Supporting Information

Photo-induced controlled radical polymerization of methyl acrylate and vinyl acetate by xanthate

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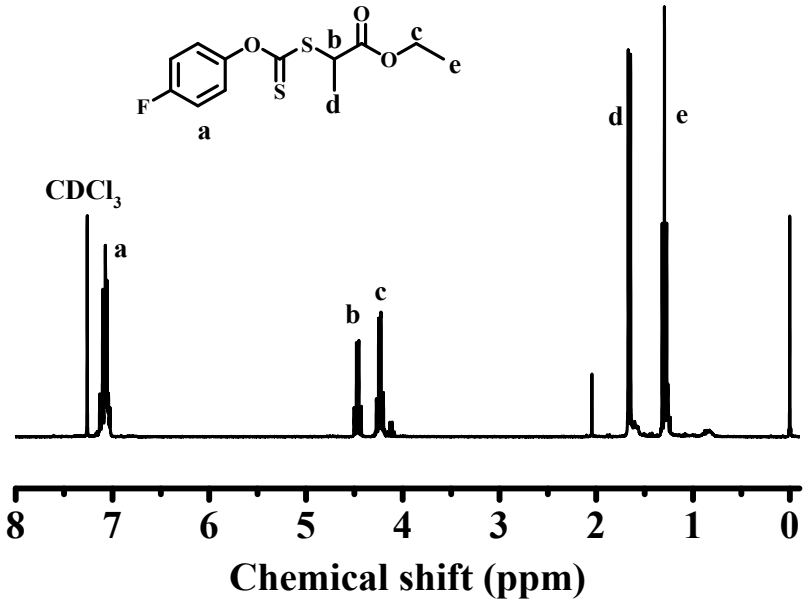


Figure S1. ^{1}H NMR spectrum of FPXEP in $CDCl_3$.

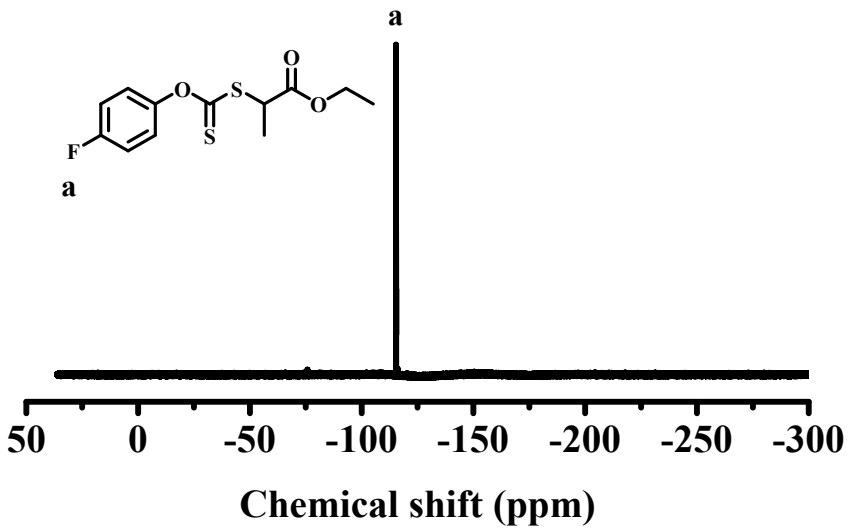


Figure S2. ^{19}F NMR spectrum of FPXEP in $CDCl_3$.

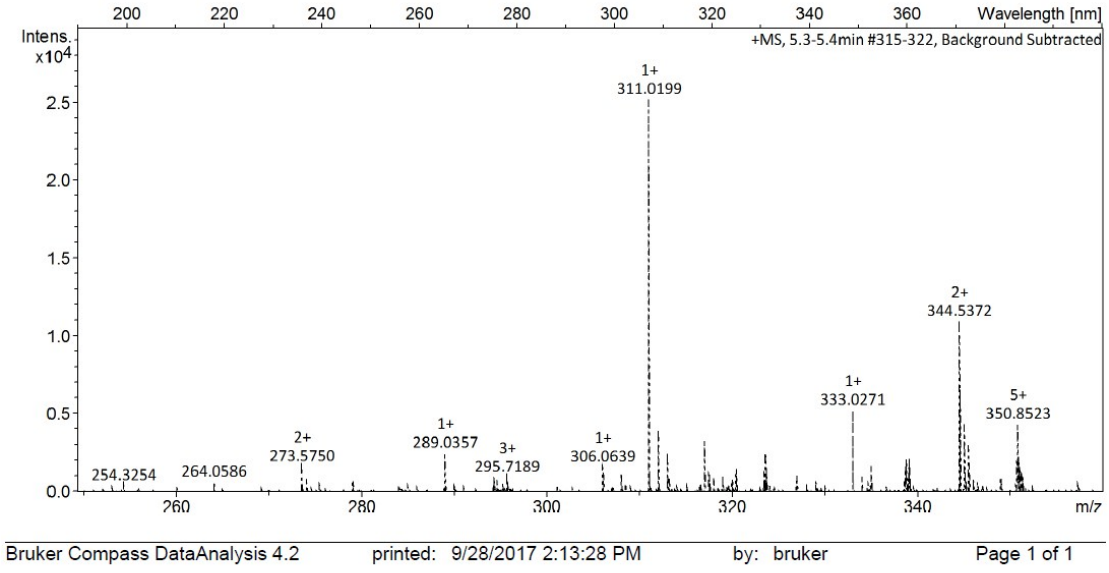


Figure S3. Mass spectrum of FPXEP

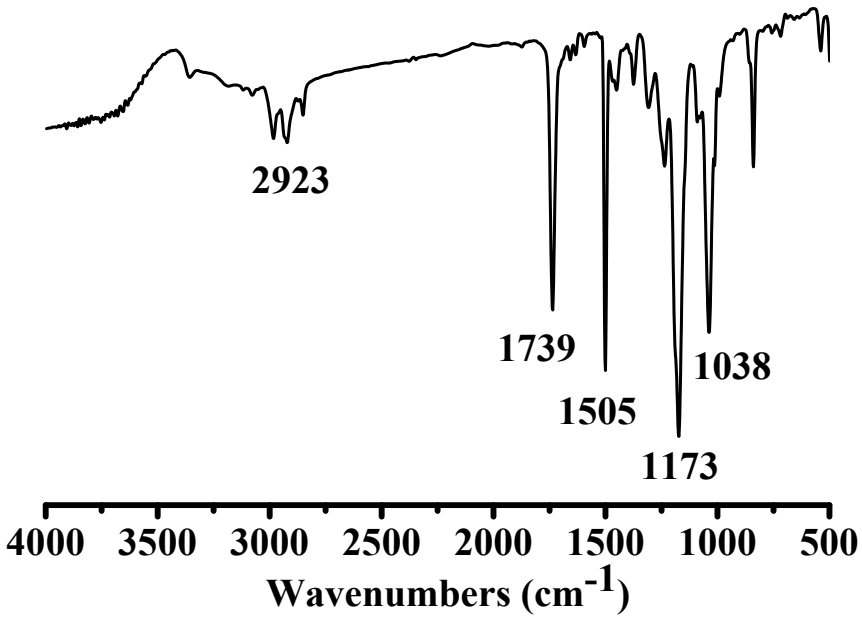


Figure S4. IR spectrum of FPXEP.

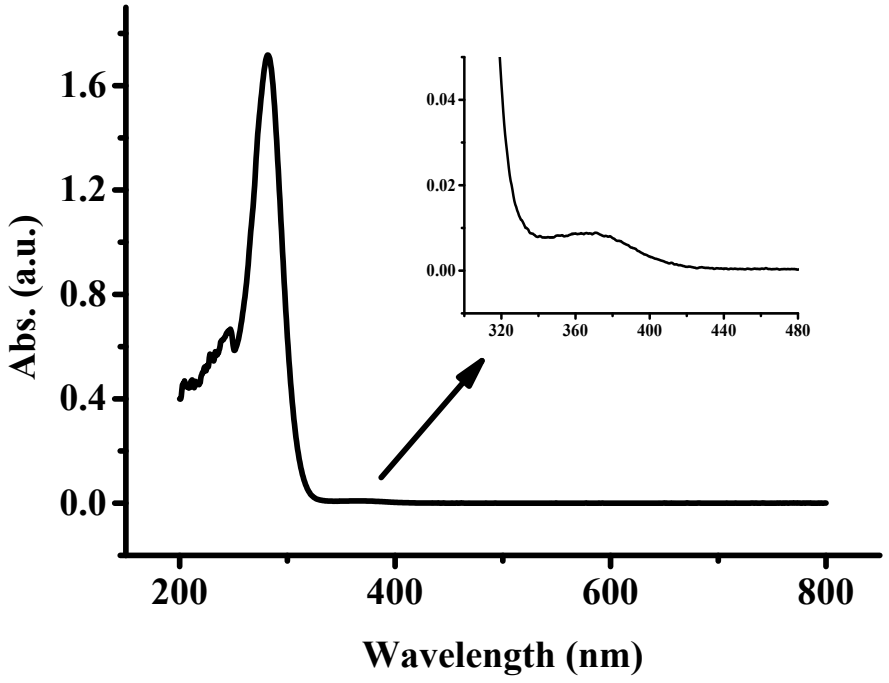


Figure S5. UV-vis absorption spectrum of FPXEP.

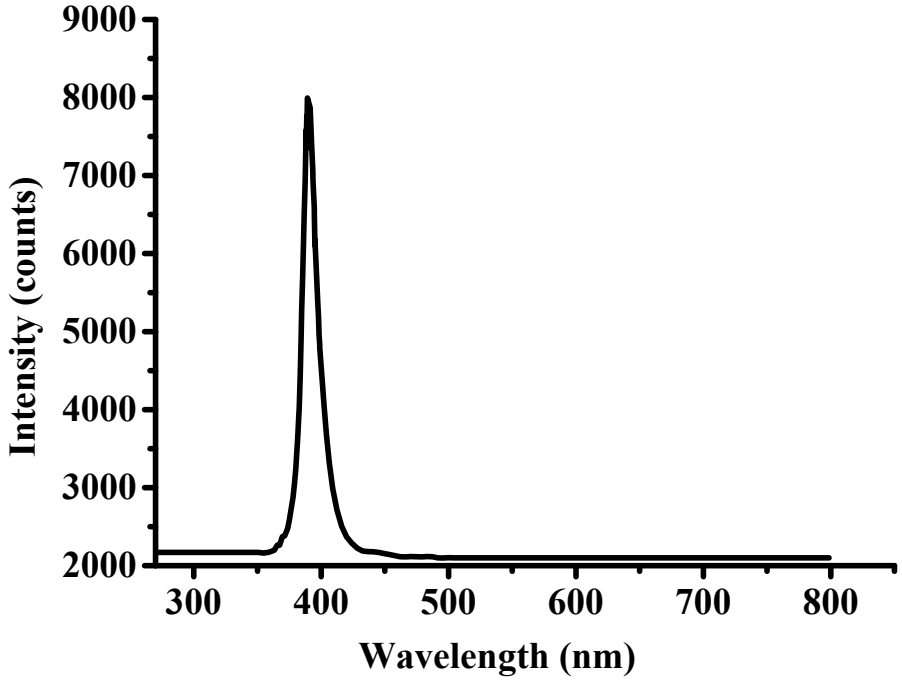


Figure S6. LED light source emission characterization.

Structure of PXEP (XYZ Cartesian coordinates)

C	-4.78815083	-0.34166490	1.15253606
C	-5.16730135	-1.27203598	0.18599693
C	-4.39714219	-1.43439421	-0.96504395
C	-3.24611575	-0.67226528	-1.15413507
C	-2.88461307	0.24152549	-0.17445467
C	-3.63893705	0.42653980	0.97489609
O	-1.77891288	1.08057083	-0.39981850
C	-0.53319937	0.69723658	-0.04093000
S	0.51958577	2.00957667	-0.58592462
S	-0.13141844	-0.69821170	0.71845523
C	2.20495842	1.53616854	-0.01775550
C	2.67311340	0.21687765	-0.65058958
O	3.49373077	-0.45282824	0.17386762
C	4.03060826	-1.70339986	-0.33248906
C	2.41583917	1.69585755	1.48895077
O	2.41709656	-0.12667899	-1.77620225
C	4.90622477	-2.29750994	0.75079016
H	-5.38676499	-0.20964919	2.04636270
H	-6.06232463	-1.86657542	0.32745263
H	-4.69159878	-2.15371294	-1.72041061
H	-2.63490310	-0.78122475	-2.04137506
H	-3.32770414	1.15701311	1.71122672

H	2.79350255	2.30257640	-0.53784724
H	4.58830817	-1.49584049	-1.24834126
H	3.19197527	-2.35410306	-0.58868982
H	3.46632549	1.53338302	1.73581211
H	1.81914759	0.97839211	2.05016295
H	2.13720918	2.70591710	1.79486137
H	5.32633115	-3.24496643	0.40269443
H	4.32987803	-2.49085647	1.65801685
H	5.73291883	-1.62831401	1.00017649

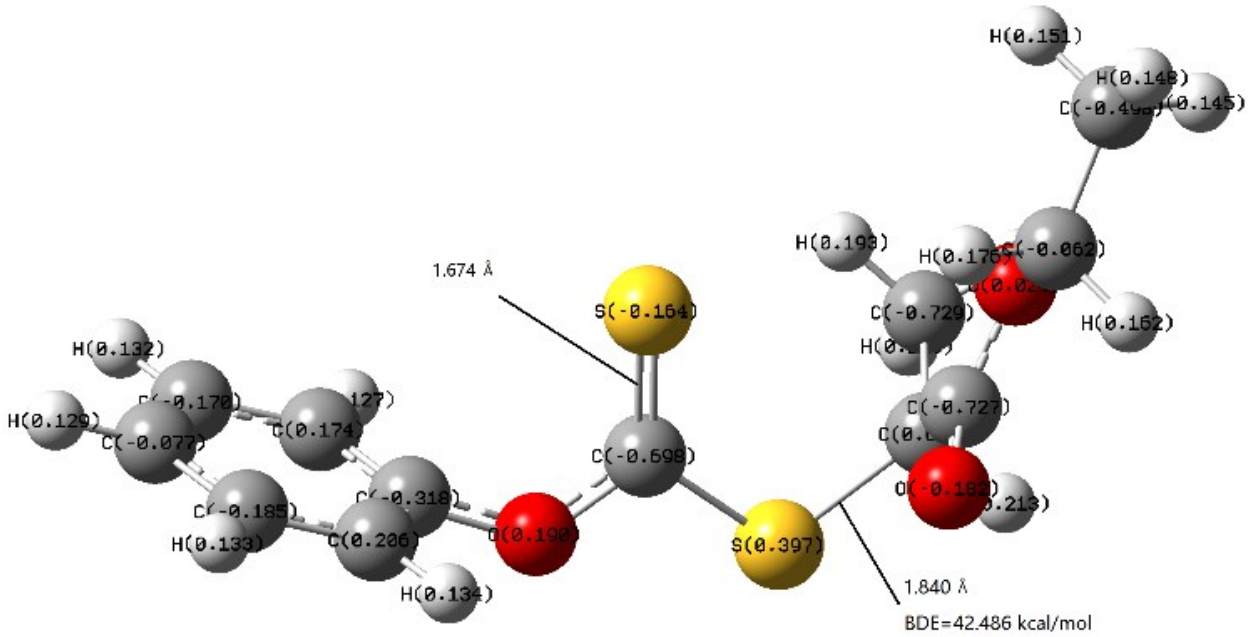


Figure S7. The Mulliken charges optimized geometries of PXEP at the level of B3LYP/6-311++G (d,p).

Bond length of PXEP

Bond	Bond length/Å
C1S2	1.7685056
C1S3	1.6387103
C1O20	1.3518687
S2C4	1.8404923
C4C5	1.5362862
C4C8	1.5297498

C4H11	1.0973882
C5O6	1.3422559
C5O9	1.2043996
C8H14	1.0912649
C8H15	1.0889244
C8H16	1.0915296
O6C7	1.4520898
C7C10	1.5143195
C7H12	1.0921975
C7H13	1.0919518
C10H17	1.0933131
C10H18	1.0920706
C10H19	1.0924466
O20C21	1.4061860
C21C22	1.3876126
C21C23	1.3871709
C22H25	1.0828884
C23H27	1.0828851
C22C24	1.3933625
C23C26	1.3941124
C24H29	1.0838367
C26H30	1.0838334
C24C28	1.3933625
C28H31	1.0837678

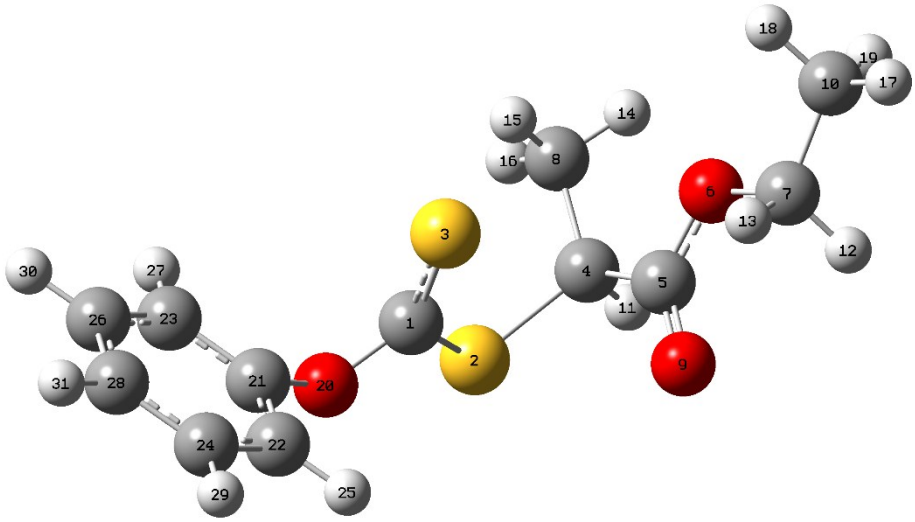


Figure S8. The atom numbers of PXEP at the level of B3LYP/6-311++G (d,p).

Structure of FPXEP (XYZ Cartesian coordinates)

C	-3.36515966	-1.57686611	-0.90838651
C	-4.14663950	-1.34608645	0.21402099
C	-4.05750417	-0.17909725	0.95809508
C	-3.14260185	0.79411345	0.56519108
C	-2.34089192	0.56351087	-0.54664078
C	-2.45150216	-0.60113824	-1.29758244
O	-1.48669977	1.58586494	-0.99274046
C	-0.19078323	1.67114160	-0.61404971
S	0.28554904	0.38455325	0.52862632
S	0.73488248	2.88636778	-1.20438037
C	2.06305569	0.78923886	0.86614444
C	2.79291841	-0.54927065	0.91249488
O	3.23621634	-0.90057242	-0.30475564
C	3.91743487	-2.18004019	-0.40523454
C	2.22665697	1.58862820	2.15396269
O	2.95427797	-1.20618683	1.91185381
C	4.33707817	-2.36214181	-1.84858817
F	-5.03626833	-2.29261374	0.59243014
H	-3.47901506	-2.49870726	-1.46430710
H	-4.69601659	-0.03911726	1.82090474
H	-3.04784954	1.72276745	1.11368293
H	-1.82977280	-0.73849387	-2.17326754
H	2.39252400	1.35442422	-0.00573519
H	3.23130302	-2.96211041	-0.07243102
H	4.77154849	-2.17064020	0.27522430

H	3.28467818	1.81621160	2.31370546
H	1.86797246	1.02486923	3.01560145
H	1.68094527	2.53035129	2.08219010
H	4.85499314	-3.31835248	-1.96082635
H	5.01526537	-1.56597896	-2.16313454
H	3.47020864	-2.36123544	-2.51283755

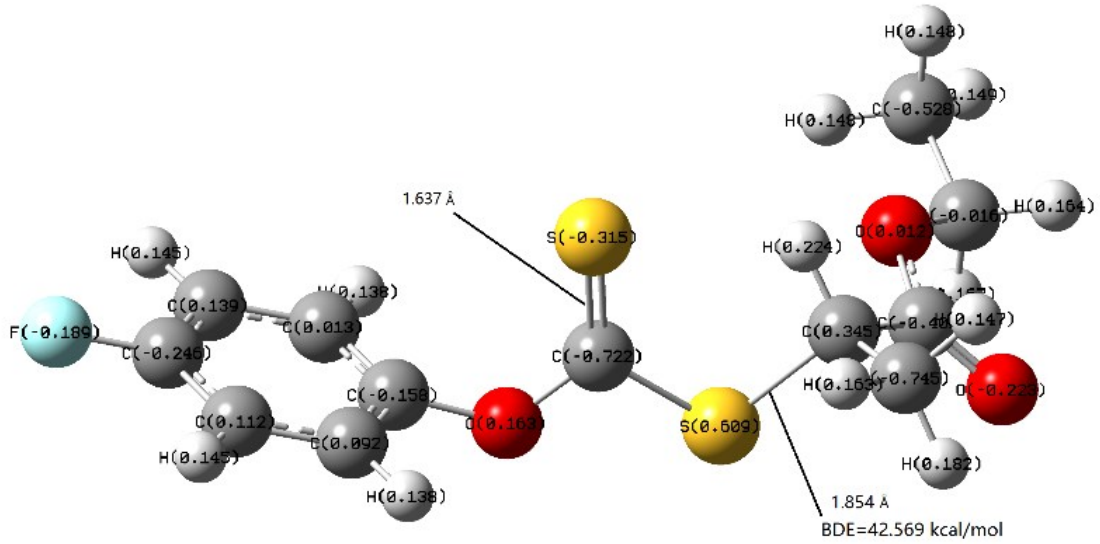


Figure S9. The Mulliken charges and optimized geometries of FPXEP at the level of B3LYP/6-311++G (d,p)

Bond length of FPXEP

Bond	Bond length/Å
C1S2	1.7746351
C1S3	1.6384592
C1O20	1.3527888
S2C4	1.8535559
C4C5	1.5249015
C4C8	1.5251840
C4H11	1.0898610
C5O6	1.3424082
C5O9	1.2068176
C8H14	1.0940657
C8H15	1.0903726
C8H16	1.0908223

O6C7	1.4530223
C7C10	1.5141629
C7H12	1.0921637
C7H13	1.0921172
C10H17	1.0932445
C10H18	1.0921745
C10H19	1.0920725
O20C21	1.4048330
C21C22	1.3877865
C21C23	1.3877851
C22H25	1.0825809
C23H27	1.0825685
C22C24	1.3926067
C23C26	1.3926688
C24H29	1.0824925
C26H30	1.0824896
C26C28	1.3865136
C28F31	1.3542385

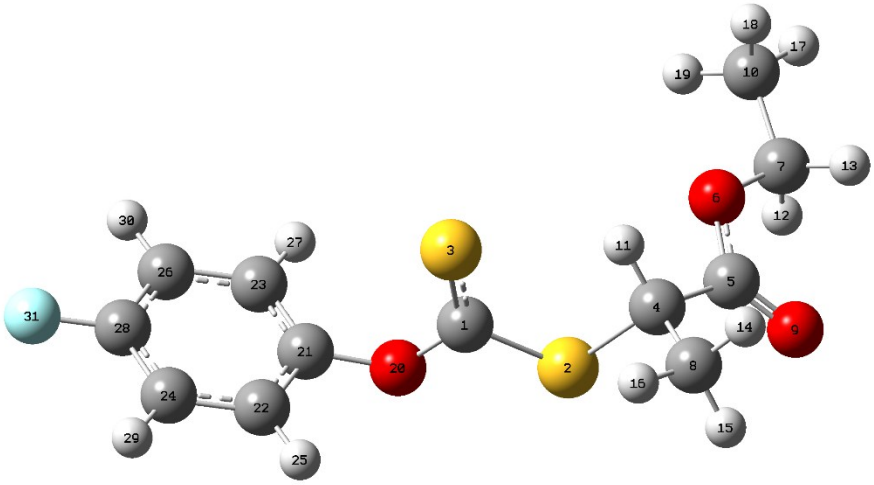


Figure S10. The atom numbers of FPXEP at the level of B3LYP/6-311++G (d,p).

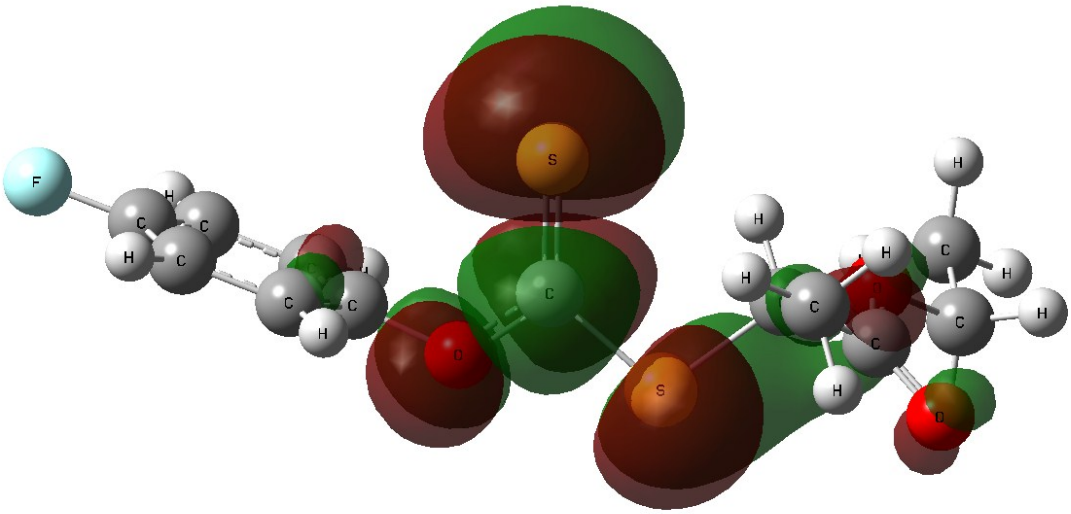


Figure S11. LUMO for FPXEP.

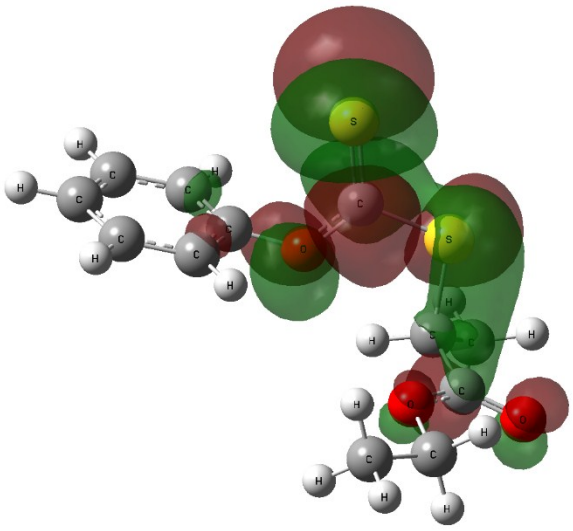
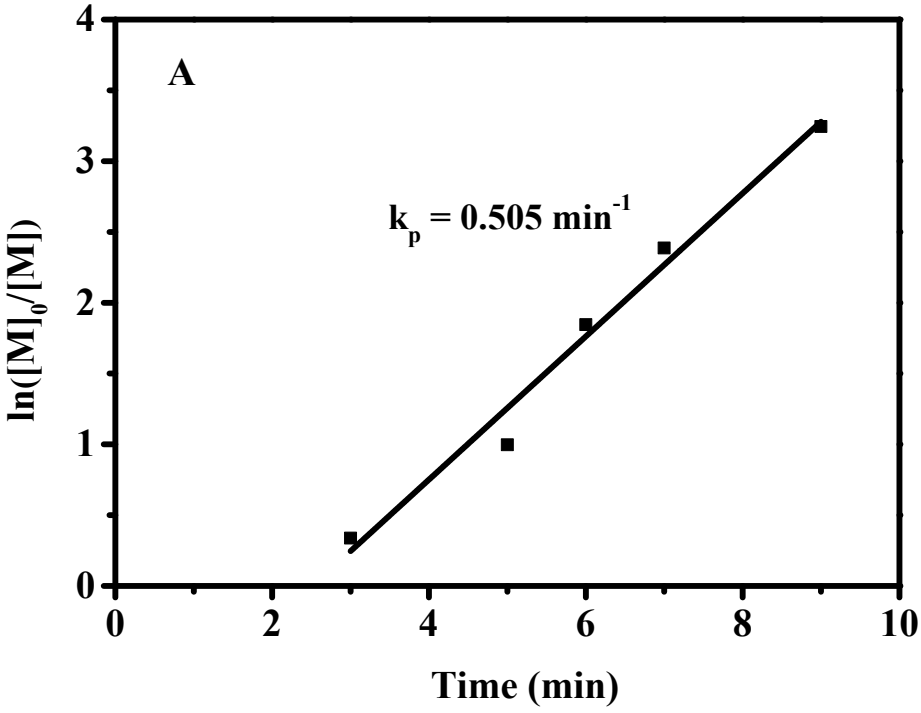
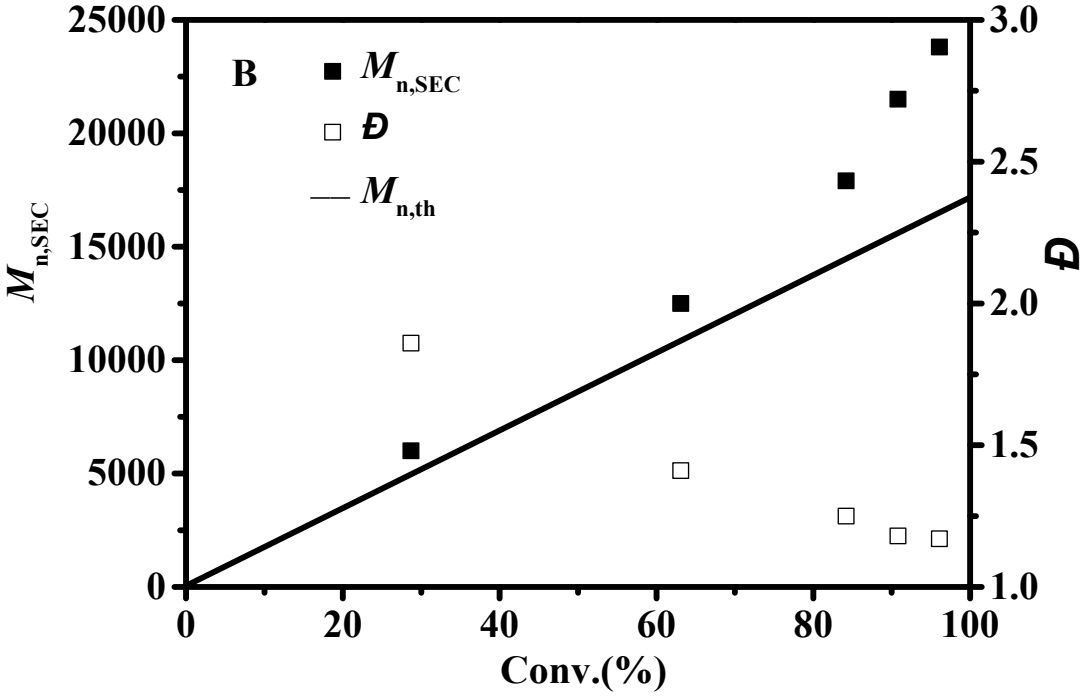


Figure S12. LUMO for PXEP.


A
k_p = 0.505 min^{-1}
ln([M]$_0$/[M])
Time (min)
0
1
2
3
4
0
2
4
6
8
10


B
$M_{n,SEC}$
Đ
$M_{n,th}$
$M_{n,SEC}$
Đ
Conv.(%)
0
5000
10000
15000
20000
25000
1.0
1.5
2.0
2.5
3.0
0
20
40
60
80
100

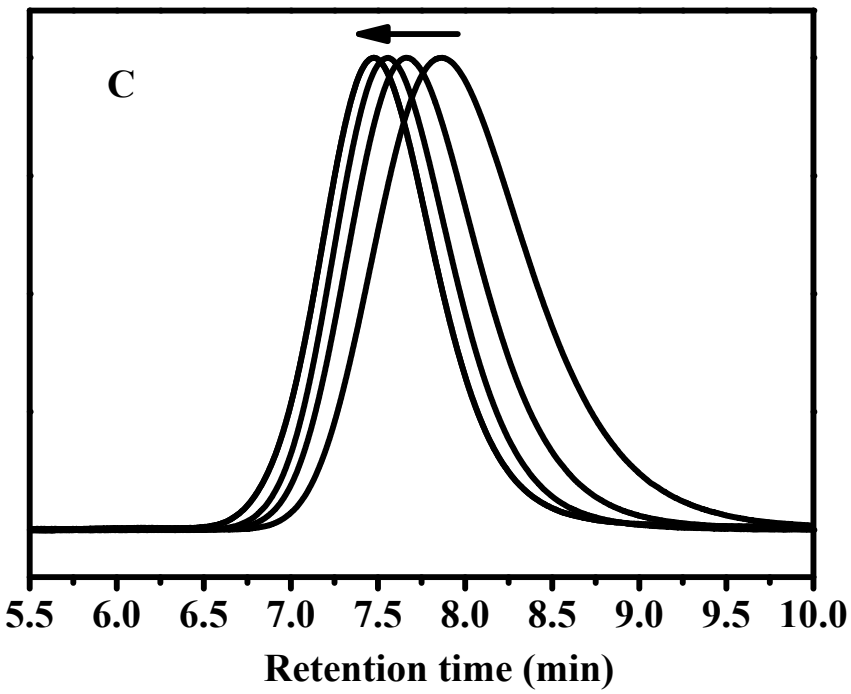
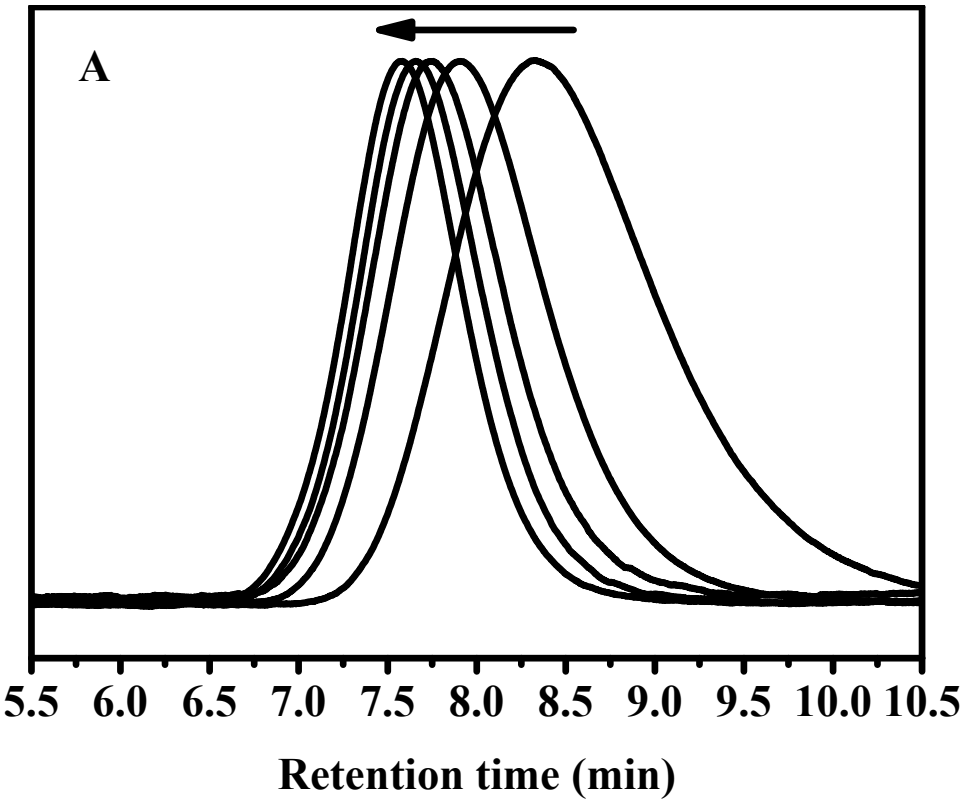


Figure S13. Polymerization results for MA in the presence of PXEP with the molar ratio $[MA]_0$:$[PXEP]_0$ = 200:1 in bulk with purple LED at 25 °C. A) $\ln([M]_0/[M])$ versus time; B) molar mass (M_n) and molar mass distribution ($Đ$) versus conversion. C) SEC traces.



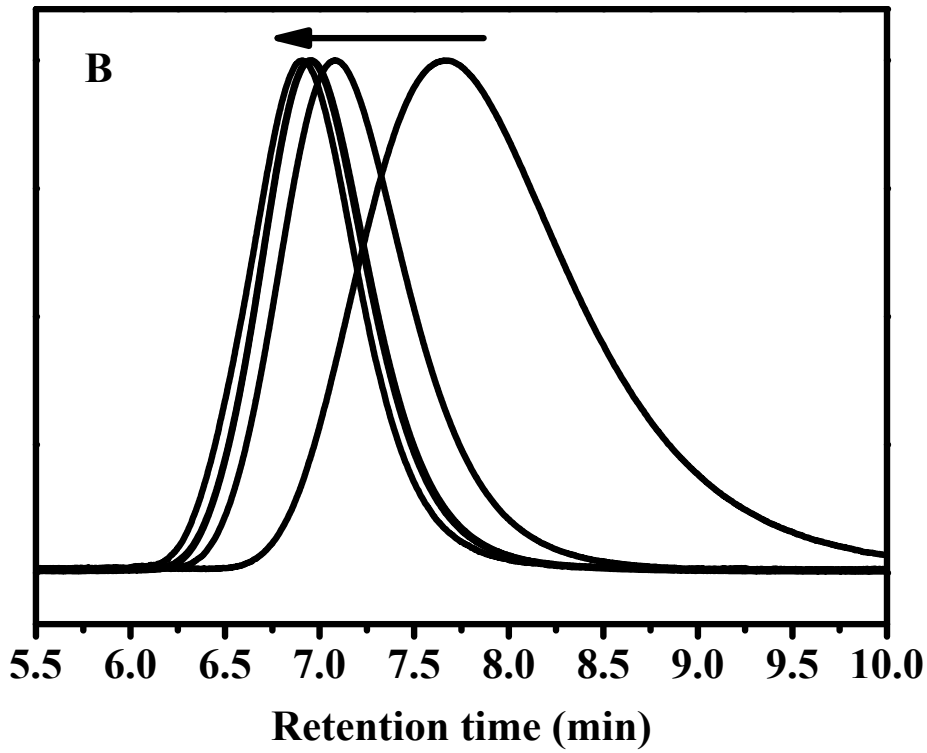


Figure S14. SEC traces of PMA obtained by the bulk polymerization using FPXEP as the mediator with purple LED at 25 °C: A) the molar ratio $[MA]_0$:$[FPXEP]_0$ = 200:1; B) the molar ratio $[MA]_0$:$[FPXEP]_0$ = 500:1.

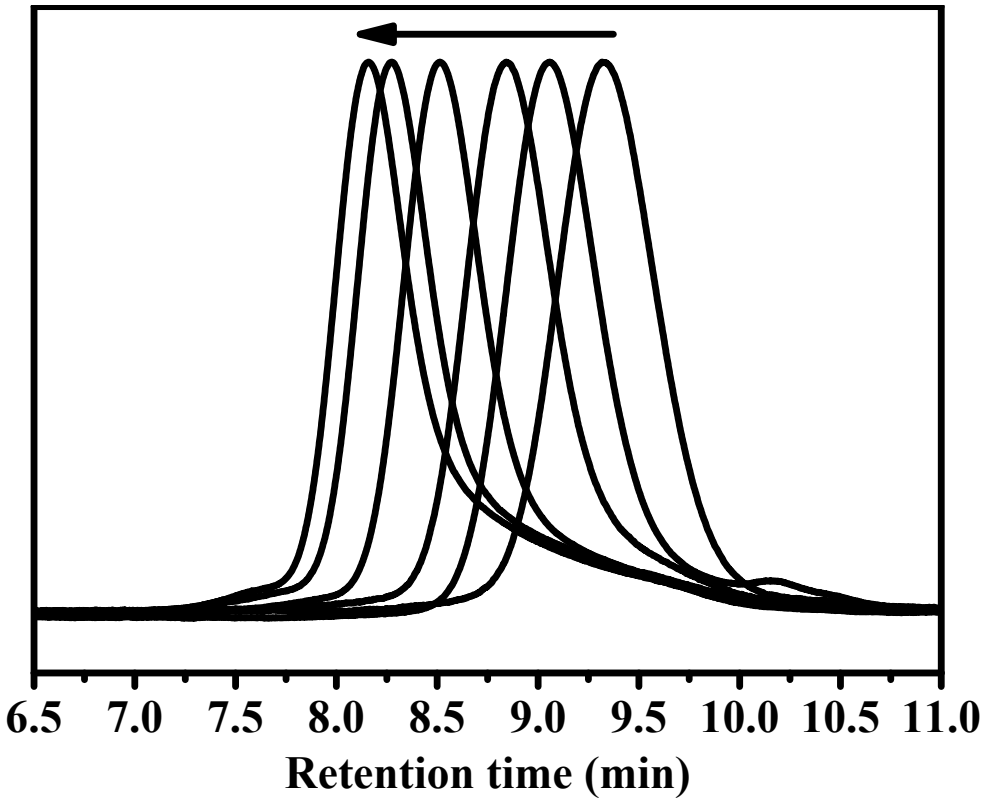
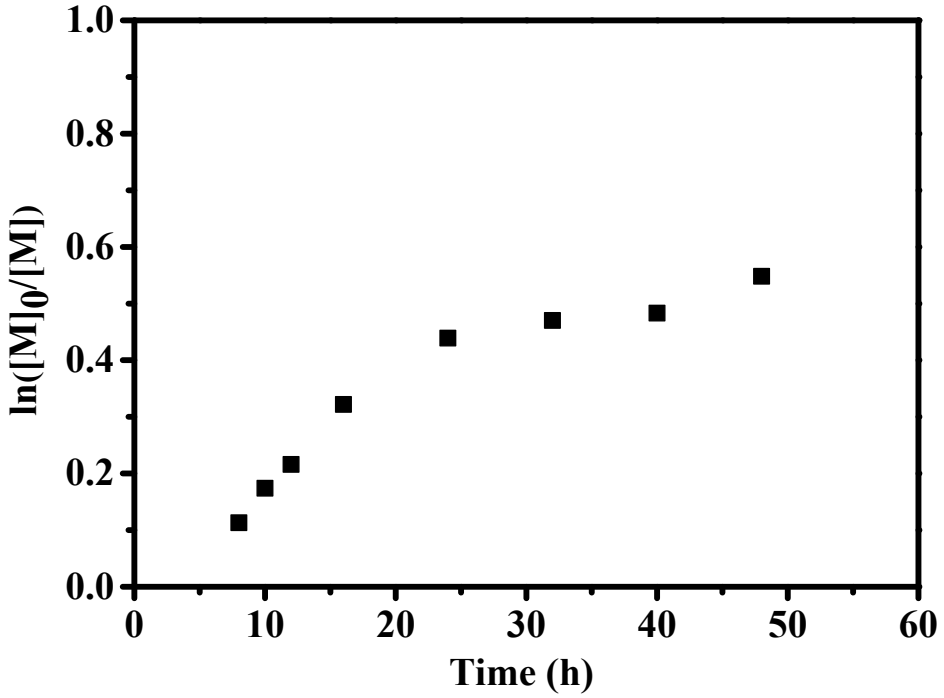


Figure S15. SEC traces of PVAc polymerized in bulk using FPXEP as the mediator under irradiation of purple LED at 25°C with the molar ratio $[VAc]_0$:$[FPXEP]_0$ = 200:1.



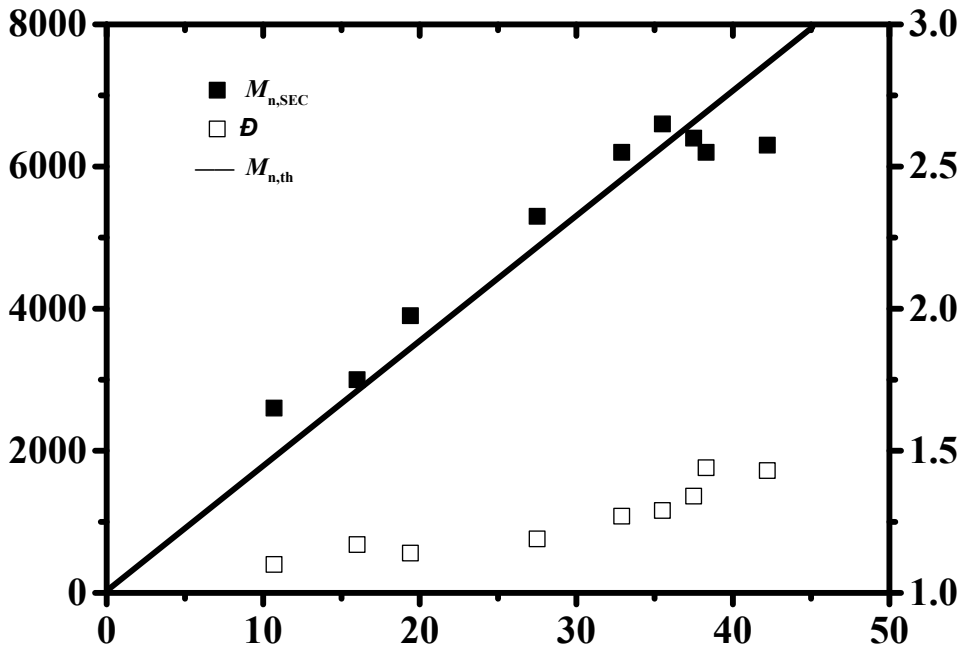


Figure S16. Polymerization results of ln([M]$_0$/[M]) versus time for VAc in the presence of the FPXEP with the molar ratio [VAc]$_0$:[FPXEP]$_0$ = 200:1 in bulk with purple LED at 25 °C; B) molar mass (M_n) and molar mass distribution (*Đ*) versus conversion.

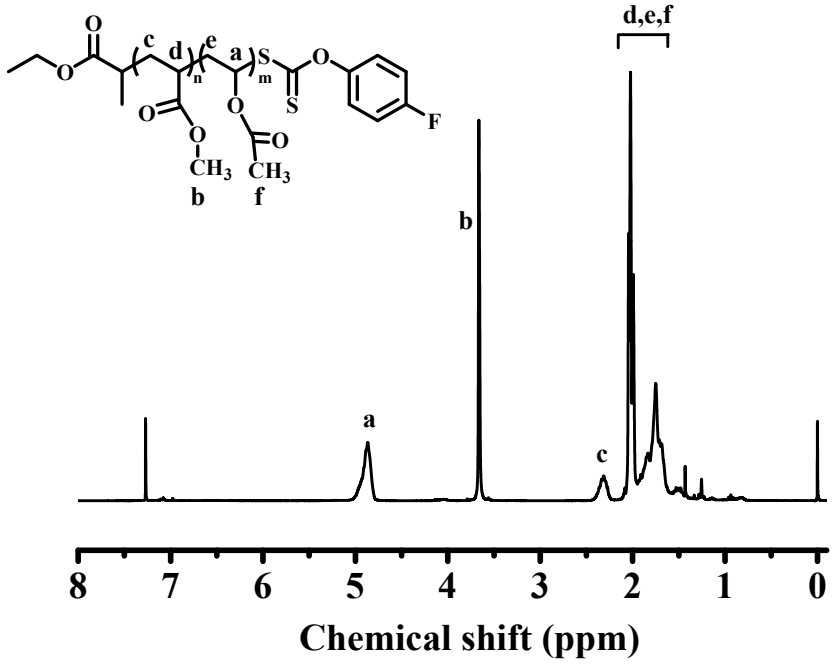


Figure S17. ^{1}H NMR spectrum of PMA-*b*-PVAc in $CDCl_3$ (Mn,SEC = 29800 g mol^{-1}, $Đ$ = 1.33)

Table S1. Polymerization of MMA and St with the molar ratio $[M]_0$:$[FPXEP]_0$ = 200:1 at 25 °C, V_M = 1 mL

Monomer	Time	Conv.%	M_n,th(g/mol)	M_n,SEC(g/mol)	$Đ$
St	24h	74.8	15900	12500	1.71
MMA	80min	84.3	17200	38100	1.97

Table S2. Polymerization of VAc and MA with the molar ratio $[M]_0$:$[FPXEP]_0$:$[AIBN]_0$ = 200:1:0.5 at 60 °C, V_M = 1 mL

Monomer	Time	Conv.%	M_n,th(g/mol)	M_n,SEC(g/mol)	$Đ$
VAc	3.5h	30.6	5600	4800	1.20
VAc	6h	73.3	12900	12600	1.68
MA	20min	58.2	10300	10900	1.46
MA	30min	83.1	14600	16700	1.22