

## **Trithiocarbonates as intrinsic photoredox catalysts and RAFT agents for oxygen tolerant controlled radical polymerization**

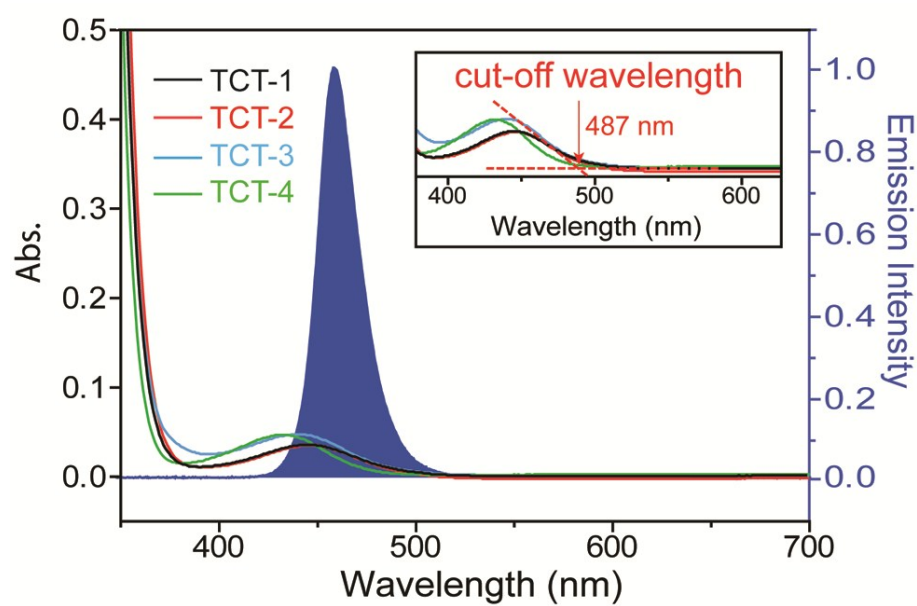
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## 1. Blue LED light source


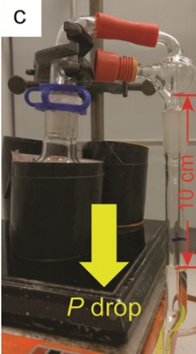

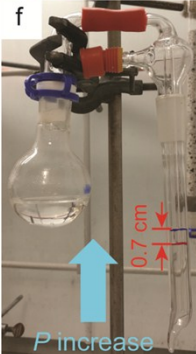

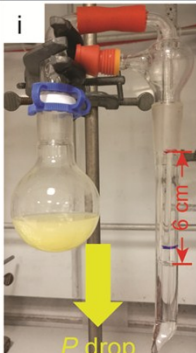


**Figure S1.** The UV-vis spectra of TTCs and blue LED light source emission characterization. The insert chart represents the cut-off wavelength ( $\lambda_{\text{cut-off}} = 487 \text{ nm}$ ) of the TTCs *via* UV-vis analysis.

## 2. Supplementary data for the investigation on photoredox mechanism

### a. Module experiments

A round bottom flask (50 mL) charged with various components (Fig.S2a, d and g) was connected to a graded seal. The levels of the oil in graded seal were marked as blue lines (Fig.S6b, e and h). Then, the blue LED light source (4.0 mW/cm<sup>2</sup>) was switched “on” and the reaction mixture was stirred. After 24 hours irradiation, the levels of the oil were recorded as red lines (Fig.S2c, f and i). The increase (or decrease) of the oil level indicates a decrease (or increase) of pressure within the closed reaction vessel.

Components	Before irradiation	After 24 h irradiation
<b>a</b> TTC-1 50 mM  TEOA 340 mM  MA 9.05 mL  DMSO 9.05 mL	<b>b</b> 	<b>c</b> 
<b>d</b> TEOA 340 mM  MA 9.05 mL  DMSO 9.05 mL	<b>e</b> 	<b>f</b> 
<b>g</b> NH <sub>2</sub> -MIL-125(Ti) 20 mg  TEOA 340 mM  DMSO 18.1 mL	<b>h</b> 	<b>i</b> 

**Figure S2.** (a, d and g) The list of reaction mixture, (b, e and h) the reaction setups before and (c, f and i) after 24 hours blue light irradiation. (a-c) The photoredox reaction using TTC-1/TA. (d-f) The reaction in which TTC was selectively omitted. (g-i) The photoredox reaction in which a MOF, NH<sub>2</sub>-MIL-125(Ti) was used.

In another reaction, a round bottom flask (50 mL) charged with MA (9.05 mL, 100 mmol), TTC-1 (0.346 g, 1 mmol), TEOA (1.0 g, 6.7 mmol) and DMSO (9.05 mL) was sealed with a rubber septa. The mixture was degased by bubbling CO<sub>2</sub>/N<sub>2</sub> (10/90 v/v) for 20 min. The composition of the initial headspace was assessed via gas chromatography (490 Micro GC, Agilent). Then, the blue LED light source (4.0 mW/cm<sup>2</sup>) was switched “on” and the reaction mixture was stirred. Samples of the reaction vessel headspace were taken at timed intervals and characterized by gas chromatography (Fig. S3).

**Figure S3.** The consumption rate of CO<sub>2</sub> within the TTC/TA two-component photocatalyst system.

The electron transfer procedure from TEOA to [TTC]\* (exited state of TTC) could be represented as:

This can be estimated by evaluating the total energy changes of the two reagents:

For the reaction-1,  $\Delta E_{\text{TTC}}$  is defined as the energy variation of the reaction from  $[\text{TTC}]^*$  to  $[\text{TTC}]^-$ . Because the energy for electron transfer to  $[\text{TTC}]^*$  can be further deduced from the following diagram:

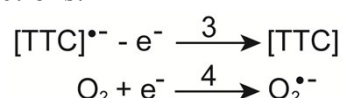
The TTC (*i.e.* 2-cyano-2-propyl dodecyl trithiocarbonate) could be excited by blue light irradiation to afford [TTC]\* (i). The absorption energy ( $E_i$ ) can be calculated from its cut-off wavelength: 2.55 eV ( $\lambda_{\text{cut-off}} = 487$  nm, Fig. S1, ESI†), corresponding to +245.6 kJ/mol. The direct formation of [TTC]<sup>-</sup> from TTC requires energy ( $E_{\text{iii}}$ ), which can be calculated from an electrochemical measurement of the TTC (Fig. S4):

where  $n$  refers to the number of electrons transferred in this procedure,  $F$  is the faraday constant: 96,485 C/mol, and  $V_{red}$  represents the reduction potential of the TTC. The midpoint potential is -0.929 V vs. Ppy-SS (reference electrode determined as +0.135 V vs. SHE in acetonitrile), indicating the  $V_{red}$  is -0.794 V vs. SHE. Accordingly, the  $E_{ij}$  is 76.6 kJ/mol.

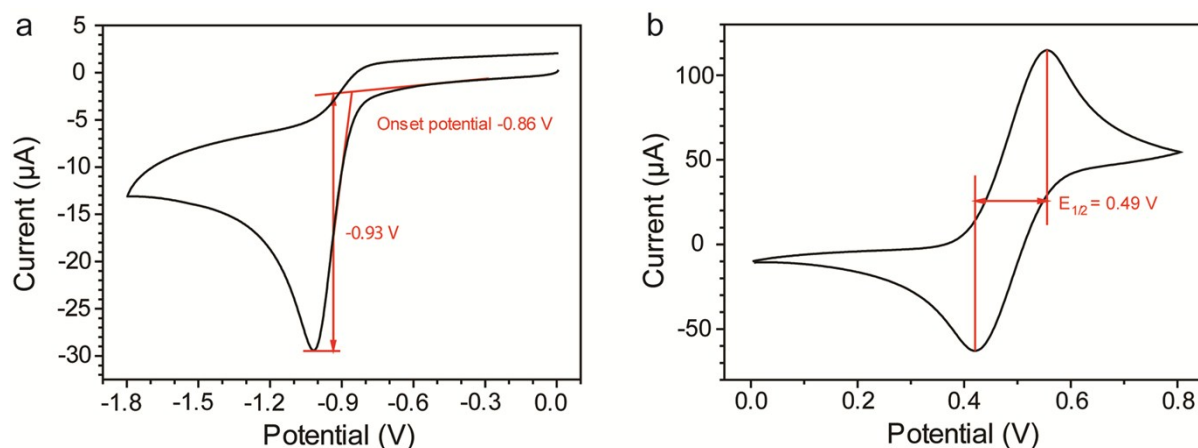
Thus,  $\Delta E_{\text{TTC}}$  is able to be calculated by subtracting  $E_i$  from  $E_{\text{iii}}$ . This provides a value of -169.0 kJ/mol for  $\Delta E_{\text{TTC}}$ .

It has been established that the electrochemical oxidation of any TA species must follow the principle of ‘*electron transfer followed by a chemical reaction*’, where the amine radical cation  $[\text{TA}]^{+\bullet}$  is evoked at the beginning of this procedure.<sup>1</sup> Therefore, the onset potential of TEOA oxidation (+0.930 V *vs.* SHE as reported by Girousi *et al.*<sup>2</sup>) can be used to evaluate the energy variation of reaction-2 ( $\Delta E_{\text{TA}}$ ) *via* the same formula as equation (S1), which gives a value of +89.7 kJ/mol. Therefore, the Gibbs free-energy variation for the first ET reaction is -79.3 kJ/mol, meaning it is energetically favourable.

The validity of electron transfer from  $[\text{TTC}]^{\bullet-}$  to  $\text{O}_2$  can also be estimated by evaluating the potentials of the two half-cell reactions:



The potential of half-cell reaction-3 was obtained by measuring its potential using cyclic voltammetry. The midpoint potential of TTC is -0.929 V *vs.* Ppy-SS (Fig. S4a) (reference electrode 0.135 V *vs.* SHE in acetonitrile, as calibrated in Fig. S4b), indicating the potential of reaction-3 is -0.794 V *vs.* SHE. Meanwhile the potential of reaction-4 was reported to be +0.07 V *vs.* SHE.<sup>3</sup> Therefore, the total reduction potential for this electron transfer from  $[\text{TTC}]^{\bullet-}$  to  $\text{O}_2$  is +0.864 V. The Gibbs free-energy variation for the second electron transfer can be calculated by equation (2) to yield a value of -83.4 kJ/mol, meaning it is also energetically favourable.



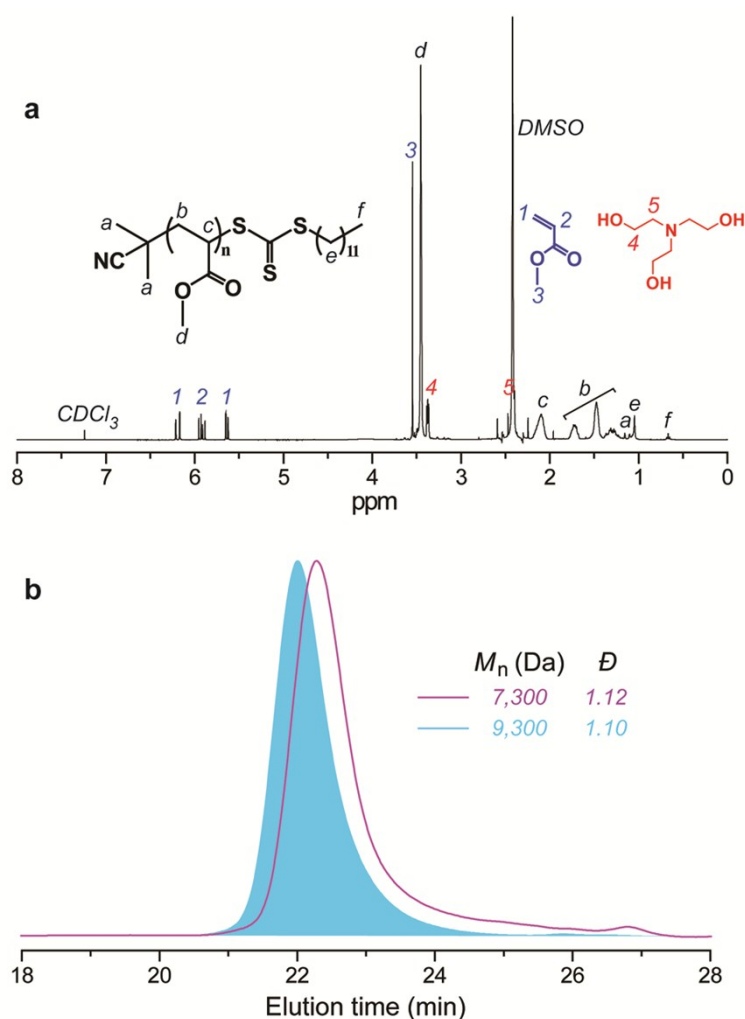
**Figure S4.** The cyclic voltammetry (CV) measurements for (a) 15 mM TTC-1 and (b) 10 mM Fc<sup>+</sup>/Fc (+0.624 V *vs.* SHE).<sup>4</sup> The  $E_{1/2}$  is +0.489 V *vs.* polypyrrole coated stainless steel rod (Ppy-SS), meaning the Ppy-SS is +0.135 V *vs.* SHE. The measurement was carried out in 0.1 M TBA<sup>+</sup>/BF<sub>6</sub><sup>-</sup>/acetonitrile electrolyte using glassy carbon, platinum mesh and Ppy-SS as working, counter and reference electrodes respectively.

### 3. Kinetic study of poly(methyl acrylate) for Figure 1

The MA conversion was estimated from  $^1\text{H}$  NMR by integrating the peaks corresponding to methyl group (**d**, Figure S2) at  $\delta_{\text{H}} = 3.45$  ppm, (s, 3H,  $-\text{COOCH}_3$ ) and the protons corresponding to the unsaturated methyl acrylate double bond (**1** and **2** in Figure S2,  $\delta_{\text{H}} = 5.5\text{--}6.3$  ppm, m, 3H,  $\text{CH}_2=\text{CH}-$ ). These peaks account for all protons derived from the monomer species, from which the percentage of remaining unreacted monomer can be calculated. The theoretical molecular weight was calculated using the equation:

$$M_{\text{n,theo}} = [\text{MA}]_0 / [\text{TTC}]_0 \times \text{conv. \%} \times M_{\text{M}} + M_{\text{TTC}} \quad (\text{S2})$$

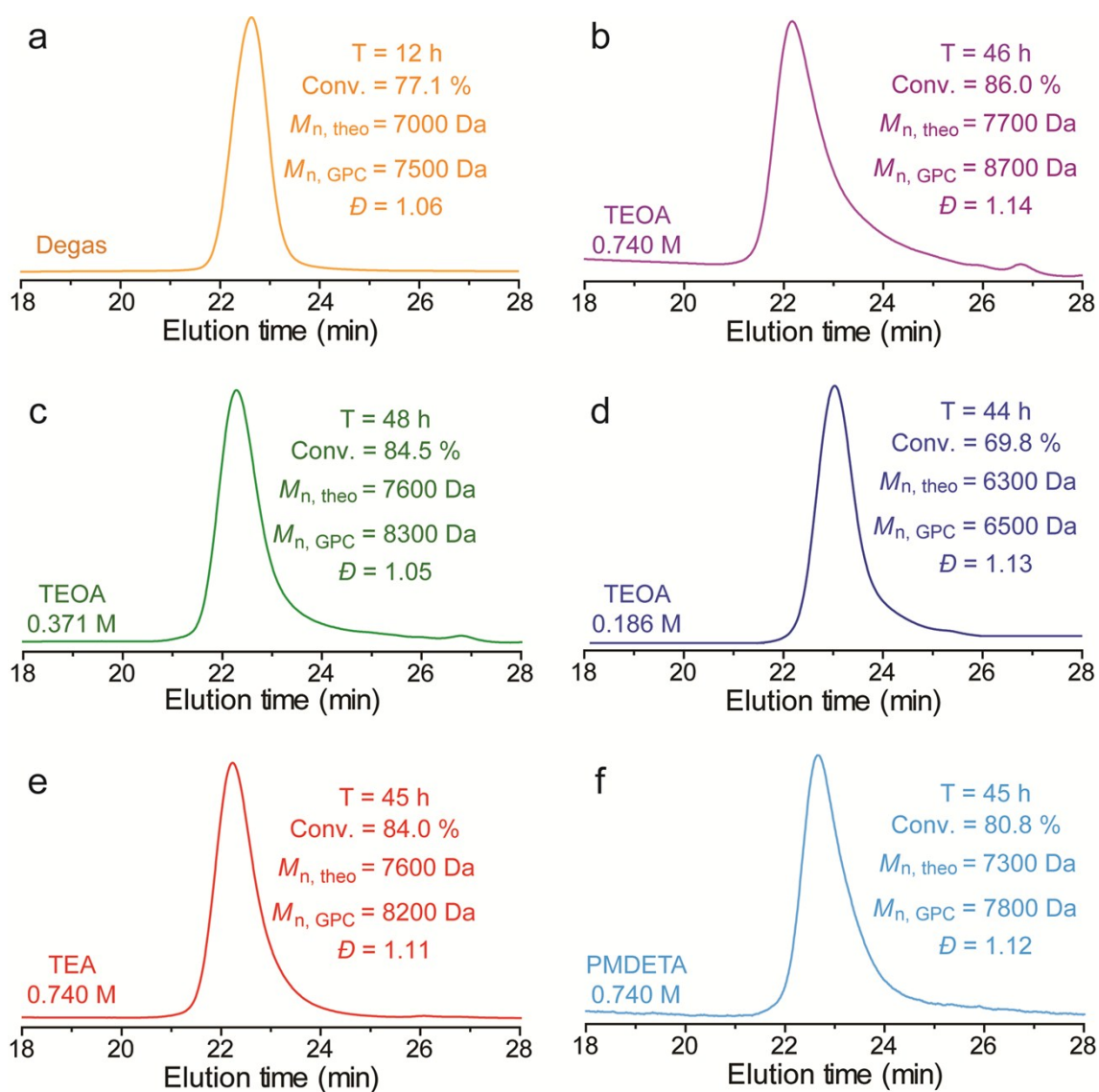
where  $[\text{MA}]_0$  is the initial concentration of monomer,  $[\text{TTC}]_0$  is initial chain transfer agent concentration, conv. % is the monomer conversion estimated from  $^1\text{H}$  NMR,  $M_{\text{M}}$  and  $M_{\text{TTC}}$  are the molecular weights of monomer and TTC, respectively.



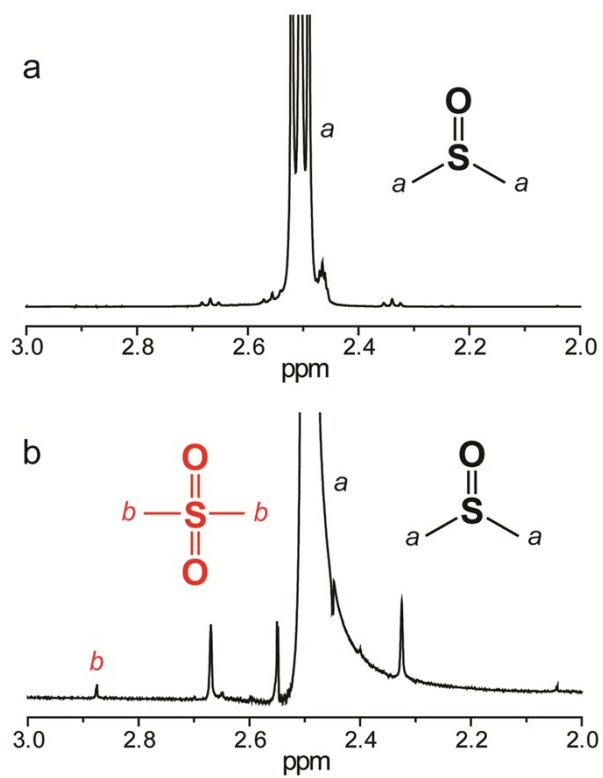
**Figure S5.** (a)  $^1\text{H}$  NMR spectrum of the reaction mixture in  $\text{CDCl}_3$ . (b) GPC profiles of the reaction mixture sample (purple) and the purified PMA (blue).

We have estimated the rates of  $\text{O}_2$  and monomer consumption and found that their reaction rates are ca. 0.04 mmol/h ( $\text{O}_2$ ) and ca. 0.042 mmol/h (monomer). This result reveals a similar rate for TTC photoexcitation in the induction period and the subsequent polymerization process, confirming the involvement of this species in both processes.

#### 4. Supplementary data for Figure 2

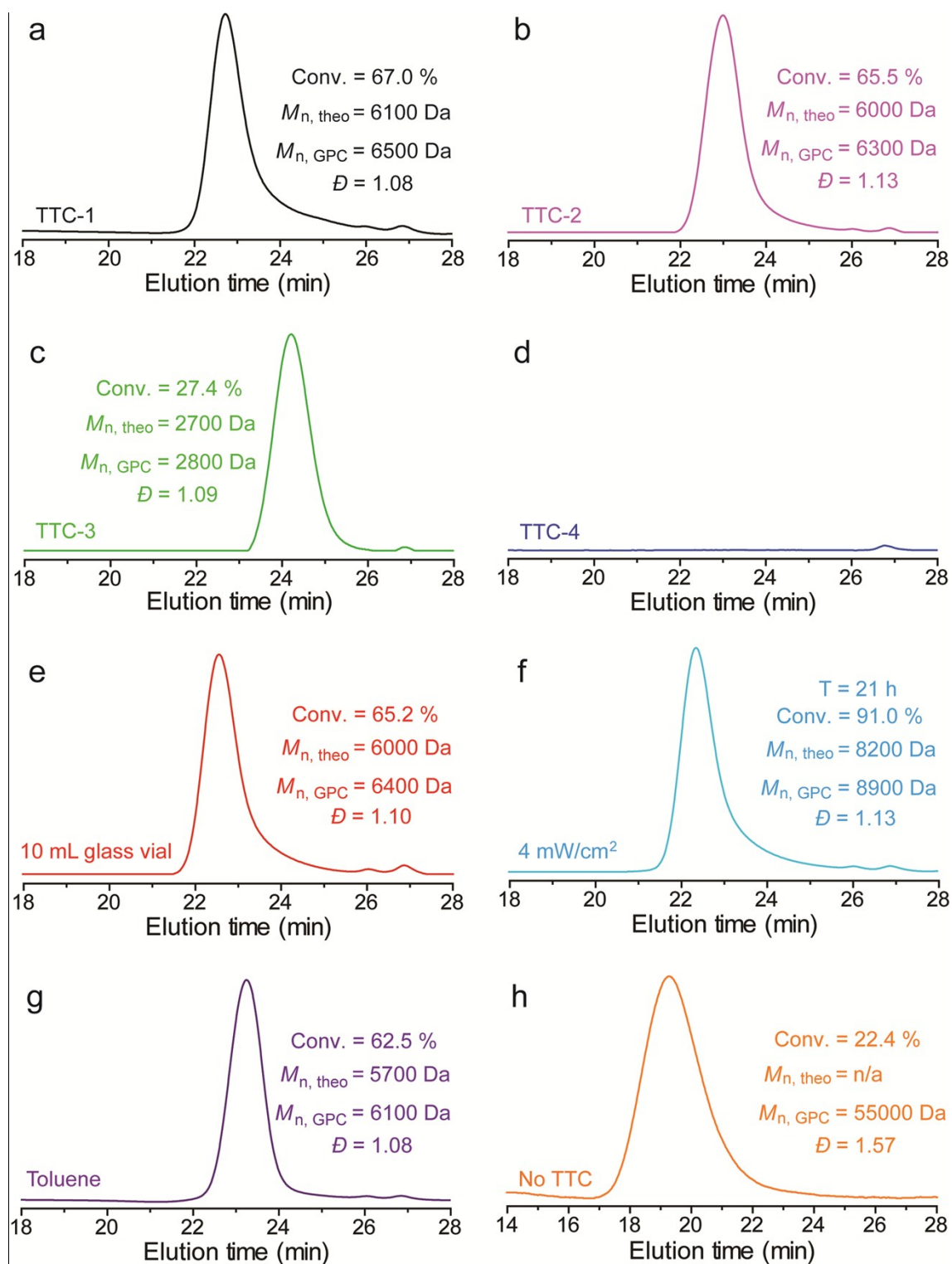


**Figure S6.** (a-d) GPC profiles of the synthesized PMAs in Fig. 3a and (e-f) GPC curves of the resultant PMAs in Figure 3b.



**Figure S7.** Enlarged  $^1\text{H}$  NMR spectra (in  $\text{CDCl}_3$ ) of the reaction mixture (a) before irradiation and (b) after 3 hours of irradiation.

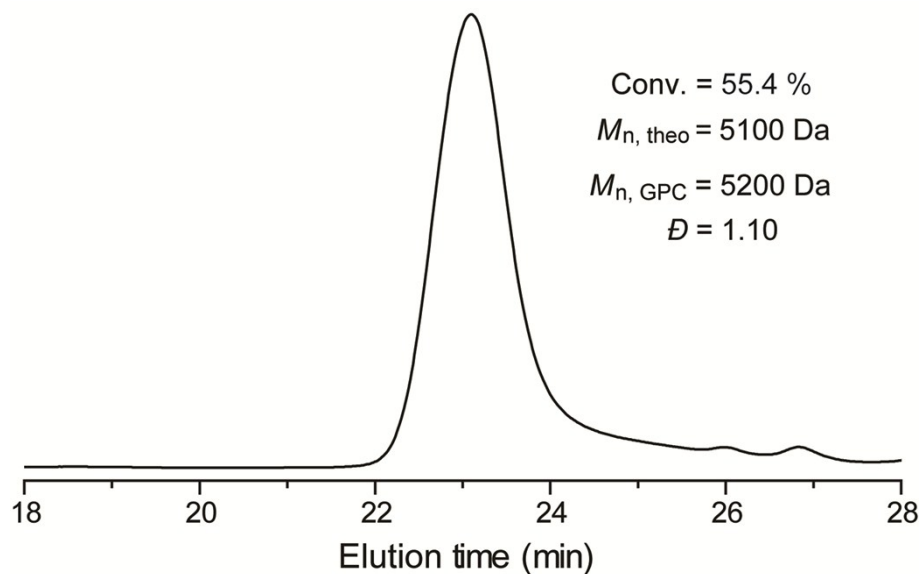
## 5. Supplementary data for Table 1



**Figure S8.** GPC profiles of the synthesized PMAs listed in Table 1.

## 5. Supplementary data for Figure 3

### a. “On/Off” reactions



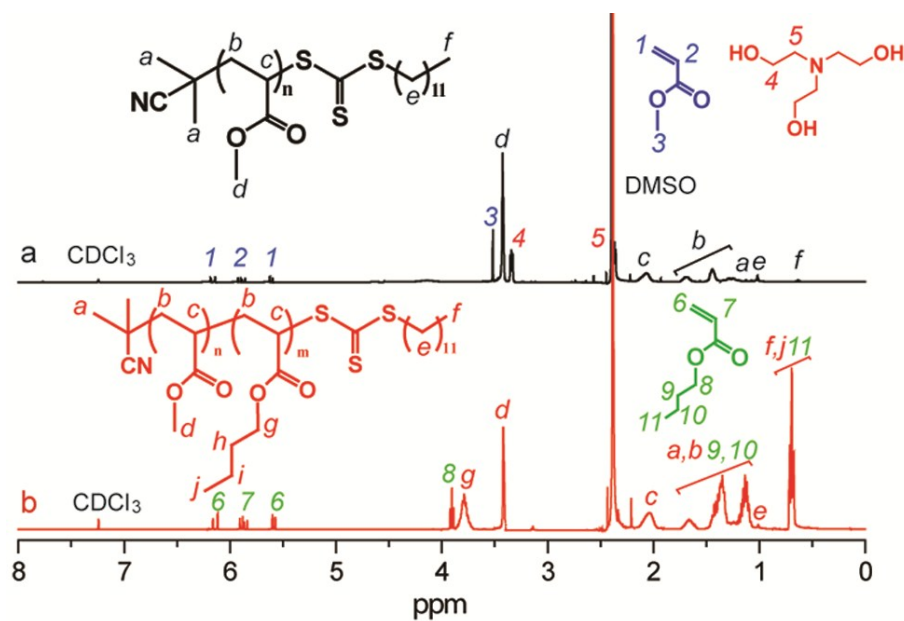
**Figure S9.** GPC DRI chromatogram of the synthesized PMA in the “On/Off” experiment.

### b. Chain extension

**Table S1.** Chain extension experiment for PMA-*b*-PBA.<sup>a</sup>

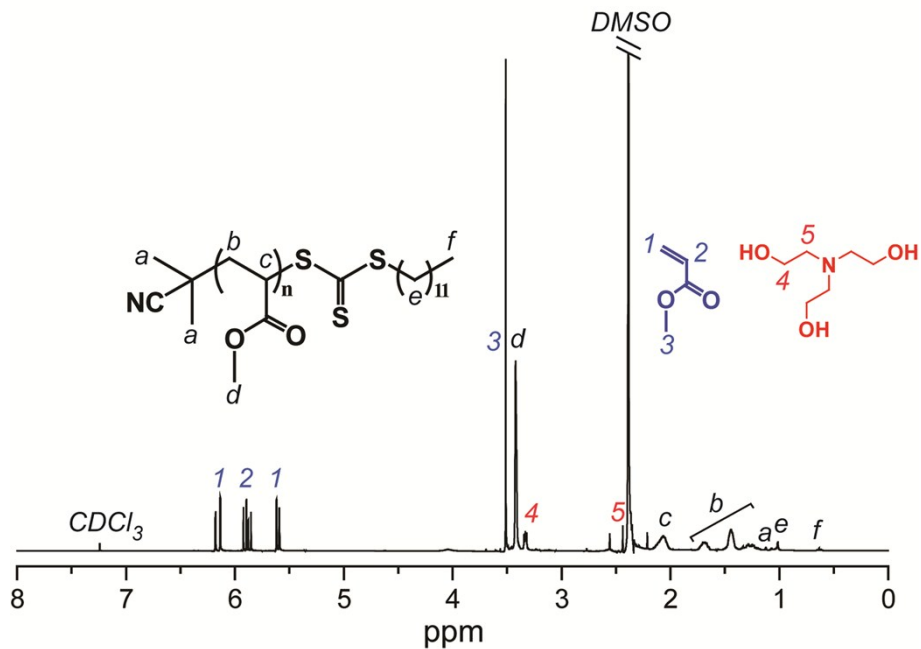
Entry	Feed ratio [(macro)-TTC]	Time (h)	Conv. <sup>b</sup> (%)	$M_{n, \text{GPC}}^c$ (kDa)	$\bar{D}^c$
1	100	21	91.0	8.8	1.13
2	50	24	80.3	14.3	1.26

<sup>a</sup> A stronger blue LED light source (4 mW/cm<sup>2</sup>) was applied. <sup>b</sup> Obtained by <sup>1</sup>H NMR spectroscopic analysis. <sup>c</sup> Determined by GPC characterization.



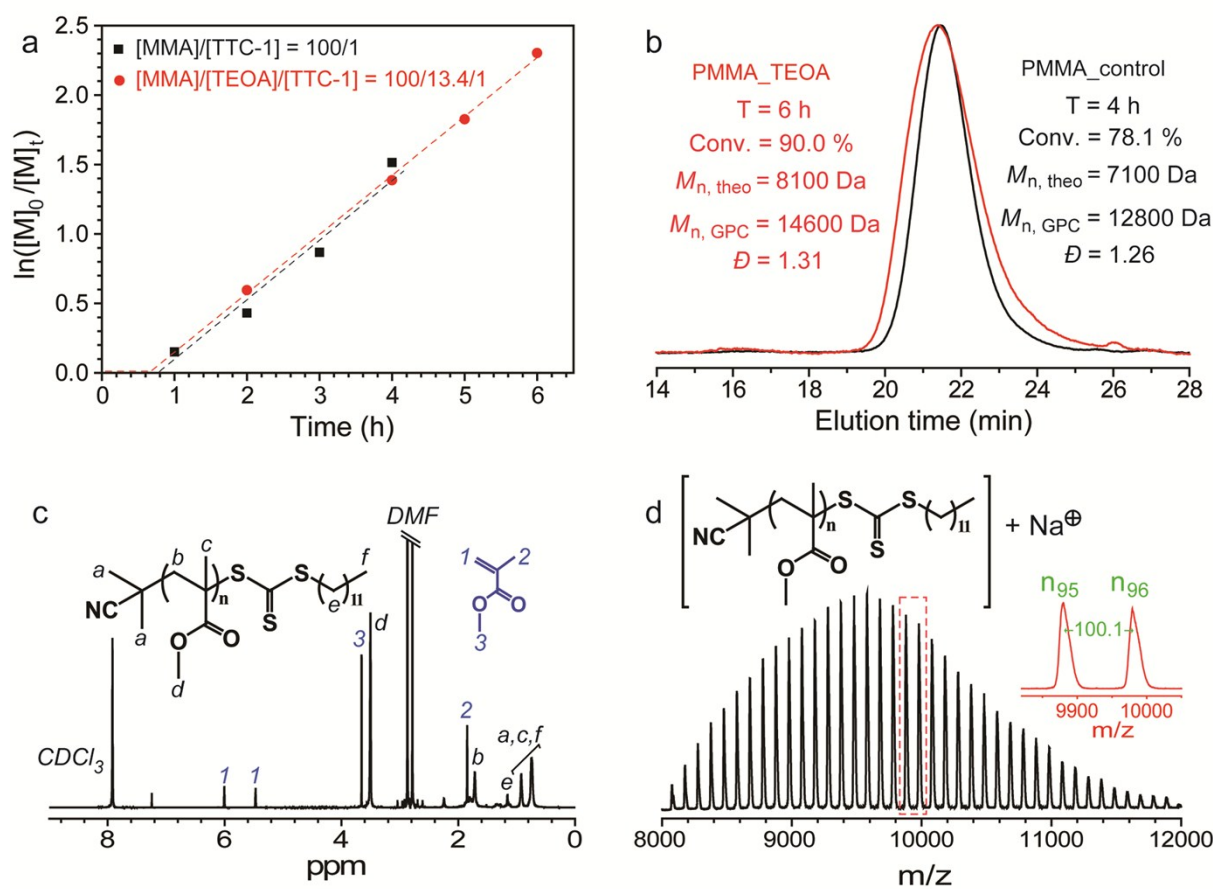
**Figure S10.**  $^1\text{H}$  NMR spectra of the raw products (a) PMA and (b) PMA-*b*-PBA block copolymer in  $\text{CDCl}_3$ .

### c. Scalable synthesis of PMA

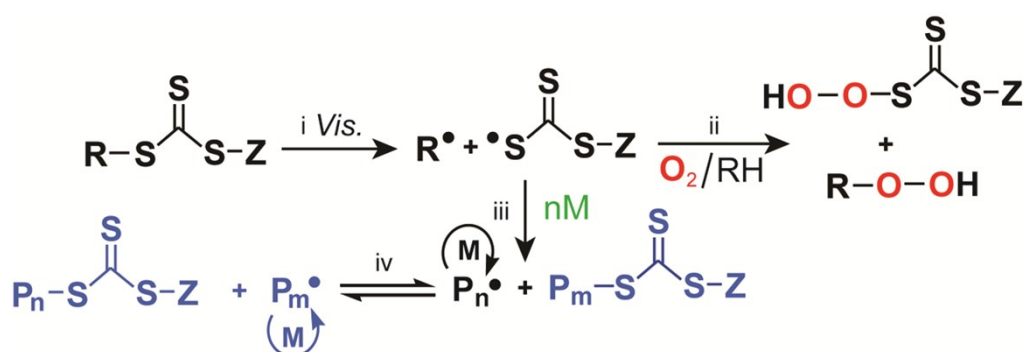


**Figure S11.**  $^1\text{H}$  NMR spectrum of the reaction mixture in  $\text{CDCl}_3$ .

## 6. The preparation of PMMA



**Figure S12.** (a) Kinetic study on the PMMAs prepared in the control experiments by photo-CRPs. (b) GPC DRI chromatogram of the synthesized PMMAs. (c)  $^1\text{H}$  NMR spectrum of the raw product (PMMA\_control) in  $\text{CDCl}_3$ . (d) MALDI-ToF MS of the PMMA\_control.



**Scheme S1.** Proposed mechanism for photo-CRP of MMA in the presence of oxygen.

## References

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