE) (C) obtained in photo-mediated cationic RAFT polymerization with **C1**/**A2** in *n*-hexane/CH_2Cl_2 (4/1) at –40 °C under irradiation of blue LED: $[M]_0/[\mathbf{C1}]_0/[\mathbf{A2}]_0$ = 500/5.0/0.20 mM.

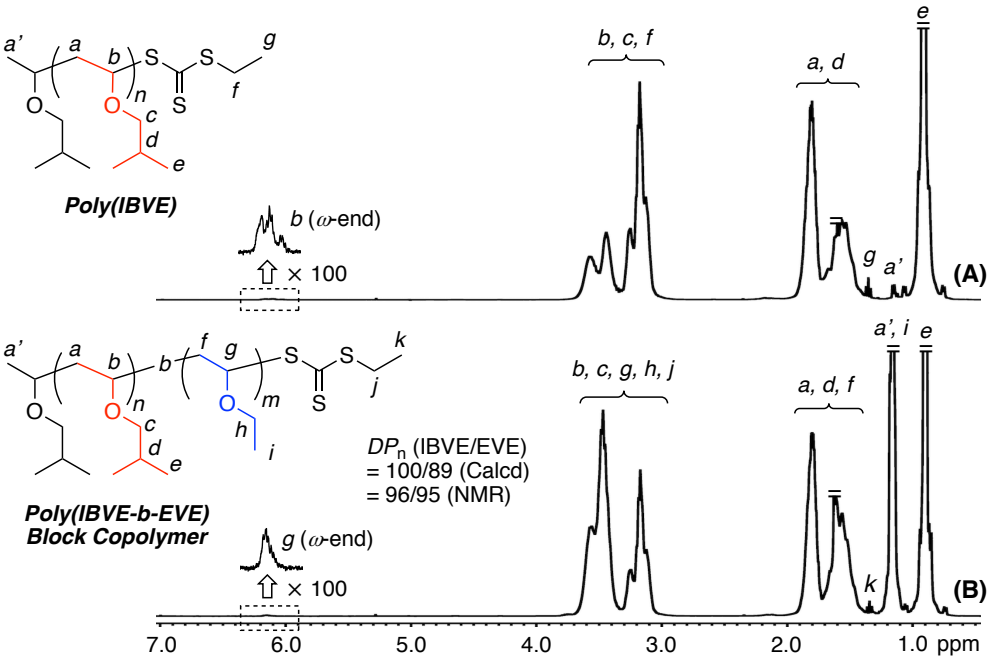

Fig. S6 ^{1}H NMR spectra ($CDCl_3$, 55 °C) of poly(IBVE) (A) and poly(IBVE-*b*-EVE) (B) obtained in photo-mediated cationic RAFT block polymerization of IBVE and EVE with **C1**/**A2** in *n*-hexane/CH_2Cl_2 (4/1) at –40 °C under irradiation of blue LED: $[IBVE]_0/[EVE]_{add}/[\mathbf{C1}]_0/[\mathbf{A2}]_0$ = 500/500/5.0/0.20 mM.

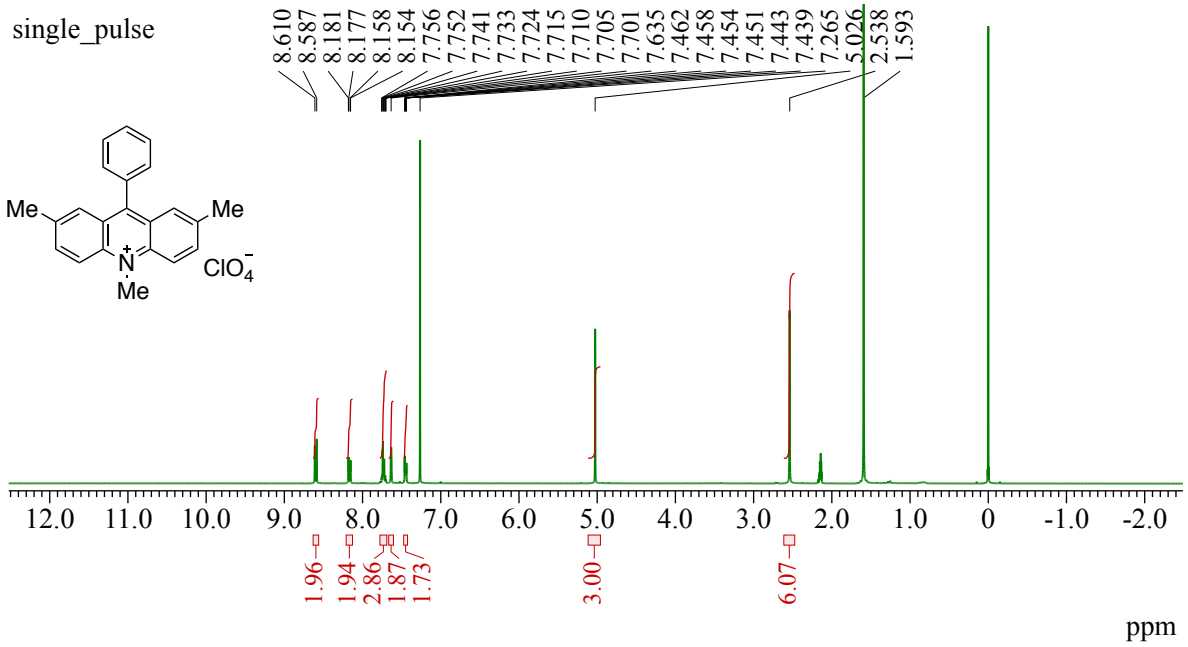

Fig. S7 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of 2,7,10-trimethyl-9-phenylacridinium perchlorate (**A5**).

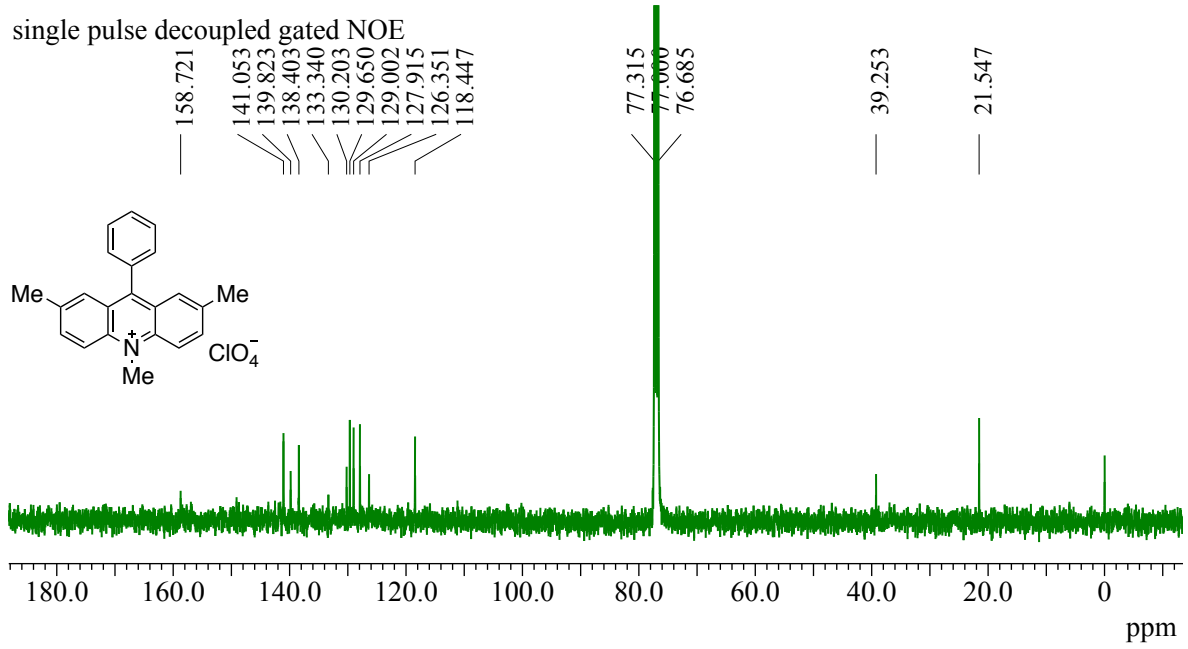

Fig. S8 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of 2,7,10-trimethyl-9-phenylacridinium perchlorate (**A5**).

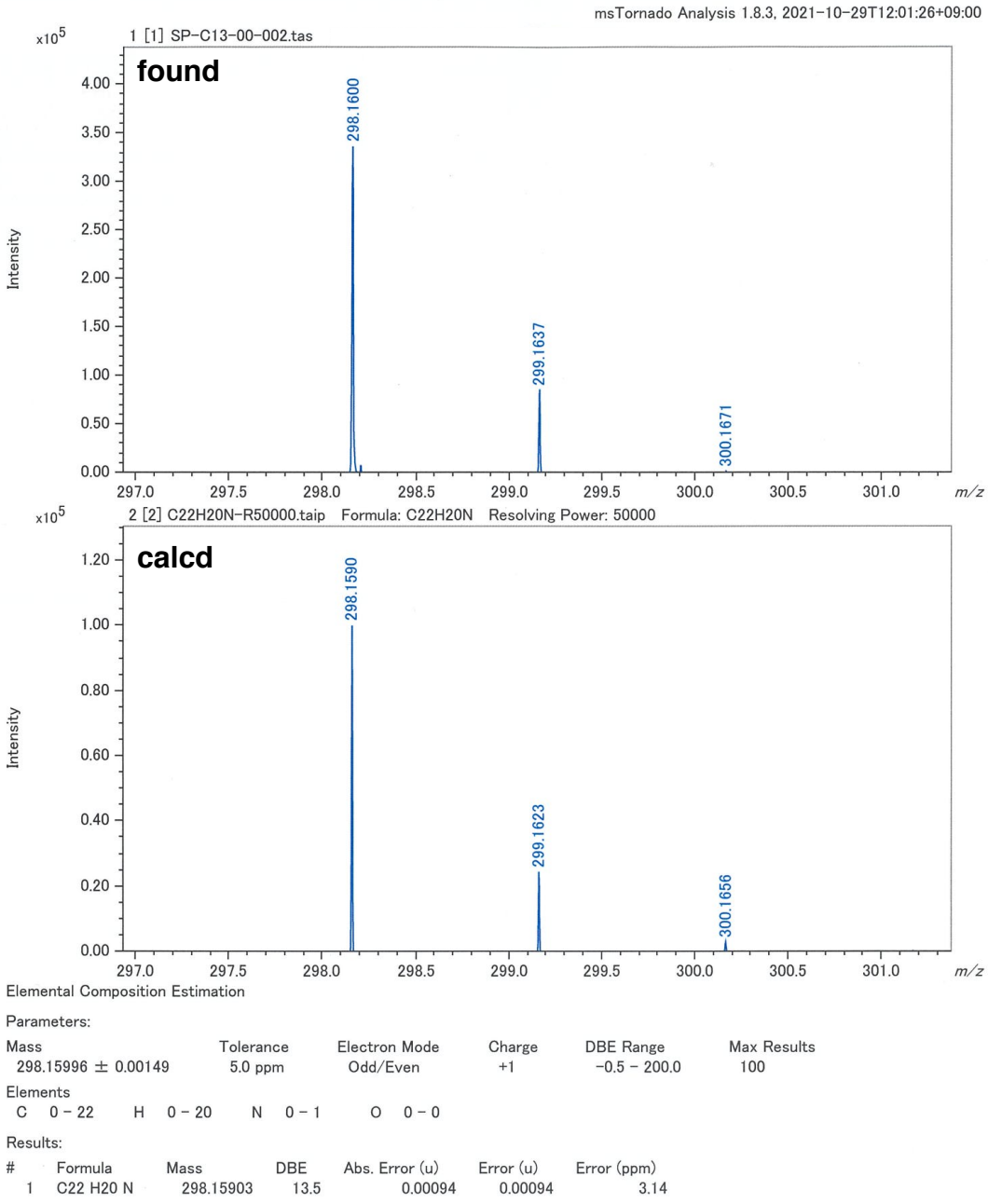

Fig. S9 HRMS spectrum of 2,7,10-trimethyl-9-phenylacridinium perchlorate (**A5**).

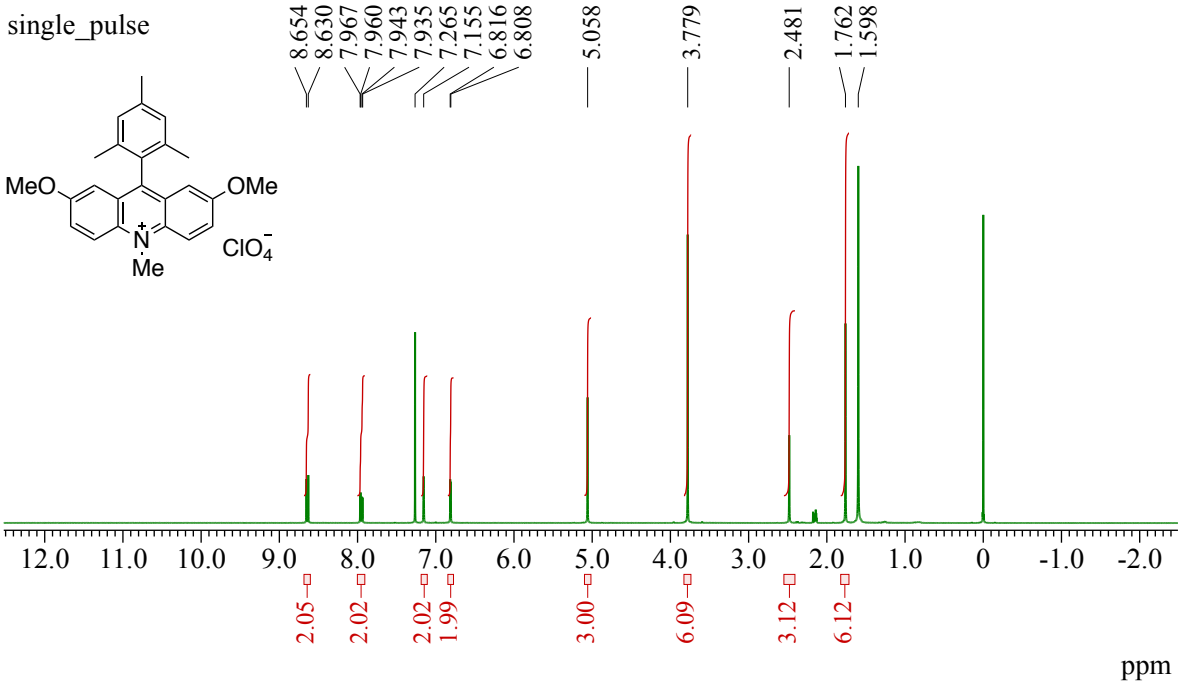

Fig. S10 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of 9-mesityl-2,7-dimethoxy-10-methylacridinium perchlorate (**A6**).

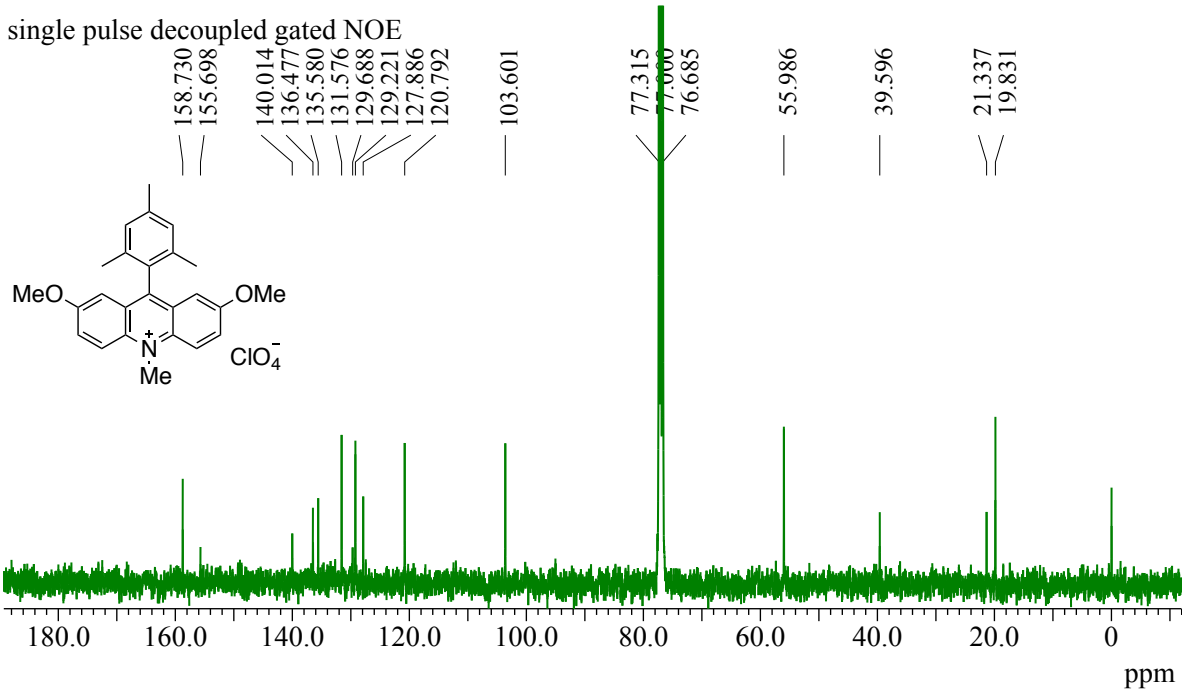

Fig. S11 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of 9-mesityl-2,7-dimethoxy-10-methylacridinium perchlorate (**A6**).

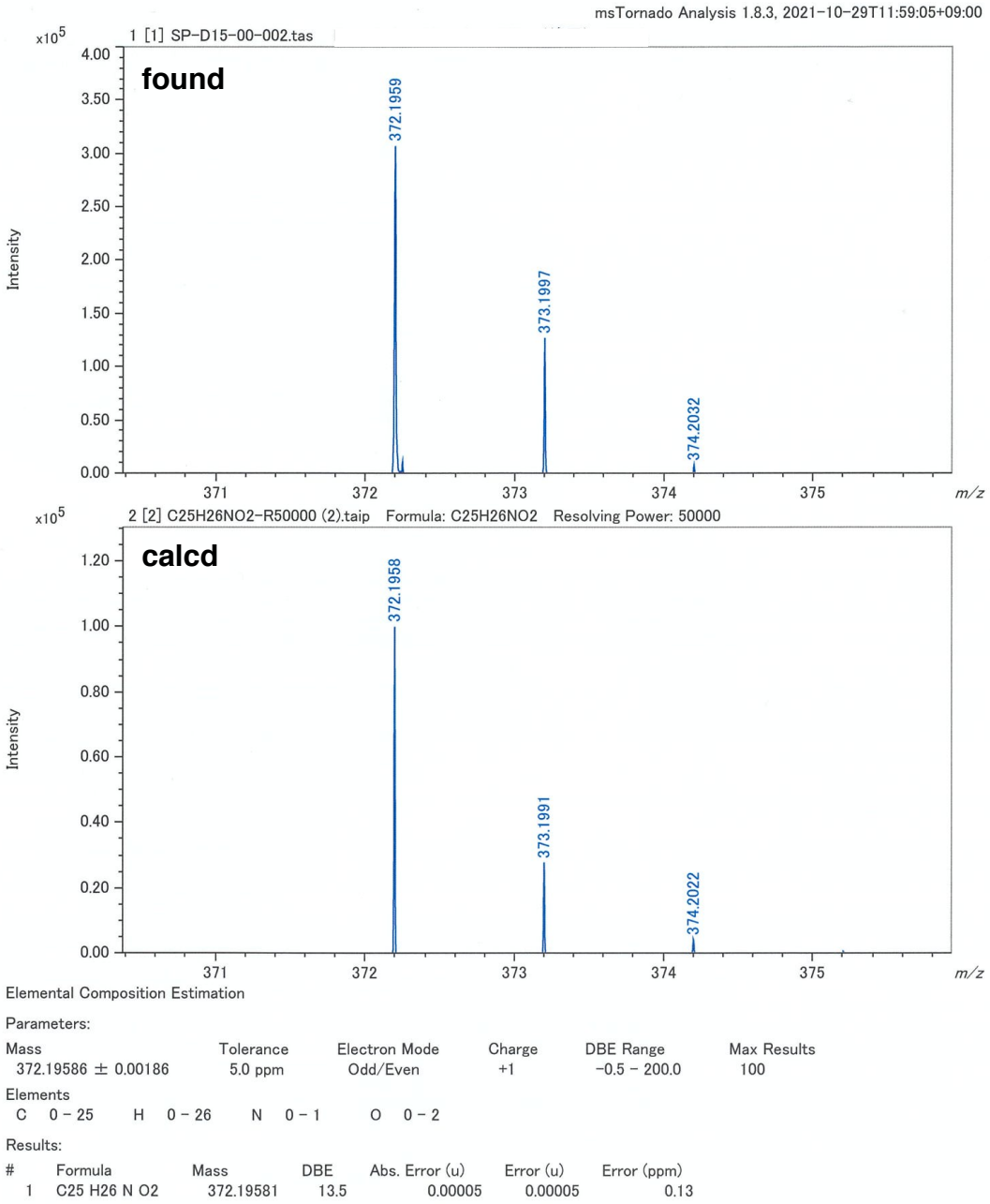

Fig. S12 HRMS spectrum of 9-mesityl-2,7-dimethoxy-10-methylacridinium perchlorate (**A6**).

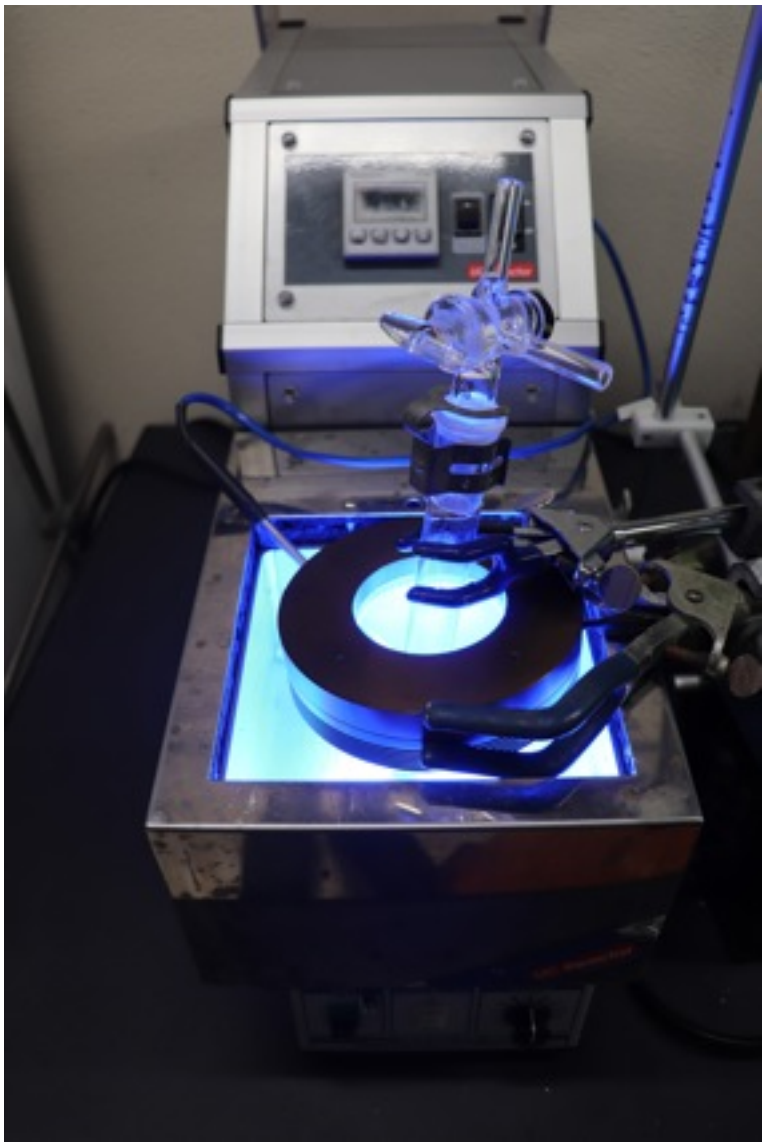

Fig. S13 Experimental setup for photo-mediated cationic polymerization under blue LED irradiation (470 nm, 70 mW).