Supporting Information

The development of highly efficient monophosphonium photocatalysts for the visible light-regulated metal-free cationic polymerization of vinyl ethers

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Experimental section

Materials

Ethyl vinyl ether (EVE; 99%, J&K), Isobutyl vinyl ether (IBVE) (TCI, >95%), *n*-propyl vinyl ether (PVE; 99%, TCI), and n-butyl vinyl ether (NBVE; 99%, TCI), 2,3dihydrofuran (DHF) (99%, TCI), 2-chloroethyl vinyl ether (Cl-EVE) (97%, TCI) were distilled over CaH₂ under reduced pressure and stored under argon atmosphere at -20 °C. DCM (HPLC; water content, <0.001%) was purchased from J&K and distilled over CaH₂ under argon atmosphere and deoxygenized by freeze–pump–thaw cycle three times and stored in Schlenk bar under argon atmosphere. S-1-Isobutoxyethyl S'-2-ethyl BPS trithiocarbonate and were synthesized according to literature procedures.¹Acetonitrile dried using 4 Å molecular sieves were purchased from Energy Chemical and Shanghai Chemical Reagents Co., Ltd. All other chemicals were used as received unless mentioned.

Characterisation

¹H NMR, ¹³C NMR, ¹⁹F NMR and ³¹P NMR were recorded on a Bruker AVIII 400 MHz or JEOL-ECZ500R 500M nuclear magnetic resonance instrument by using tetramethylsilane as the internal standard.

The number-average molecular weight (*M*n, GPC) and molecular weight distributions(*D*) of the obtained polymers were determined by a Waters 1515 series gel permeation chromatograph (GPC) equipped with a Waters 2414 refractive-index detector, using a Styragel HR3THF (7.8×300 mm) Column and a Styragel HR4THF (7.8×300 mm) Column with measurable molecular weights ranging from 102 to 106 g mol⁻¹. THF was used as eluent at a flow rate of 1.0 mL/ min at 40 °C. GPC samples were injected manually and Shodex Polystyrene samples of known molecular weight were used as calibration standards for the experimental number-average molecular weight (*M*_n) and polydispersity (*M*_w/*M*_n).

UV/vis spectra were recorded on a Shimadzu UV2600 and steady-state emission spectra were acquired using an Edinburgh Instruments, FLS920 spectrometer.

Cyclic voltammetry (CV) experiments were carried out with a. CHI760E. electrochemical workstation (Shanghai Chenhua Instrument Plant, China) using a one compartment electrolysis cell consisting of a typical glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode, and an Ag/AgCl reference electrode. The measurements were done in 0.2 mM CH₃CN solution with 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu4NPF₆) as supporting electrolyte at a scan rate of 100 mV/s.

Typical procedure for the cationic RAFT polymerization of vinyl ethers under visible light

In an argon filled glove box, a flame dried three times Schlenk tube was equipped with a stir bar and charged with isobutyl vinyl ether (0.39 mL, 3.0 mmol, 100.0 equiv), 5-200 µL of a stock solution of PC **5aa-ac** in DCM (3.0 mM), 0.1 mL of a stock solution of S-1-isobutoxylethyl-S'- ethyltrithiocarbonate (CTA) in DCM (0.3 M, 0.03 mmol, 1.0 equiv) and 0.5 mL DCM (M = 3) were added. The Schlenk tube was sealed with a septum cap under an atmosphere of argon, placed in the blue LEDs reactor (6 W, λ_{max} = 460 nm, 30 mW/cm²) or green LEDs reactor (6 W, λ_{max} = 520 nm, 30 mW/cm²) outside of the glove box. After desired reaction time, benzene (89.0 µL, 1.0 mmol) was added as an internal standard for NMR analysis, and aliquots were taken out for NMR and GPC analysis. The solvent was removed under vacuo to yield the polymer products. A typical ¹H NMR for poly(isobutyl vinyl ether) is shown in Figure S1.



Figure S1. ¹H NMR spectrum of poly(IBVE)

Procedure for the kinetic study on the photocontrolled cationic RAFT polymerization of IBVE with 5aa-ac as the photocatalyst

In an argon filled glove box, a flame dried three times Schlenk tube was equipped with a stir bar and charged with isobutyl vinyl ether (0.39 mL, 3.0 mmol, 100.0 equiv), 50 μ L (Figure 4a) or 5 μ L (Figure 4b) of a stock solution of PC **5aa-ac** in DCM (3.0 mM), 0.1 mL of a stock solution of S-1-isobutoxylethyl-S'- ethyltrithiocarbonate (CTA) in DCM (0.3 M, 0.03 mmol, 1.0 equiv) and 1.5 mL (Figure 4a) or 2.5 mL (Figure 4b) DCM (M = 1.5 or 1 M, r.t. ~10 °C) were added, benzene (89.0 μ L, 1.0 mmol) was added as an internal standard for NMR analysis. The Schlenk tube was sealed with a septum cap under an atmosphere of argon, placed in the blue LEDs reactor (6 W, λ_{max} = 460 nm, 30 mW/cm²). After each desired amount of reaction time, aliquots were taken out for NMR and GPC analysis.

Procedure for the chain extension experiment

In an argon filled glove box, a flame dried three times Schlenk tube was equipped with a stir bar and charged with isobutyl vinyl ether (0.39 mL, 3.0 mmol, 50.0 equiv), 10 µL of a stock solution of PC **5ac** in DCM (3.0 mM), 0.2 mL of a stock solution of S-1-isobutoxylethyl-S'- ethyltrithiocarbonate (CTA) in DCM (0.3 M, 0.03 mmol, 1.0 equiv) and 0.4 mL DCM (M = 3) were added. The Schlenk tube was sealed with a septum cap under an atmosphere of argon, placed in the blue LEDs reactor (6 W, λ_{max} = 460 nm, 30 mW/cm²) outside of the glove box. After the desired amount of reaction time, aliquots were taken out for NMR and GPC analysis. After that, another 100 equivalents of IBVE were added, the Schlenk tube was sealed with a septum cap under an atmosphere of argon again, and then exposed to light again for 0.5 h.

Synthesis of PC 5aa-ac



A mixture of trisubstituted phosphines **4a-c** (0.2 mmol, 1.0 equiv), alkyne (0.24 mmol, 1.2 equiv), and Cu(OTf)₂ (0.4 mmol, 2.0 equiv) was weighed in a sealed Schlenk tube equipped with a stir bar. Dry CH₃CN (2.0 mL) was added and the mixture was stirred at 100 °C for 12 h under an Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by a silica gel column using acetone/CH₂Cl₂ (1/8) as eluent to give pure product **5aa-ac**. The trisubstituted phosphines **4a-c** were synthesized according to literature procedures.²

Characterization data of PC 5aa-ac



PC 5aa

PC 5aa (122 mg, 80%)

¹H NMR (400 MHz, CD₂Cl₂) δ 8.07 (d, J = 8.8 Hz, 1H), 8.01 - 1.89 (m, 1H), 7.79 (d, J = 8. 8 Hz, 1H), 7.75 - 7.64 (m, 14H), 7.52 - 7.31 (m, 5H), 7.29-7.24 (m, 5H), 7.16 (t, J = 7.98 Hz, 1H)7.02 (t, J = 8.0 Hz, 2H), 6.45(d, J = 7.6 Hz, 2H).

¹⁹F NMR (376 MHz, CD_2Cl_2) δ -78.85.

³¹P NMR (162 MHz, CD₂Cl₂) δ -2.98.

¹³C NMR (101 MHz, CD₂Cl₂) δ 157.82, 151.43, 151.39, 138.47 (d, J = 8.0 Hz), 137.21, 137.0 7, 135.12 (d, J = 1.2 Hz), 134.62, 134.49 (d, J = 2.8 Hz), 134.17, 132.44 (d, J = 2.8 Hz), 131.88, 131.84, 131.32, 131.25, 131.21, 130.71, 130.44 (q, J = 12.4 Hz), 130.02, 129.29, 129. 08, 129.05, 129.03, 128.64, 128.61, 128.24, 128.10, 127.20, 125.98, 125.88, 125.84, 119.93(d, J = 91.9 Hz), 118.48, 117.71, 103.29. The quartet signal of the quaternary carbon atom of the triflate counter anion was not detected due to its very low intensity.

HRMS: (EI) calcd for C₄₆H₃₂P [M]⁺ 615.2238; found 615.2229.



PC 5ba

PC 5ba (116 mg, 71%)

¹H NMR (400 MHz, CD₂Cl₂) δ 8.11 (d, J = 8.6 Hz, 1H), 8.01 – 7.90 (m, 2H), 7.82 – 7.64 (m, 13H), 7.52 – 7.40 (m, 5H), 7.34 – 7.19 (m, 5H), 7.15 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 7.6 Hz, 2H), 6.44 (d, J = 7.1 Hz, 2H), 1.49 (s, 9H).

¹⁹F NMR (376 MHz, CD₂Cl₂) δ -78.87.

³¹P NMR (162 MHz, CD₂Cl₂) δ -2.98.

¹³C NMR (101 MHz, CD₂Cl₂) δ 157.95, 152.66, 152.05, 138.57, 137.25 (d, *J* = 13.2 Hz), 135.15 (d, *J* = 3.1 Hz), 134.94, 134.60 (d, *J* = 6.6 Hz), 134.18 (d, *J* = 10.4 Hz), 133.99, 132.55 (d, *J* = 7.4 Hz), 131.95 (d, *J* = 4.1 Hz), 131.59, 131.48, 131.38, 130.67 – 130.34 (m), 130.09, 129.14, 128.89 – 128.59 (m), 128.29, 128.14, 127.17, 126.08, 125.93, 125.79, 120.15(d, *J* = 91.9 Hz), 118.50, 103.00, 102.14, 35.23, 31.55. The quartet signal of the quaternary carbon atom of the triflate counter anion was not detected due to its very low intensity.

HRMS: (EI) calcd for C₅₀H₄₀P [M⁺] 671.2862; found 671.2821.



PC 5ab

PC 5ab (106 mg, 61%)

¹H NMR (400 MHz, CD₂Cl₂) δ 8.04 (dd, *J* = 8.7, 4.8 Hz, 1H), 8.02 – 7.96 (m, 1H), 7.86 (m, 1H), 7.77 (t, *J* = 7.7 Hz, 2H), 7.73 – 7.64 (m, 7H), 7.55 – 7.61 (m, 4H), 7.51 – 7.44 (m, 5H), 7.27 (d, *J* = 7.3 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.31 (d, *J* = 8.4 Hz, 2H), 1.23 (s, 9H), 1.17 (s, 9H).

¹⁹F NMR (376 MHz, CD₂Cl₂) δ -78.90.

³¹P NMR (162 MHz, CD₂Cl₂) δ -3.29.

¹³C NMR (101 MHz, CD₂Cl₂) δ 158.32 (d, *J* = 5.4 Hz), 152.51 (d, *J* = 2.5 Hz), 151.94, 151.36 (d, *J* = 3.7 Hz), 138.39 (d, *J* = 2.7 Hz), 137.20, 135.03 (d, *J* = 3.1 Hz), 134.58, 134.50 (d, *J* = 3.4 Hz), 134.25 (d, *J* = 6.6 Hz), 134.14 (d, *J* = 3.8 Hz), 131.53 (d, *J* = 4.1 Hz), 131.30 (d, *J* = 6.2 Hz), 131.27, 130.79, 130.54 – 130.27 (m), 129.93, 129.74 (d, *J* = 7.6 Hz), 129.36, 129.16, 128.55, 128.40, 127.23, 126.09, 125.99, 125.93, 125.46 (d, *J* = 1.8 Hz), 125.40, 123.05, 120.35 (d, *J* = 91.1 Hz), 118.39, 117.63, 103.61, 102.76, 34.87, 34.80, 31.24, 31.15. The quartet signal of the quaternary carbon atom of the triflate counter anion was not detected due to its very low intensity.

HRMS: (EI) calcd for C₅₄H₄₈P [M⁺] 727.3488; found 727.3443.



PC 5ca

PC 5ca (117 mg, 65%)

¹H NMR (400 MHz, CD₂Cl₂) δ 8.26 (s, 1H), 8.08 – 8.01(m, 3H), 7.89 – 7.76 (m, 4H), 7.75 – 7.52 (m, 12H), 7.37 – 7.21 (m, 5H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.00 (td, *J* = 7.8, 4.0 Hz, 2H), 6.45 (t, *J* = 7.0 Hz, 2H).

¹⁹F NMR (376 MHz, CD₂Cl₂) δ -63.04, -78.91.

³¹P NMR (162 MHz, CD₂Cl₂) δ -3.06.

¹³C NMR (101 MHz, CD₂Cl₂) δ 157.86 (d, *J* = 4.8 Hz), 146.57, 139.67 (d, *J* = 6.4 Hz), 138.56 (d, *J* = 2.7 Hz), 137.08 – 136.84 (m), 135.40 (d, *J* = 3.2 Hz), 134.42 (d, *J* = 6.6 Hz), 134.21 (dd, *J* = 10.5, 2.4 Hz), 133.33, 133.18, 133.01, 132.99, 132.65, 132.32, 131.92, 131.89, 131.86, 131.31 – 130.90 (m), 130.76, 130.74, 130.60, 130.32, 130.21, 130.13, 130.10, 129.37, 129.26, 128.94 – 128.70 (m), 128.65, 128.28, 127.68, 127.01, 126.37 (d, *J* = 9.1 Hz), 123.60 (q, *J* = 274.7 Hz), 123.68, 123.03, 119.64 (d, *J* = 91.0 Hz), 119.08, 118.32, 105.77, 104.96. The quartet signal of the quaternary carbon atom of the triflate counter anion was not detected due to its very low intensity.

HRMS: (EI) calcd for C₄₈H₃₀F₆P [M⁺] 751.1984; found 751.1970.



PC 5ac

PC 5ac (107 mg, 52%)

¹H NMR (400 MHz, CD₂Cl₂) δ 8.19 (ddd, J = 8.8, 2.9, 1.2 Hz, 1H), 8.08 – 7.99 (m, 1H), 7.95 (dt, J = 8.1, 2.4 Hz, 1H), 7.88 – 7.64 (m, 15H), 7.62 – 7.49 (m, 4H), 6.88 (s, 2H).

¹⁹F NMR (376 MHz, CD₂Cl₂) δ -63.63, -63.99, -79.03.

³¹P NMR (162 MHz, CD₂Cl₂) δ -1.78

¹³C NMR (101 MHz, CD₂Cl₂) δ 156.40 (d, *J* = 5.1 Hz), 152.77 (d, *J* = 4.0 Hz), 139.44 (d, *J* = 2.6 Hz), 138.88 (d, *J* = 13.1 Hz), 136.75, 136.56, 135.95 (d, *J* = 3.3 Hz), 135.04 (d, *J* = 7.5 Hz), 134.77 (dd, *J* = 17.8, 8.4 Hz), 132.77, 132.59, 132.42 (brs), 132.25, 132.09, 131.60, 131.16 (q, *J* = 14.4 Hz), 130.84, 130.66, 130.54, 130.33 (brs), 129.59, 129.22, 128.70 (q, *J* = 200.0 Hz), 126.50, 126.36, 125.95, 125.76 (d, *J* = 10.8 Hz), 124.41, 123.38 – 122.97 (m), 122.92, 121.29, 120.71 (q, *J* = 232.3 Hz), 118.78 (d, *J* = 90.4 Hz), 116.93, 101.53, 100.65. The quartet signal of the quaternary carbon atom of the triflate counter anion was not detected due to its very low intensity.

HRMS: (EI) calcd for $C_{50}H_{28}F_{12}P$ [M⁺] 887.1732; found 887.1718.

UV-Vis absorption spectra



Figure S2. UV-Vis spectra of PC 5 at different concentration in DCM





Figure S3. Fluorescence emission spectra of PC 5 in DCM



Time-resolved emission decay curves of PC 5

Figure S4. Time-resolved emission decay curves of PC 5 in DCM





Figure S5. Cyclic voltammograms (vs. Ag/AgCl) of PC 5 in MeCN



Figure S6. Fluorescence decay of PC 5 with CTA as a quencher.

Fluorescence quenching of PC 5aa with CTA



Figure S7. Fluorescence quenching of PC 5aa using CTA as quencher.



UV-Fluorescence emission junction of PC 5

Figure S8. UV-Fluorescence emission junction of PC.

NMR spectra



Figure S9. ¹H NMR of PC 5aa



Figure S10. ¹⁹F NMR of PC 5aa.



Figure S11. ³¹P NMR of PC 5aa



Figure S12. ¹³C NMR of PC 5aa



Figure S14. ¹⁹F NMR of PC 5ba



Figure S15. ³¹P NMR of PC 5ba

-40 -60 f1 (ppm) -80

100

-120

-140

-160

-180

-200

-20

-240

-220



140

120

100

80

40

 $\frac{1}{20}$

Figure S16. ¹³C NMR of PC 5ba







Figure S18. ¹⁹F NMR of PC 5ab



Figure S20. ¹³C NMR of PC 5ab



Figure S22. ¹⁹F NMR of PC 5ca



Figure S24. ¹³C NMR of PC 5ca

---3.06



Figure S26. ¹⁹F NMR of PC 5ac



Figure S28. ¹³C NMR of PC 5ac

---1.78



Table S1. A comparison of catalytic activity between PC 5ac and BPS.



10.0 9.5 9.0 8.5 S. 0 6.5 6.0 5.5 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 7.5 7.0 5.0 f1 (ppm)

Figure S29. ¹H NMR of poly(EVE)



















`11.0`10.5`10.0`9.5`9.0`5.5`5.0`7.5`7.0`6.5`6.0`5.5`5.0`4!5`4.0`3.5`2.0`2.5`2.0`1.5`1.0`0.5`0.0`−0.5`−1.0`−1. £1 (ppm)

Figure S33. ¹H NMR of poly(DHF)

GPC traces and NMR analysis of chain extension.



Figure S35. Chain end fidelity analysis (~91%, based on g/a') before chain extension.

Reference

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