# Supporting Information for

## A Light-mediated Metal-free Atom Transfer Radical Chain Transfer

## **Reaction for the Controlled Hydrogenation of Poly(vinylidene**

### fluoride-chlorotrifluoroethylene)

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 Table S1. Assignments of <sup>1</sup>H NMR spectra of P(VDF-CTFE), P(VDF-TrFE-CTFE)

and	P(V	/DF-	-Trl	FE)
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Signal no.	Assignment	Chemical shift / ppm
$I_1$	$-CF_2CH_2CH_2CF_2-$	2.2-2.7
$I_2$	-CF <sub>2</sub> C <b>H</b> <sub>2</sub> CF <sub>2</sub> C <b>H</b> <sub>2</sub> -	2.7-3.2
$I_3$	$-CF_2CH_2CFClCF_2-$	3.3-3.7
$I_4$	-CF <b>H</b> CF <sub>2</sub> -	5.1-5.9
$I_5$	$-CF_2CH_2CFHCF_2-$	2.6-2.9



**Figure S1.** DSC curves of pristine P(VDF-CTFE), the resultant P(VDF-TrFE-CTFE) (91/4.3/4.7 mol%) and P(VDF-TrFE).

Table S2. The cryst	talline data of the pr	ristine P(VDF-CT)	FE), the resultant P(VDF-
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Copolymer	$T_{\rm c}^{\rm a}$ (°C)	$\Delta H_{\rm c}{}^{\rm a}({\rm J}{\rm g}^{-1})$	$T_{\rm m}^{\rm a}(^{\rm o}{\rm C})$	$\chi_{c}^{c}(\%)$	
P(VDF-CTFE)	-	-	162.1/170.0	15.1	
P(VDF-TrFE-CTFE) <sup>b</sup>	106.6	1.9	165.7	14.7	
P(VDF-TrFE)	119.1	2.9	163.2	14.5	

TrFE-CTFE)	and P	(VDF-1	ſrFE)
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<sup>a</sup>Determined by DSC during the second heating process.  $\Delta H_c$  is the heat enthalpy of the Curie transition for the copolymer. <sup>b</sup>P(VDF-TrFE-CTFE) containing 4.3 mol% TrFE (91/4.3/4.7). <sup>c</sup> $\chi_c$  is calculated from the integral of curves using the formula  $\chi_c = \Delta H_f / \Delta H_f^* \times 100\%$ , where the heat of fusion for the perfect PVDF crystal ( $\Delta H_f^*$ ) is 102.5 J g<sup>-1</sup>.

Table S3. Hydrogenation of P(VDF-CTFE) via light-mediated radical chain transfer

Entry	[TBA]/[HCOOH] (mmol)	Time (h)	VDF/TrFE/CTFE (mol%)
1	0/0	2	91/0.4/8.6
2	0/0	4	91/1.1/7.9

#### process under varied conditions<sup>a</sup>

3	0/0	8	91/2.0/7.0
4	0/0	16	91/3.4/5.6
5	0/0	24	91/4.3/4.7
6	0.13/0.13	24	91/1.2/7.8
7	0.26/0.26	24	91/1.5/7.5
8	0.52/0.52	24	91/5.0/4.0
9	1.3/1.3	0.5	91/1.5/7.5
10	1.3/1.3	1	91/2.3/6.7
11	1.3/1.3	2	91/3.1/5.9
12	1.3/1.3	4	91/6.2/2.8
13	1.3/1.3	8	91/9/0
14 <sup>b</sup>	1.3/1.3	24	gel

<sup>a</sup>Reaction condition: 0.2 g of P(VDF-CTFE) (0.26 mmol Cl atoms), Me-PTZ (0.1 equiv, 0.026 mmol) at room temperature with irradiation from 386 nm LED (4 W). <sup>b</sup>Reaction run with Ph-PTZ (0.1 equiv, 0.026 mmol).



Figure S2. <sup>1</sup>H NMR spectrum of photocatalyst Ph-PTZ in CDCl<sub>3</sub>.



Figure S3. UV-Vis spectra of photocatalysts Me-PTZ and Ph-PTZ in DMF.